Synthesis and Structure Analysis of Poly(2,3-quinoxaline)s

Eiji Ihara

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Preface

The studies presented in this thesis have been carried out under the direction of Professor Yoshihiko Ito at the Department of Synthetic Chemistry of Kyoto University during 1989-1992. The thesis is concerned with synthesis and structure analysis of poly(2,3-quinoxaline)s.

The author wishes to express his sincerest gratitude to Professor Yoshihiko Ito for his constant guidance, valuable suggestions and encouragement throughout this work. The author is deeply grateful to Dr. Masahiro Murakami for his constant advice and valuable discussions during the course of this study. The author also wishes to express his gratitude to Assistant Professor Kohei Tamao and Dr. Masaya Sawamura for their helpful suggestions. The author is particularly indebted to Associate Professor Masahiko Sisido, Tokyo Institute of Technology, for his contribution to this work. The author is fortunate to have had the great assistance of Mr. Tetsuya Uesaka.

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CONTENTS

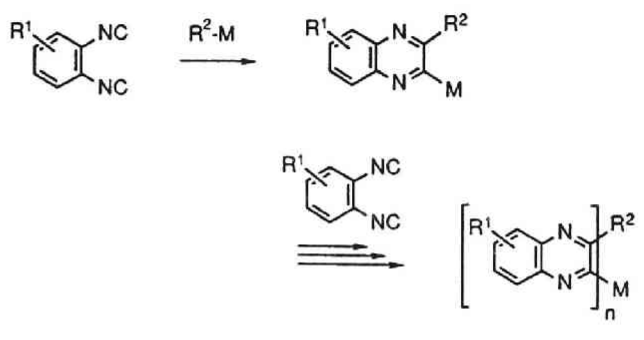
GENERAL INTRODUCTION.

Polymerization of Isocyanides.

Isocyanides are known to be polymerized by transition metal catalysts, to afford poly(N-substituted iminomethylene)s. Drenth, Nolte et al. have shown that Ni(II) salts are very effective for the polymerization and the reaction proceeds via consecutive insertion reactions of coordinated isocyanides to a propagating species on transition metal coordination sphere.[1] Furthermore, they clarified that the poly(iminomethylene) took a rigid helical conformation and prepared various functional polymers by utilizing the main chain structure as a rigid matrix.[1]

On the other hand, Yamamoto and Yamazaki attempted to polymerize isocyanides by organo-palladium complexes as initiators.[2] They isolated mono-, di- and tri-iminomethylpalladium complexes as a result of successive insertion reactions of one to three isocyano groups into carbon palladium bond. However, they found that nitrogen of imino group from firstly inserted isocyanide strongly coordinated to palladium, resulting in the deactivation of polymerization.

If two isocyano groups are substituted on 1,2 positions of aromatic ring, successive insertion of these two isocyano groups into carbon-metal bond results in the formation of quinoxalinyl-metal complex. In this thesis, the author tried to develop new aromatizing polymerization of 1,2-diisocyanoarenes to afford polyquinoxaline by applying the reaction to polymerization.



In chapter 1, Grignard reagents were used as initiators. Actually, up to hexa oligomers of quinoxaline were obtained as a result of aromatizing oligomerization of 1,2-diisocyanoarenes. Higher polymers could not be obtained due to the instability of propagating quinoxalinyl magnesium complexes.

Organopalladium complex were found to be effective for the polymerization of diisocyanoarenes in chapter 2. Propagating quinoxalinyl-Pd complexes were very stable and isolated to be analyzed by X-ray crystallography. Same kind of coordination of nitrogen as described above was observed, but the nitrogen is from quinoxaline ring not from imino group. This difference results in the success of polymerization without deactivation of the propagating species. Furthermore, because of the anomalous stability of the propagating species, the polymerization proceeded in a living manner.

In chapter 3, organo nickel(II) catalyzed polymerization are described. By accurate choice of the phosphine ligands and monomer substituents, living polymerization was possible. Mechanistic difference from the polymerization of monoisocyanide by nickel(II) salts is discussed.

Screw-sense Selective Polymerization.

There have been several reports on the synthesis of chiral polymers whose optical activity is derived from their helical sense. In screw-sense selective polymerization, helical polymer with one screw-sense is predominantly obtained. Okamoto et al. have succeeded in screw-sense selective polymerization of poly(tritylmethacrylate) by using optically active amines as additives.[3] As for the polymerization of monoisocyanide mentioned above, Nolte et al. obtained chiral helical polymers by using chiral amine as an activator of the initiation.[4] Helical polychloral with one screw sense was obtained by Vogl et al.[5]

From the X-ray crystal analysis of quinoxaline oligomer, it is suggested that the main chain of polyquinoxaline have a helical conformation. Chapter 4 deals with screw-sense selective polymerization of 1,2-diisocyanoarenes. Because of the anomalous stability of the quinoxalinylpalladium complexes, it is possible to isolate the oligomeric propagating species. After separating the oligomer into two isomers in terms of their helical sense, the author succeeded to prepare polyquinoxalines with exclusively one screw sense.

Empirical Energy Calculation and Theoretical Circular Dichroism.

Circular dichroism has been used for investigation of stereochemistry of organic compound since its spectrum relates to spatial arrangement of chromophoric groups. Especially, Nakanishi and Harada established the general rule to determine stereochemistry of two substituents on vicinal positions on the basis of quantum mechanics.[6] Woody extended this theory to polymeric system to investigate the conformation of polypeptide.[7]

In chapter 5, empirical energy calculation was performed on polyquinoxaline to determine its stable conformation. Theoretical CD was calculated to determine helical sense of the optically active polyquinoxalines synthesized in chapter 4.

Synthesis of Novel Liquid Crystalline Polymers.

Generally, liquid crystalline polymers are classified into three types i.e., a)main chain LC polymers, b)side chain LC polymers and c)rigid rod LC polymers.[8] While monomeric unit of type a) and b) has mesogenic property itself, rigid core of type c) is constructed by the progress of polymerization. In that sense, LC polymers of type c) is different from those of type a) and b). Though there have been a lot of examples of type a) and b), examples of type c) are limited in polyisocyanate,[9] polypeptide[8], polyester[10] and cellulose[11] derivatives, due to the difficulty of synthesis of such polymeric rigid core.

In chapter 6, the author attempts to synthesize LC polymer of type c) in which polyquinoxaline main chain plays a role of rigid core segment. Furthermore, by using the living nature of the polymerization, polyquinoxalines with various degrees of polymerization and very narrow molecular weight distribution were prepared. The relation between thermal phase behavior and molecular weight is discussed.

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Chapter 1

Aromatizing Oligomerization of 1,2-Diisocyanoarene to Quinoxaline Oligomers

Abstract

The reaction of Grignard reagents with 1,2-diisocyanoarene results in the formation of quinoxaline oligomers up to hexa-oligomer, which may be derived from successive insertion of the two ortho isocyano groups of 1,2-diisocyanoarene into carbon-magnesium bond.

Introduction

Isocyanides are known to be polymerized by transition metal catalysts, especially by nickel(II) salts, to afford poly(N-substituted iminomethylenes).[1] The polymerization reaction proceeds via consecutive insertions of coordinated isocyanides to a propagating species on transition metal coordination sphere. On the other hand, various organometallic compounds of typical metals undergo an insertion reaction with isocyanide. As reported by Ugi[2] and Walborsky[3], Grignard reagents reacted with isocyanide to give magnesium aldimines, of which synthetic utilities have been limited. However, successive insertions of isocyanides into carbon-typical metal bond have been not extensively studied. In this chapter, the author describes oligomerization of 1,2-diisocyano-3,4,5,6-tetramethylbenzene (1) promoted by Grignard reagents to give quinoxaline oligomers (2) up to hexa-oligomers.

Results and Discussion

1,2-Diisocyano-3,4,5,6-tetramethylbenzene (1) was treated with Grignard reagents in THF at 0 C to give a variety of quinoxaline oligomers (2) after hydrolysis.(Scheme 1, Table 1)

These oligomers were separated and isolated by preparative T.L.C. on silica gel and/or recycling H.P.L.C. on polystyrene gel, and characterized by ^{1}H-NMR, IR and mass spectrum. The quinoxaline skeleton was regularly constructed by successive insertion of two ortho isocyano groups into carbon-magnesium linkage. Of noteworthy was the formation of hexa-oligomer (2f), in which up to twelve isocyano groups underwent consecutive insertions into carbon-magnesium linkage.

Scheme 1

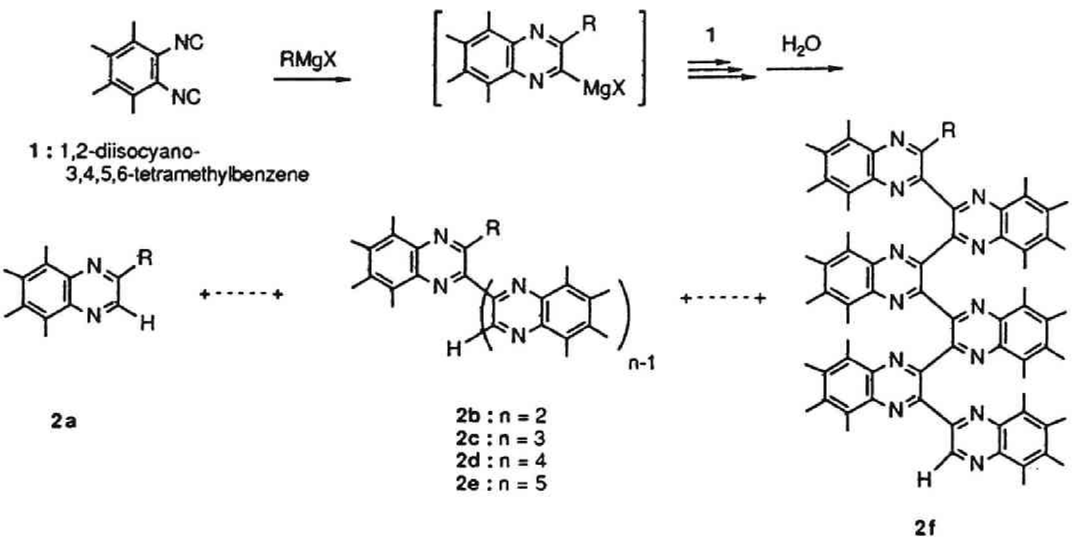


Table 1. Reaction of 1 with Grignard reagents.

Entry	R	1 / RMgX	% Yield[a)] of 2					
			2a	2b	2c	2d	2e	2f
1	i-Pr	0.7	89	4	-	-	-	-
2	i-Pr	2	9	14	15	8	2	-
3	i-Pr	3	5	3	7	5	8	3
4	n-Bu	2	2	4	8	10	10	-
5	i-Bu	2	5	6	6	4	6	3
6	t-Bu	2	12	3	3	3	4	

a) Yields of 2 are based on chromatographically isolated products (silica gel and/or polystyrene gel).

As shown in Table 1, when excess of Grignard reagent was used to the monomer (1), monomeric quinoxaline (2a) was obtained in high yield (90%). Higher oligomers were obtained on increasing the feed ratio of 1 to Grignard reagent. However, total yield of the oligomers was relatively low (30-50%). This may be ascribed to the instability of the propagating species, i.e., oligoquinoxalinyl-magnesium complexes in THF. To improve the stability of the complexes, the oligomerization was carried out in various solvent.(Table 2)

Table 2. Reaction of **1** with i-PrMgBr in various solvent.

Entry	Solvent	1 / i-PrMgBr	Yield of 2 (%)						
			2a	2b	2c	2d	2e	2f	Total
1	THF	2	9	14	15	8	2	-	48
2	THF	3	5	3	7	5	8	3	31
3	THP	2	14	39	16	4		-	73
4	THP	3	6	15	20	18	6	3	68
5	Dioxane	2	21	25	20	8	-	-	74
6	DME	2	10	5	8	-		-	23
7	Toluene	2	11	17	21	7	-	-	56

Compared to the reaction in THF, quinoxaline oligomers were obtained in good yield in the feed ratio (1 / i-PrMgBr) of 0.33 and 0.5 in THP and dioxane. Furthermore, distribution of the product were corresponded to the feed ratio. This result suggests that the propagating species are more stable in THP and dioxane than in THF. However, even in THP, the yield of quinoxaline oligomers decreased to 30% on decreasing the feed ratio to less than 0.25.

To examine the lifetime of the propagating species, after the reaction of 1,2-diisocyanoarene with excess of Grignard reagent, resulting mono-quinoxalinylmagnesium complex was quenched by D_2O.(Scheme 2) The result of D content incorporated into the product indicates same trend of the stability as described above.(Table 3)

Scheme 2

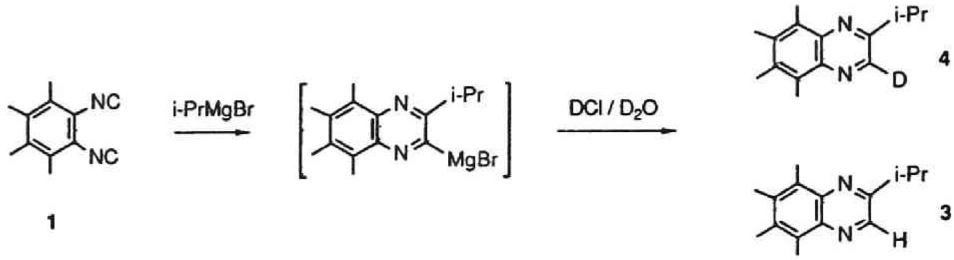


Table 3. D_2O quench of mono-quinoxalinyl-Mg complex.

Entry	Solvent	Time	100 x [4 / (3+4)]
1	THF	1h	20
2	THP	1h	45
3	THP	5min	59

UV spectra of the quinoxaline oligomers revealed an interesting structural feature ; quinoxaline monomer possessed an intense π-π^* transition band at 252 nm, while quinoxaline dimer showed additionally a red shifted absorption at 280 nm. The two absorptions may be ascribed to single isolated quinoxaline chromophore and conjugated dimeric quinoxaline chromophore, respectively. For trimer, the absorption band of conjugated quinoxaline chromophore moved to 290 nm due to slight contribution of the resonance. However, tetramer and pentamer absorbed at the same position as trimer with an increased absorption intensity indicating that an effective resonance conjugation over more than three sequential quinoxaline ring chain may be inhibited by steric interaction.

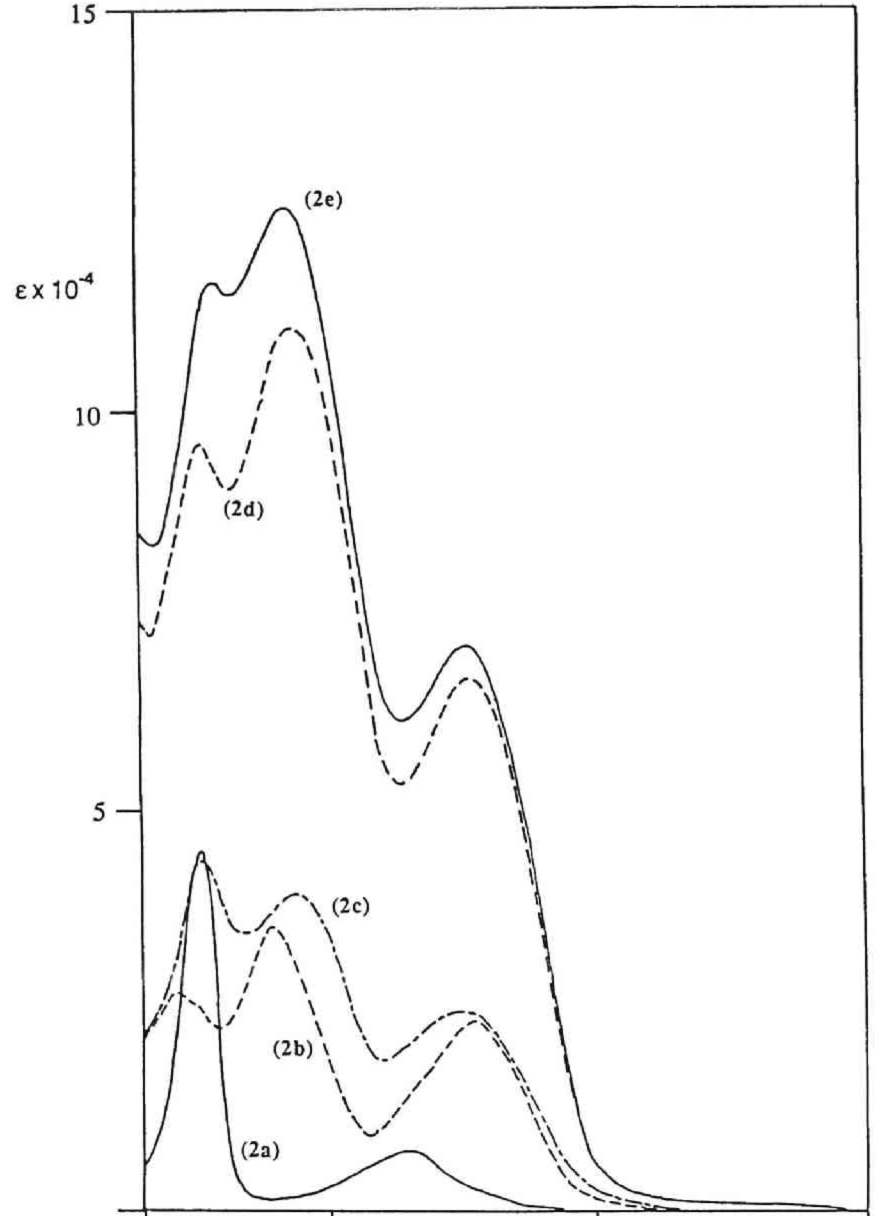


Figure 1. UV spectra of **2a-e** (R = n-Bu) in CH_2Cl_2.

Experimental Section

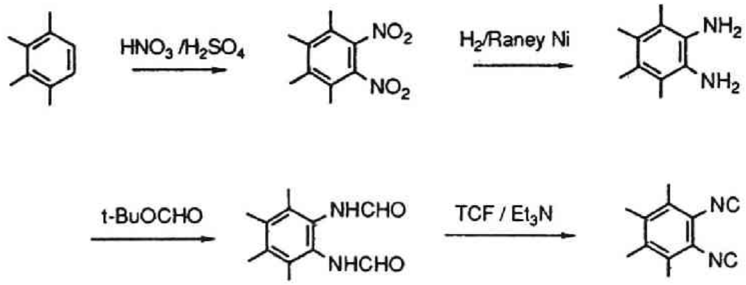
General. ^{1}H-NMR spectra were measured with a Varian VXR-200 and Gemini-200 spectrometer in $CDCl_3$. Chemical shifts are reported in δ ppm. Infrared spectra were measured with a Hitachi 270-30 spectrometer. Data are given in cm^{-1}. Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. UV spectra were measured with a UVIDEC-660. Preparative GPC on polystyrene was performed on a JAI LC-908 equipped with JAIGEL-1H and -2H columns($CHCl_3$).

Materials. All solvents were dried over appropriate desiccants and distilled under nitrogen. 1,2,3,4-Tetramethylbenzene was commercially available. Pivaloyl formate was prepared according to the reported procedure.[4]

Preparation of 1,2-diisocyano-3,4,5,6-tetramethylbenzene(1)

Diisocyanobenzene (1) was prepared following the scheme below.

Scheme 3



Preparation of 1,2-dinitro-3,4,5,6-tetramethylbenzene (5).

To ice-cooled conc. H_2SO_4(150ml) in a three necked flask equipped with thermometer, mechanical-stirrer and dropping funnel, tetramethylbenzene (27 g, 200 mmol) in $CHCl_3$(200 ml) was added dropwise at the temperature under 10°C and 250 ml of fuming HNO_3 under 50°C. After the addition, the reaction mixture was transferred to separate-funnel and acid layer was removed. The organic layer was neutralized by 10% Na_2CO_3aq. (1l) and washed twice with 2.5% Na_2CO_3aq. The $CHCl_3$ solution was dried with $CaCl_2$ and the solvent was evaporated after filtration. Resulting solid was recrystallized from EtOH. Yield 60%. ;

^{1}H-NMR ($CDCl_3$) 2.28 (s, 6H), 2.34 (s, 6H). IR (KBr) 2910, 1530, 1465, 1400, 1370, 870, 790, 730 cm^{-1}.

Preparation of 1,2-diamino-3,4,5,6-tetramethylbenzene (6).

To a solution of **5** (24 g, 107 mmol) in EtOH (300 ml) and AcOEt (300 ml) was added 2 g of raney-Ni(W1) and 0.3 g of H_2PtCl_6. The reaction mixture was stirred under H_2 atmosphere (1 atm) at r.t. for 30 hrs. Removal of the catalyst by filtration followed by evaporation of the solvent gave **6** in 90% yield.

^{1}H-NMR ; ($CDCl_3$) 2.15 (s, 6H), 2.18 (s, 6H), 3.32 (br-s, 4H). IR (KBr) 3300, 2924, 1684, 1464, 1334, 902, 822 cm^{-1}. MS m/e 164 (M+).

Preparation of 1,2-diformamido-3,4,5,6-tetramethylbenzene (7).

To a solution of **6** (0.93 g, 5.7 mmol) in $CHCl_3$(3 ml), pivaloyl formate (1.63 g, 12.5 mmol) was added dropwise at 0°C and stirred overnight at 0°C to r.t. The resulting suspension was filtered and the remaining white solid was washed with CH_2Cl_2 and dried in vacuo. Yield 80%.

IR (KBr) 3232, 2936, 1660, 1528, 1386, 1196, 790 cm^{-1}.

Preparation of 1,2-diisocyano-3,4,5,6-tetramethylbenzene (1).

To a suspension of **7** (0.92 g, 4.2 mmol) in CH_2Cl_2(4.2 ml) and triethylamine (3.4 ml), trichloromethyl chloroformate (0.84 ml, 7.0 mmol) in CH_2Cl_2(12.6 ml) was added dropwise at -78°C from dropping funnel. The mixture was stirred for 10 hrs at -78°C, then, gradually warmed up to -20°C. 10% Na_2CO_3aq. (23 ml) was added dropwise at that temperature and the organic layer was extracted with CH_2Cl_2 and washed twice with 10% Na_2CO_3aq. The solution was passed through a column of Florisil with CH_2Cl_2 and the solvent was removed by evaporation. The remaining solid was recrystallized from diisopropylether. Yield 70%.

^{1}H-NMR ($CDCl_3$) 2.25 (s, 6H), 2.38 (s, 6H). IR (KBr) 2940, 2124, 1456, 1390, 1048, 998 cm^{-1}. MS m/e 184 (M+). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.56; N, 15.20. Found: C, 78.51; H, 6.74; N, 15.13.

General Procedure of Oligomerization of 1,2-diisocyano-3,4,5,6-tetramethylbenzene by Grignard Reagent.

The reaction was carried out under a nitrogen atmosphere. In a two-necked flask, were placed 1,2-diisocyano-3,4,5,6-tetramethylbenzene (1) and dry solvent. To the homogeneous mixture was added Grignard reagent by syringe dropwise at 0°C. After the reaction finished, H_2O was added to the reaction mixture and the organic layer was washed with water twice and dried over Na_2SO_4. Evaporation of the solvent following the filtration gave the crude mixture of quinoxaline oligomers. The mixture was separated into each oligomer by preparative T.L.C. on silica gel and/or recycling H.P.L.C on polystyrene gel.

Spectral Data of Quinoxaline Oligomers

2A (R=i-Pr)

2A-a (n=1) ; ^{1}H-NMR ($CDCl_3$) 1.43 (d, 6H, J=7.0 Hz), 3.29 (sep, 1H, J=7.0 Hz), 2.41 (s, 6H), 2.74 (s, 3H), 2.75 (s, 3H), 8.67 (s, 1H). IR (KBr) 2986, 2932, 2876, 1472, 1382, 1286, 1192, 1150, 1116, 1066 cm^{-1}. MS m/e 228 (M+). Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.94; H, 9.04; N, 12.28.

2A-b (n=2) ; ^{1}H-NMR ($CDCl_3$) 1.45 (d, 6H, J=7.0 Hz), 2.46 (s, 3H), 2.48 (s, 3H), 2.50 (s, 6H), 2.82 (s, 12H), 4.44 (sep, 1H, J=7.0 Hz), 9.70 (s, 1H). IR (KBr) 2932, 2860, 1462 1380, 1264, 1134, 824, 804 cm^{-1}. MS m/e 412 (M+).

2A-c (n=3) ; ^{1}H-NMR ($CDCl_3$) 1.41 (d, 6H, J=7.0 Hz), 1.61 (s, 3H), 2.19 (s, 6H), 2.27 (s, 3H), 2.36 (s, 3H), 2.41 (s, 3H), 2.51 (s, 3H), 2.53 (s, 3H), 2.74 (s, 3H), 2.79 (s, 3H), 2.82 (s, 3H), 2.93 (s, 3H), 3.66 (sep, 1H, J=7.0 Hz), 9.92 (s, 1H). IR (KBr) 2968, 2932, 2872, 1732, 1466, 1380, 1276, 1150, 1120, 1072, 1052, 822 cm^{-1}. MS m/e 596 (M+).

2A-d (n=4) ; ^{1}H-NMR ($CDCl_3$) 1.33 (d, 6H, J=7.0 Hz), 1.75 (s, 3H), 1.77 (s, 3H), 2.13 (s, 3H), 2.21 (s, 3H), 2.31 (s, 6H), 2.32 (s, 6H), 2.36 (s, 3H), 2.38 (s, 3H), 2.41 (s, 3H), 2.47 (s, 3H), 2.72 (s, 3H), 2.75 (s, 3H), 2.80 (s, 3H), 2.82 (s, 3H), 3.90 (sep, 1H, J=7.0 Hz), 9.73 (s, 1H). IR (KBr) 2932, 1566, 1458, 1384, 1340, 1272, 1186, 1144, 1130, 1050, 822, 458 cm^{-1}. MS m/e 781 (M+).

2A-e (n=5) ; ^{1}H-NMR ($CDCl_3$) 1.48 (d, 6H, J=7.0 Hz), 1.87 (s, 3H), 1.92 (s, 3H), 1.95 (s, 3H), 1.99 (s, 3H), 2.14 (s, 3H), 2.16 (s, 6H), 2.17 (s, 3H), 2.19 (s, 3H), 2.20 (s, 6H), 2.25 (s, 3H), 2.35 (s, 3H), 2.38 (s, 6H), 2.42 (s, 3H), 2.76 (s, 3H), 2.77 (s, 3H), 2.79 (s, 3H), 2.90 (s, 3H), 4.12 (sep, 1H, J=7.0 Hz), 9.85 (s, 1H). IR (KBr) 2936, 1566, 1458, 1384, 1136, 1052, 822, 458 cm^{-1}. MS m/e 965 (M+).

2A-f (n=6) ; ^{1}H-NMR ($CDCl_3$) 1.42 (d, 6H, J=7.0 Hz), 1.85 (s, 3H), 1.88 (s, 3H), 1.96 (s, 3H), 2.03 (s, 6H), 2.07 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 2.15 (s, 3H), 2.18 (s, 3H), 2.21 (s, 3H), 2.23 (s, 6H), 2.25 (s, 3H), 2.38 (s, 3H), 2.41 (s, 6H), 2.79 (s, 6H), 2.83 (s, 3H), 2.90 (s, 3H), 4.22 (sep, 1H, J=7.0 Hz), 9.91 (s, 1H). IR (KBr) 2936, 1734, 1566, 1464, 1382, 1266, 1138, 1052, 820, 466 cm^{-1}. MS m/e 1149 (M+).

2B (R=n-Bu)

2B-a (n=1) ; ^{1}H-NMR ($CDCl_3$) 0.97 (t, 3H, J=7.0 Hz), 1.44 (sex, 2H, J=7.0 Hz), 1.84 (qu, 2H, J=8.0 Hz) 2.13 (s, 6H), 2.74 (s, 6H), 2.99 (t, 3H, J=8.0 Hz), 8.61 (s, 1H). IR (neat) 2961, 2937, 2877, 1570, 1468, 1380, 1340, 1300, 1172, 1110, 1050, 830, 756 cm^{-1}. MS m/e 242 (M+).

2B-b (n=2) ; ^{1}H-NMR ($CDCl_3$) 0.91 (t, 3H, J=7.0 Hz), 1.43 (sex, 2H, J=8.0 Hz), 1.88 (qu, 2H, J=8.0 Hz), 2.46 (s, 3H), 2.47 (s, 3H), 2.50 (s, 6H), 2.82 (s, 6H), 2.83 (s, 6H), 3.65 (t, 2H, J=8.0 Hz), 9.75 (s, 1H). IR (KBr) 2932, 1552, 1458, 1380, 1342, 1282, 1160, 1128, 1112, 1096, 1052, 824, 600, 460 cm^{-1}. MS m/e 426 (M+).

2B-c (n=3) ; ^{1}H-NMR ($CDCl_3$) 0.85 (t, 3H, J=7.0 Hz), 1.38 (sex, 2H, J=7.0 Hz), 1.71 (s, 3H), 1.98 (qu, 2H, J=8.0 Hz), 2.20 (s, 6H), 2.26 (s, 3H), 2.35 (s, 3H), 2.40 (s, 3H), 2.51 (s, 3H), 2.53 (s, 3H), 2.74 (s, 3H), 2.79 (s, 3H), 2.81 (s, 3H), 2.92 (s, 3H), 3.21 (t, 3H, J=8.0 Hz), 9.88 (s, 1H). IR (KBr) 2936, 1734, 1568, 1464, 1382, 1340, 1280, 1168, 1126, 1052, 824, 600, 458 cm^{-1}. MS m/e 610 (M+).

2B-d (n=4) ; ^{1}H-NMR ($CDCl_3$) 0.81 (t, 3H, J=7.0 Hz), 1.13 (sex, 2H, J=8.0 Hz), 1.64 (s, 3H), 1.68 (qu, 2H, J=8.0 Hz), 1.73 (s, 3H), 2.15 (s, 3H), 2.23 (s, 3H), 2.34 (s, 3H), 2.39 (s, 3H), 2.41 (s, 3H), 2.43 (s, 3H), 2.45 (s, 3H), 2.50 (s, 3H), 2.54 (s, 3H), 2.55 (s, 3H), 2.69 (s, 3H), 2.73 (s, 3H), 2.74 (s, 3H), 2.78

(s, 3H), 2.78 (t, 2H, J=8.0 Hz), 9.29 (s, 1H). IR (KBr) 2936, 2864, 1730, 1568, 1460, 1380, 1276, 1130, 824, 600, 462 cm^{-1}. MS m/e 795 (M+).

2B-e (n=5) ; ^1H-NMR ($CDCl_3$) 0.93 (t, 3H, J=7.0 Hz). 1.44 (sex, 2H, J=8.0 Hz), 1.82 (s, 3H), 1.93 (s, 3H), 1.97 (qu, 2H, J=8.0 Hz), 2.07 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 2.16 (s, 3H), 2.19 (s, 3H), 2.21 (s, 6H), 2.24 (s, 3H), 2.29 (s, 3H), 2.35 (s, 3H), 2.39 (s, 6H), 2.44 (s, 3H), 2.72 (s, 3H), 2.74 (s, 3H), 2.77 (s, 3H), 2.88 (s, 3H), 3.30 (t, 3H, J=8.0 Hz), 9.69 (s, 1H). IR (KBr) 2936, 2868, 1728, 1566, 1462, 1380, 1136, 1052, 822, 600, 460 cm^{-1}. MS m/e 979 (M+).

2C (R=iso-Bu)

2C-a (n=1) ; ^1H-NMR ($CDCl_3$) 0.98 (d, 6H, J=7.0 Hz), 2.26 (sep, 1H, J=7.0 Hz), 2.44 (s, 3H), 2.75 (s, 3H), 2.85 (d, 2H, J=7.0 Hz), 8.58 (s, 1H). IR (KBr) 2968, 2932, 2876, 1558, 1470, 1380, 1342, 1306, 1258, 1180, 1098, 1048, 822, 750, 460 cm^{-1}. MS m/e 242 (M+).

2C-b (n=2) ; ^1H-NMR ($CDCl_3$) 0.91 (d, 6H, J=7.0 Hz), 2.31 (sep, 1H, J=7.0 Hz), 2.46 (s, 3H), 2.47 (s, 3H), 2.49 (s, 6H), 2.82 (s, 9H), 2.84 (s, 3H), 3.60 (d, 2H, J=7.0 Hz), 9.72 (s, 1H). IR (KBr) 2960, 2932, 2876, 1552, 1464, 1380, 1342, 1164, 1128, 1104, 1052, 824, 598, 460 cm^{-1}. MS m/e 426 (M+).

2C-c (n=3) ; ^1H-NMR ($CDCl_3$) 0.97 (d, 6H, J=7.0 Hz), 1.70 (s, 3H), 2.20 (s, 6H), 2.27 (s, 3H), 2.36 (s, 3H), 2.41 (s, 3H), 2.50 (sep, 1H, J=7.0 Hz), 2.51 (s, 3H), 2.53 (s, 3H). 2.74 (s, 3H), 2.78 (s, 3H), 2.80 (s, 3H), 2.92 (s, 3H), 3.08 (d, 2H, J=7.0 Hz), 9,88 (s, 1H). IR (KBr) 2936, 1568, 1464, 1380, 1340, 1288, 1170, 1126, 1052, 824, 600, 460 cm^{-1}. MS m/e 611 (M+).

2C-d (n=4) ; ^1H-NMR ($CDCl_3$) 0.87 (d, 6H, J=7.0 Hz), 1.72 (s, 3H), 1.74 (s, 3H), 2.13 (s, 3H), 2.21 (s, 3H), 2.33 (s, 3H), 2.36 (s, 3H), 2.39 (s, 9H), 2.41 (s, 3H), 2.43 (s, 3H), 2.48 (s, 3H), 2.70 (s, 3H), 2.74 (s, 3H), 2.79 (s, 3H), 2.81 (s, 3H), 3.00 (d, 2H, J=7.0 Hz), 9.58 (s, 1H). IR (KBr) 2932, 1568, 1458, 1382, 1340, 1170, 1130, 1050, 822, 600, 458 cm^{-1}. MS m/e 795 (M+).

2C-e (n=5) ; ^1H-NMR ($CDCl_3$) 1.06 (d, 6H, J=7.0 Hz), 1.89 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 2.16 (s, 9H), 2.19 (s, 3H), 2.21 (s, 6H), 2.26 (s, 3H), 2.34 (s, 3H), 2.39 (s, 6H), 2.42 (s, 3H), 2.75 (s, 6H), 2.79 (s, 3H), 2.89 (s, 3H), 3.34 (d, 2H, J=7.0 Hz), 9.78 (s, 1H). IR (KBr) 2932, 1566, 1460, 1384, 1340, 1130, 1052, 822, 600, 460 cm^{-1}. MS m/e 979 (M+).

2C-f (n=6) ; ^{1}H-NMR ($CDCl_3$) 1.08 (d, 6H, J=7.0 Hz), 1.8-3.5 (m, 75H), 9.89 (s, 1H). IR (KBr) 2932, 1566, 1458, 1384, 1132, 1052, 820, 600, 458 cm^{-1}. MS m/e 1163 (M+).

2D (R=t-Bu)

2D-a (n=1) ; ^{1}H-NMR ($CDCl_3$) 1.49 (s, 9H), 2.44 (s, 6H), 2.74 (s, 3H), 2.76 (s, 3H), 8.88 (s, 1H). IR (KBr) 2964, 2936, 1556, 1480, 1464, 1376, 1368, 1148, 1110, 1046, 912, 824, 590, 466 cm^{-1}. MS m/e 242 (M+).

2D-b (n=2) ; ^{1}H-NMR ($CDCl_3$) 1.41 (s, 9H), 2.44 (s, 3H), 2.47 (s, 3H), 2.49 (s, 3H), 2.51 (s, 3H), 2.70 (s, 3H), 2.74 (s, 3H), 2.81 (s, 3H), 2.84 (s, 3H), 9.13 (s, 1H). IR (KBr) 2960, 2932, 1568, 1460, 1392, 1380, 1342, 1290, 1142, 1100, 1050, 824, 598, 458 cm^{-1}. MS m/e 426 (M+).

2D-c (n=3) ; ^{1}H-NMR ($CDCl_3$) 1.53 (S, 9H), 1.68 (s, 3H), 2.17 (s, 3H), 2.20 (s, 3H), 2.24 (s, 3H), 2.34 (s, 3H), 2.40 (s, 3H), 2.51 (s, 3H), 2.53 (s, 3H), 2.73 (s, 3H), 2.75 (s, 3H), 2.83 (s, 3H), 2.94 (s, 3H), 9.97 (s, 3H). IR (KBr) 2936, 1730, 1462, 1380, 1342, 1282, 1144, 1072, 824 cm^{-1}. MS m/e 610 (M+).

2D-d (n=4) ; ^{1}H-NMR ($CDCl_3$) 1.64 (s, 9H), 1.93 (s, 3H), 1.97 (s, 3H), 2.04 (s, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 2.21 (s, 3H), 2.27 (s, 6H), 2.32 (s, 3H), 2.37 (s, 3H), 2.39 (s, 3H), 2.43 (s, 3H), 2.77 (s, 6H), 2.79 (s, 3H), 2.81 (s, 3H), 9.82 (s, 1H). IR (KBr) 2932, 1738, 1566, 1456, 1384, 1278, 1142, 1130, 1052, 824 cm^{-1}. MS m/e 795 (M+).

2D-e (n=5) ; ^{1}H-NMR ($CDCl_3$) 1.64 (s, 9H), 1.89 (s, 6H), 1.93 (s, 3H), 1.96 (s, 3H), 2.12 (s, 3H), 2.16 (s, 6H), 2.20 (s, 6H), 2.24 (s, 3H), 2.27 (s, 3H), 2.28 (s, 3H), 2.36 (s, 3H), 2.37 (s, 6H), 2.43 (s, 3H), 2.74 (s, 3H), 2.75 (s, 3H), 2.81 (s, 3H), 2.91 (s, 3H), 9.89 (s, 1H). IR (KBr) 2936, 1568, 1464, 1384, 1142, 1052, 822, 600, 458 cm^{-1}. MS m/e 979 (M+).

References and Notes.

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Chapter 2

New Living Polymerization of 1,2-Diisocyanoarenes via (Quinoxalinyl)palladium Complexes --- Synthesis of Poly(2,3-quinoxaline)

Abstract

New Living Polymerization of 1,2-diisocyanoarene giving poly(2,3-quinoxaline) via (quinoxalinyl)palladium complexes was developed. 1,2-Diisocyano-3,4,5,6-tetramethylbenzene reacted with trans-bromobis(dimethylphenylphosphine)methylpalladium(II) (1.2 equiv) at room temperature in THF to afford trans-bromobis(dimethylphenylphosphine)(2-methylquinoxalin-3-yl)palladium(II) quantitatively. Oligomerization of 1,2-diisocyanoarene with the increased feeding ratio of diisocyanoarene to methylpalladium complex, was propagated at reflux in THF to give a mixture of oligomeric (2,3-quinoxalinyl)palladium complexes in good total yields. The reactive propagating species of this living polymerization can be isolated and fully characterized. X-ray structural analysis revealed that the (di, ter and quater-quinoxalinyl)palladium complexes exist in distorted square pyramidal five-coordination in which nitrogen atom of the second quinoxaline unit coordinates to palladium atom at an axial position. Soluble higher polymer with regular poly(2,3-quinoxaline) structure was successfully synthesized by use of 1,2-diisocyano-3,6-bis(trimethylsilylmethyl)benzene. The produced polymer was of Mn = 4830 and soluble in common organic solvents such as chloroform and THF. It should be noted that GPC using polystyrene as standard indicated very sharp distribution of molecular weight Mw/Mn = 1.08.

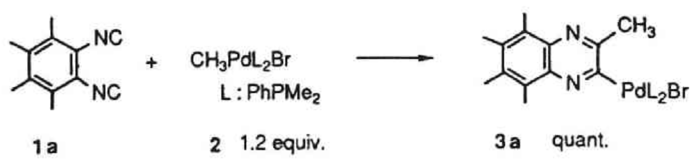
Introduction

Polymerization of isocyanides catalyzed by transition metal complexes involves a multiple successive insertion of isocyano groups into carbon-metal linkage.[1] The author's group has been studying a series of insertion reactions of isocyanides with organometallic compound.[2] In chapter 1, the author describes that Grignard reagents promote new aromatizing oligomerization of 1,2-diisocyanoarene, which may arise from successive insertion of ortho-isocyano groups on 1,2-diisocyanoarene into carbon-magnesium bond.[3] However, the propagation of the oligomerization of 1,2-diisocyanoarene is rapidly terminated to give a mixture of quinoxaline oligomers from the monomer up to the hexamer, because of instability of the propagating organomagnesium species. In this chapter, the author describes new living polymerization of 1,2-diisocyanoarene giving poly(2,3-quinoxaline) via (quinoxalinyl)palladium complexes.

Results and Discussion

1,2-Diisocyano-3,4,5,6-tetramethylbenzene (1a) reacted with trans-bromobis(dimethylphenylphosphine)methylpalladium(II) (2, 1.2 equiv) at room temperature in THF to afford trans-bromobis (dimethylphenylphosphine)(2,5,6,7,8-pentamethylquinoxalin-3-yl)palladium(II) (3a) quantitatively (Scheme 1). The (quinoxalinyl)palladium complex (3a) thus formed is stable in air and isolated by TLC on silica gel. A crystal suitable for X-ray structural analysis was obtained by recrystallization from dichloromethane-hexane and crystal structure is shown in Figure 1.

Scheme 1



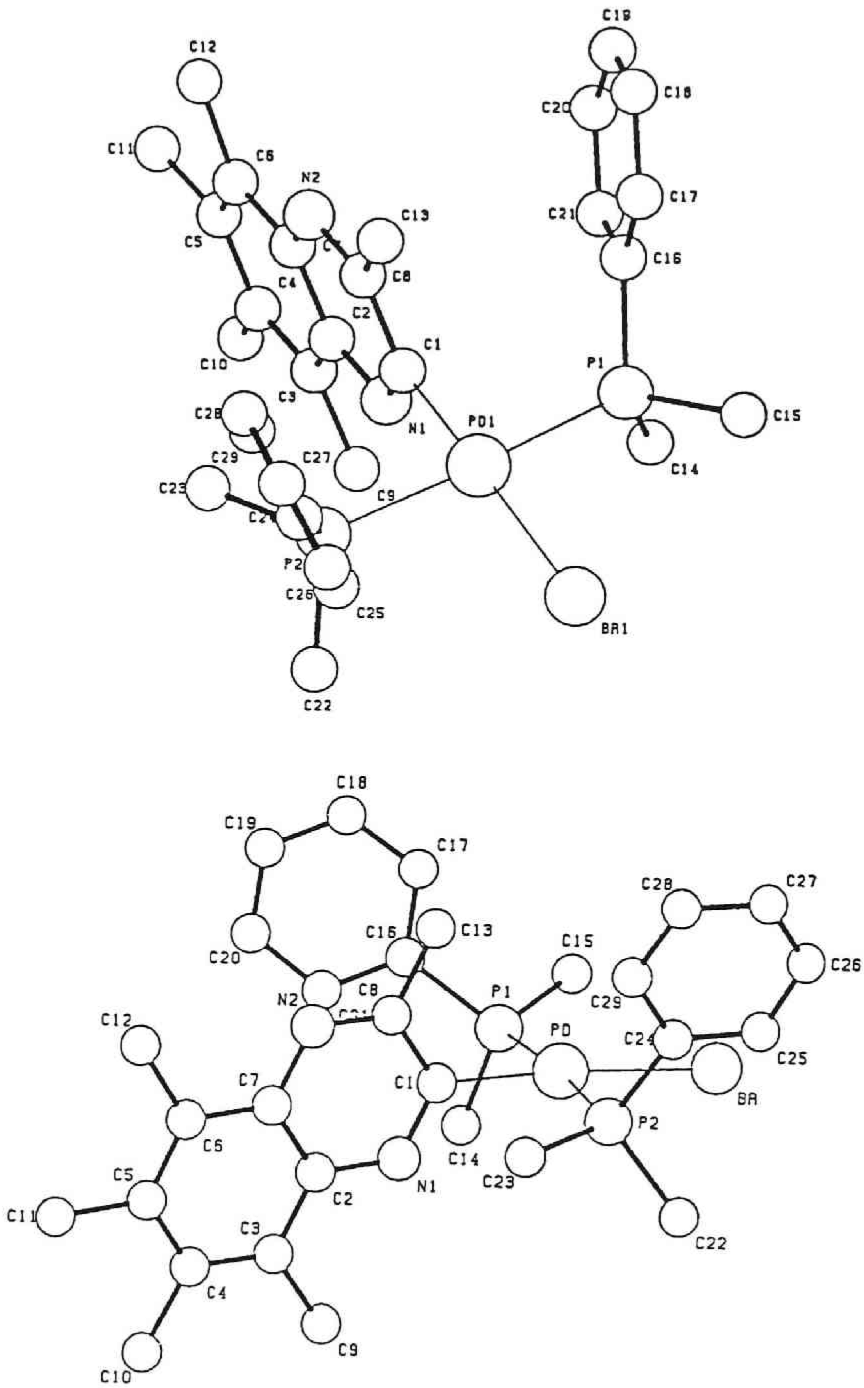


Figure 1. Structure of **3a**.

Oligomerization of 1,2-diisocyanoarene with the increasing feeding ratio of **1a**/**2**, was propagated at reflux in THF to give a mixture of oligomeric (2,3-quinoxalinyl)palladium complexes (**3b-h**) in good total yields, which were transformed to (trimethylsilylmethyl)quinoxaline derivatives (**4b-h**) for isolation by the reaction with (trimethylsilylmethyl)magnesium chloride. As seen from Table 1, the higher oligomers were produced with the higher feeding ratio of **1a**/**2**. Although further polymerization also proceeded with the feeding ratio of over 7, insoluble polymers were produced.

Scheme 2

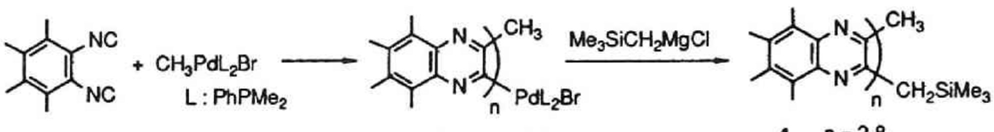


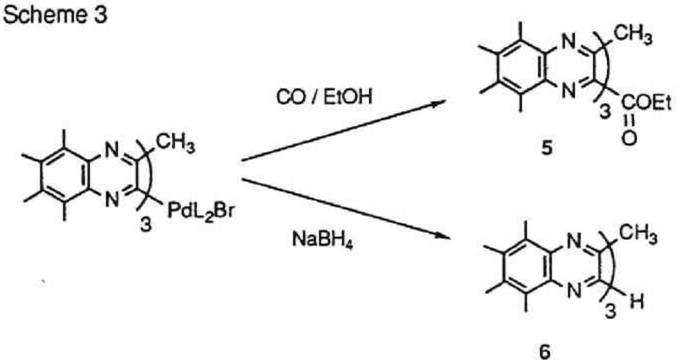
Table 1. Reaction of **1a** with **2**.

	Yield %							
1a/**2**	**4b**(n=2)	**4c**(n=3)	**4d**(n=4)	**4e**(n=5)	**4f**(n=6)	**4g**(n=7)	**4h**(n>7)	total
2	37	27	6	0	0	0	0	70
3	20	49	16	2	0	0	0	87
5	0	9	20	22	17	9	2	79
7	0	0	6	9	20	15	6	56

The living polymerization mentioned above should be propagated via (quinoxalinyl)palladium complexes which undergo successive insertion of ortho-isocyano groups on 1,2-diisocyanoarene into carbon-palladium linkage. Indeed, treatment of (biquinoxalinyl)palladium complex **3b** once isolated[4] with **1a** (2 equiv) resulted in the propagation to form a mixture of ter-quinoxaline (**3c**, 27%), quater-quinoxaline (**3d**, 28%), quinque-quinoxaline (**3e**, 17%) and sexi-quinoxaline (**3f**, 4%).[5] The structures of (bi-, ter- and quater-quinoxalinyl)palladium complexes **3c**, **3d** and **3e** were determined by X-ray crystallography (Figure 2, 3 and 4). Noteworthy is that these quinoxalinylpalladium complexes exist in distorted square pyramidal five-coordination[6] in which nitrogen atom of the second quinoxaline unit coordinates to palladium atom at an axial position. It is of much interest that the reactive propagating species of living polymerization can be isolated and fully characterized.

As shown in scheme 3, two substitution reactions were carried out on ter-quinoxalinylpalladium complex (**3c**). Reaction with carbon monoxide in the presence of ethanol gave quinoxaline trimer (**5**) which had ethyl ester group instead of Pd moiety of **3c**. Hydrogen was introduced by the reaction with $NaBH_4$.

Scheme 3



Finally, soluble higher polymer with regular poly(2,3-quinoxaline) structure was successfully synthesized by use of 1,2-diisocyano-3,6-bis(trimethylsilylmethyl)benzene (**1b**) ; the reaction of **1b** with **2** (**1b**/**2**=19) proceeded at reflux in THF to afford quinoxaline polymer **7** of Mn=4830 as determined by VPO in 65% yield, which was soluble in common organic solvents such as chloroform and THF. It should be noted that GPC using polystyrene as standard indicated very sharp distribution of molecular weight Mw/Mn = 1.08.

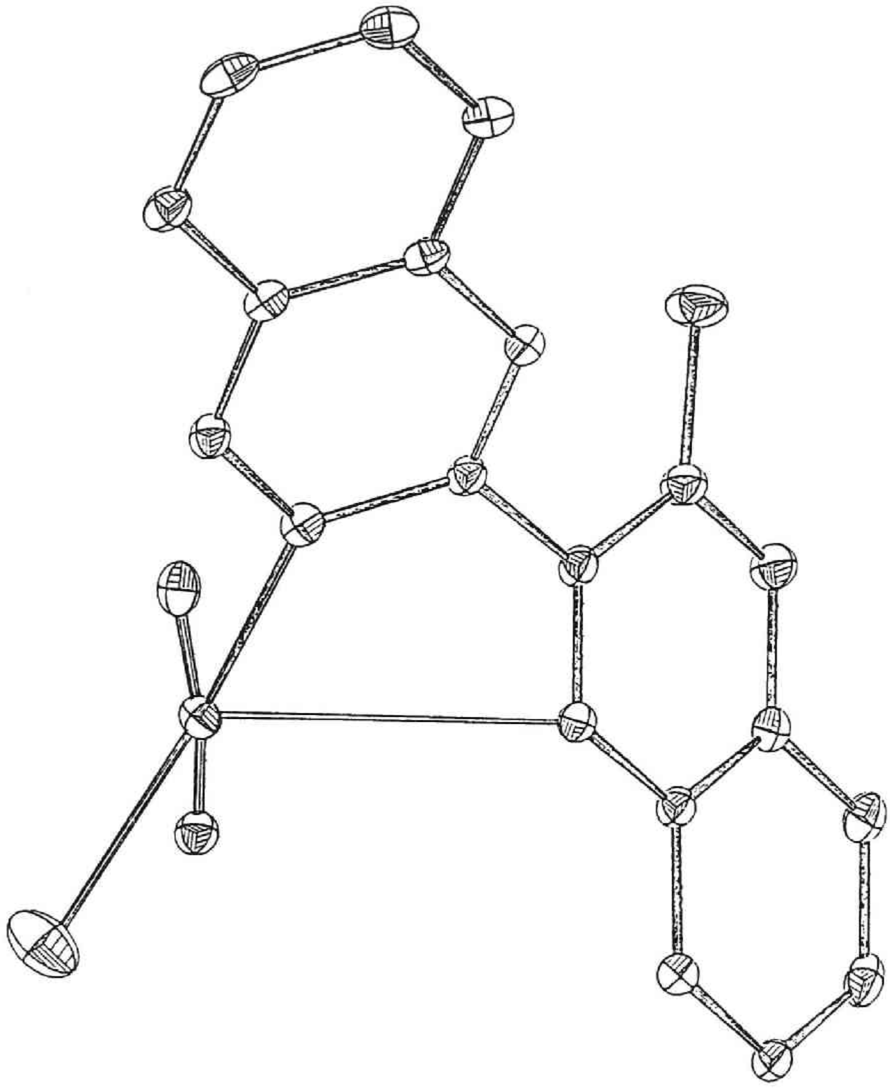


Figure 2. Structure of 3b.

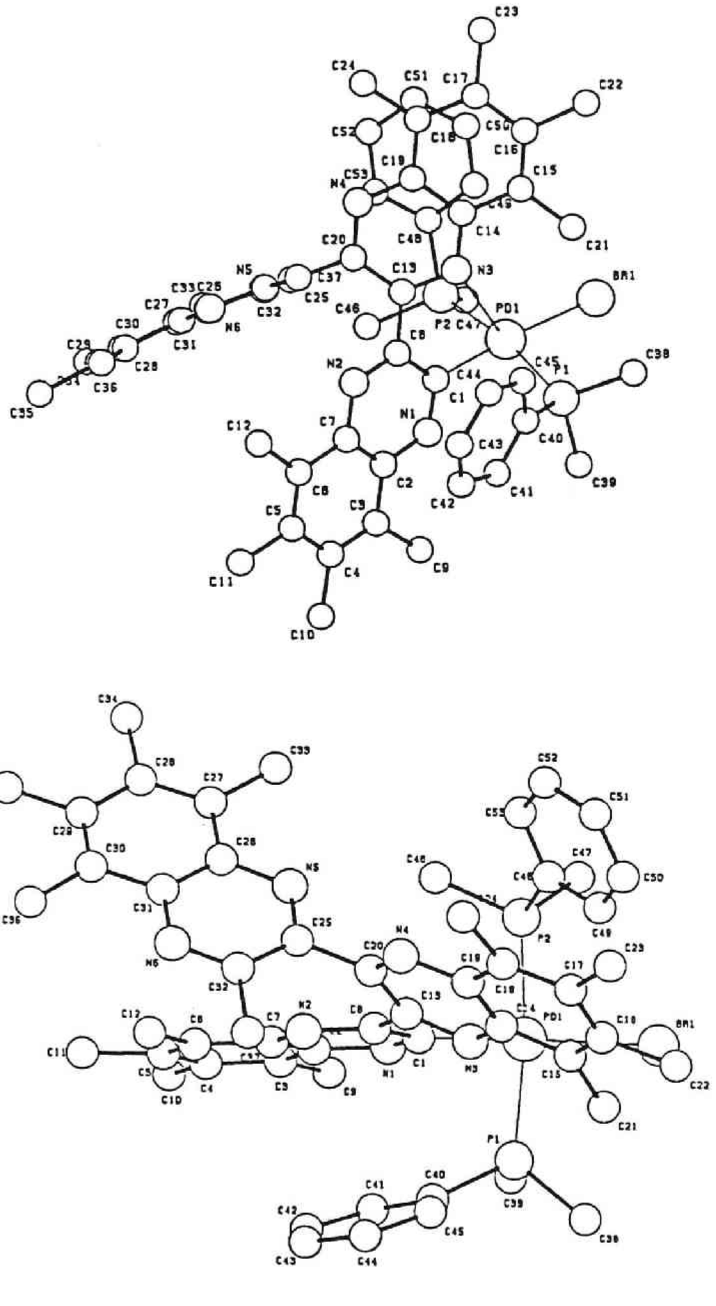


Figure 3. Structure of **3c**.

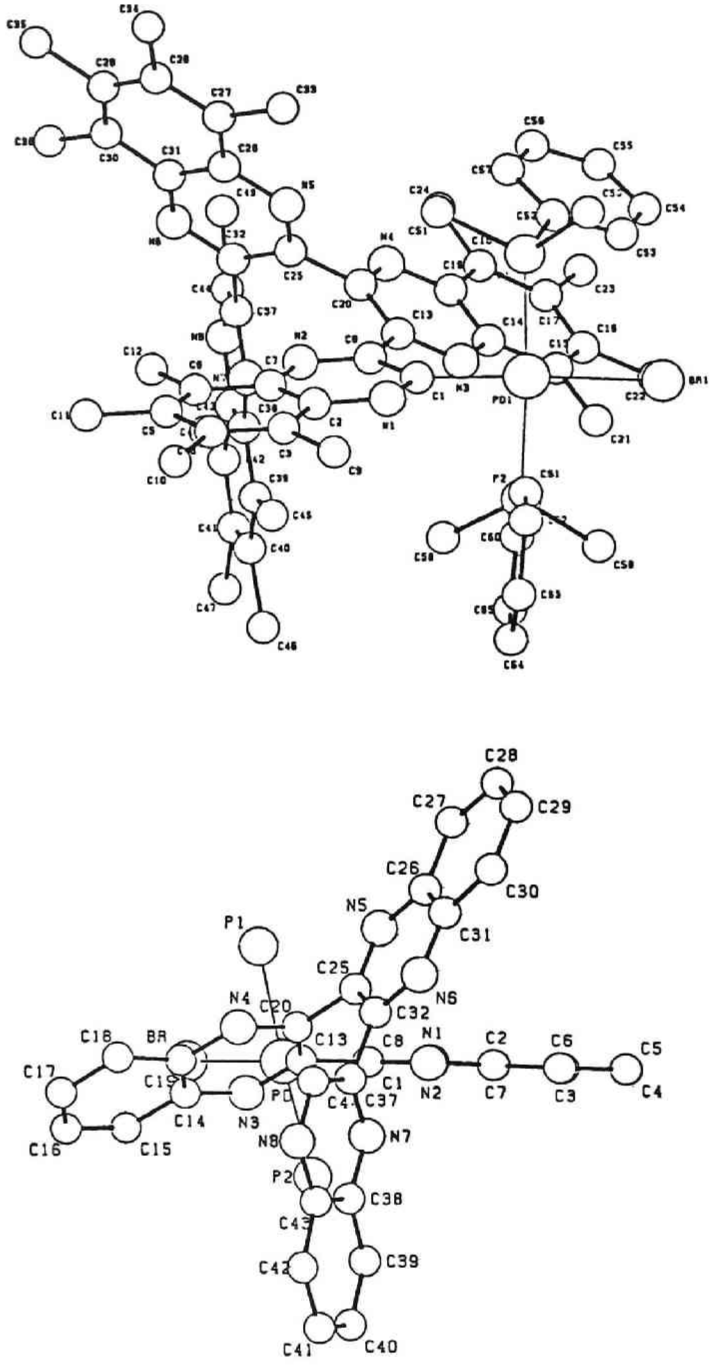
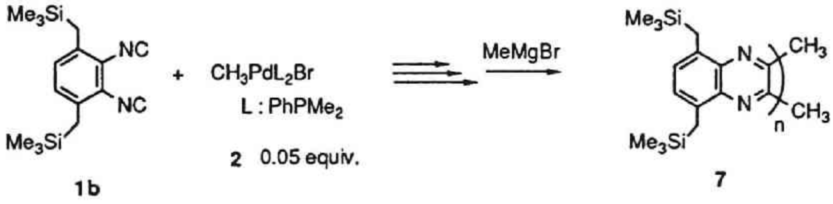


Figure 4. Structure of **3d**.

Scheme 4



This method for the controlled living polymerization offers a new entry to poly(heteroaromatics), which have attracted increasing attention owing to their interesting properties.

Experimental Section

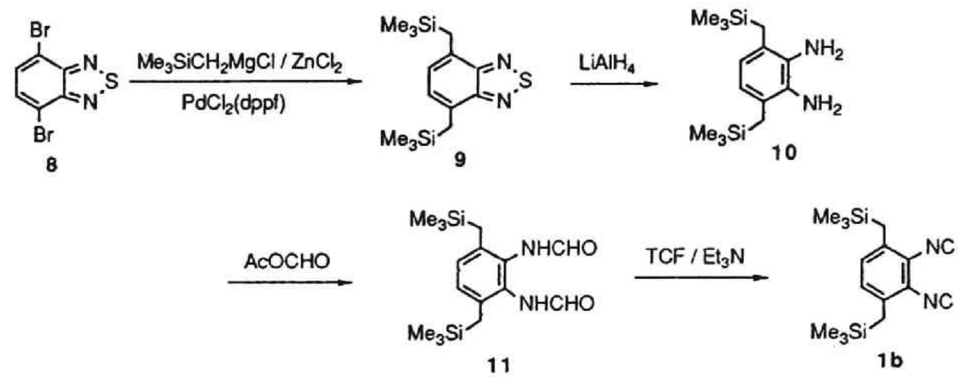
General. ^{1}H-NMR spectra were measured with a Varian VXR-200 and Gemini-200 spectrometer in $CDCl_3$. Chemical shifts are reported in δ ppm. Infrared spectra were measured with a Hitachi 270-30 spectrometer. Data are given in cm^{-1}. UV spectra were recorded with a UVIDEC-660. The molecular weights of polymers were measured by a Corona 117 vapor pressure osmometer in chloroform at 40°C. Gel permeation chromatographic analysis (GPC) were carried out on a Toyo-Soda HLC-8020 (Toyo-Soda G3000) by using THF as a eluent and polystyrene as a standard. Recycling H.P.L.C. purification was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns($CHCl_3$).

Materials. All solvents were dried over appropriate desiccants and distilled under nitrogen. Preparation of 1,2-diisocyano-3,4,5,6-tetramethylbenzene(**1a**) was described in Chapter 1. Trans-bromobis(dimethylphenylphosphine)methylpalladium(II)(**2**)[7], 4,6-Dibromo-2,1,3-benzothiadiazol[8], acetylformate[9] were prepared according to the literature method.

Preparation of 1,2-diisocyano-3,6-bis(trimethylsilylmethyl)-benzene.(1b)

1,2-Diisocyano-3,6-bis(trimethylsilyl)benzene was prepared following the scheme below.

Scheme 5



Preparation of 4,6-Bis(trimethylsilylmethyl)-2,1,3-benzothiadiazol.(9)

To a THF solution (30 mL) of $ZnCl_2$ (6 g, 43.8 mmol) was added a ether solution of of $TMSCH_2MgCl$ (22.5 mmol) dropwise and the mixture was stirred at r.t. for 30 min. Then, a mixture of **8** (2.0 g, 6.8 mmol) and $NiCl_2$dppp (0.2 g, 0.37 mmol) in THF (100 mL) was added. The mixture was heated at reflux for 10 hrs. Extractive workup with CH_2Cl_2 and water gave **9** in 91% yield.

^{1}H-NMR ($CDCl_3$) -0.05 (s, 18H), 2.56 (s, 4H), 7.03 (s, 2H). IR (KBr) 2964, 2904, 1592, 1558, 1490, 1412, 1338, 1250, 1160, 1018, 848, 696, 638 cm^{-1}. MS m/e 308 (M+).

Preparation of 3,6-Bis(trimethylsilylmethyl)-1,2-diaminobenzene.(10)

To a THF solution (100 mL) of **9** (2.3 g, 7.5 mmol), $LiAlH_4$ (2.1 g, 55 mmol) was added at 0°C. The mixture was heated at reflux for 3 hrs. After excess of $LiAlH_4$ was quenched with water, extractive work up with CH_2Cl_2 and water gave **10** in 97% yield.

^{1}H-NMR ($CDCl_3$) 0.02 (s, 18H), 1.92 (s, 4H), 3.20 (br-s, 4H), 6.37 (s, 2H). IR (KBr) 3452, 3352, 3232, 3960, 2896, 1616, 1496, 1456, 1250, 1160, 848, 696 cm^{-1}.

Preparation of 1,2-diformamido-3,6-bis(trimethylsilylmethyl)benzene.(11)

To a CH_2Cl_2 solution (10 mL) of 10 (0.53 g, 1.9 mmol), acetylformate (1.3 g, 14.7 mmol) was added at 0°C and the solution was stirred overnight gradually warming up to r.t. After removal of the solvent, column chromatography on silica gel (AcOEt) afforded **11** in 85% yield.

IR (KBr) 3256, 2964, 2904, 1678, 1520, 1482, 1388, 1300, 1250, 1152, 850, 756, 694 cm^{-1}.

Preparation of 1,2-diisocyano-3,6-bis(trimethylsilylmethyl)benzene.

A CH_2Cl_2 suspension (10 mL) of **11** (0.74 g, 2.2 mmol) and Et_3N (4 mL, 28.7 mmol) was cooled to -78°C. A CH_2Cl_2 solution (15 ml) of trichloromethylchloroformate (1.5 mL, 12.4 mmol) was added dropwise at -78°C. The mixture was stirred at -78°C for 10 hrs, then gradually warmed up to -30°C. At -30°C, 10% Na_2CO_3 aq. (50 mL) was added dropwise. Extractive workup with CH_2Cl_2 and 10% Na_2CO_3 aq. followed by column chromatography on silica gel (n-hexane : ether = 10:1) gave **1b** in 85% yield.

^{1}H-NMR 0.04 (s, 18H), 2.25 (s, 4H), 6.97 (s, 2H). IR (KBr) 2968, 2912, 2116, 1490, 1424, 1254, 1150, 978, 920, 852, 698, 634 cm^{-1}. MS m/e 300 (M+). Anal. Calcd for $C_{16}H_{24}N_2Si_2$: C, 63.94; H, 8.05; N, 9.32. Found: C, 63.64; H, 8.10; N, 9.21.

Oligo(quinoxalinyl)palladium(II) complexes(3a-d)

Oligo(quinoxalinyl)palladium(II) complexes were obtained by the reaction of **1a** and **2** in THF at r.t. and separated into each oligomer by preparative TLC (silica gel) and recrystallized from n-hexane and CH_2Cl_2.

3a : mp 190°C (dec). ^{1}H-NMR ($CDCl_3$) 1.48 (t, 6H, J_{P-H} = 3.6 Hz), 1.52 (t, 6H, J_{P-H} = 3.6 Hz), 2.29 (s, 3H), 2.37 (s, 3H), 2.41 (s, 3H), 2.57 (s, 3H), 2.68 (s, 3H), 7.10-7.45 (m, 10H) ; IR (KBr) 2916, 1530, 1438, 1376, 1340, 1284, 1218, 1188, 1102, 1056, 952, 910, 848, 758, 736, 718, 692, 486, 428 cm^{-1}. Anal. Calcd for $C_{29}H_{37}BrN_2P_2Pd$: C, 52.62; H, 5.63; N, 4.23. Found: C, 52.55; H, 5.67; N, 4.24.

3b : mp 240°C (dec). ^{1}H-NMR ($CDCl_3$) 1.43-1.56 (m, 6H), 2.39 (s, 3H), 2.40 (s, 3H), 2.42 (s, 3H), 2.50 (s, 6H), 2.53 (s, 3H), 2.61 (s, 3H), 2.72 (s, 3H), 3.17 (s, 3H), 6.8-7.3 (m, 10H). IR (KBr) 2920, 1560, 1510, 1438, 1378, 1262, 1194, 1114, 1150, 948, 910, 840, 738, 694, 484, 456, 424 cm^{-1}. Anal. Calcd for $C_{41}H_{49}BrN_4P_2Pd$: C, 58.20; H, 5.84; N, 6.62. Found: C, 58.41; H, 5.78; N, 6.48.

3c : mp 260°C (dec). ^{1}H-NMR ($CDCl_3$) 1.4-1.6 (m, 12H), 1.71 (s, 3H), 2.11 (s, 3H), 2.26 (s, 3H), 2.39 (s, 3H), 2.41 (s, 3H), 2.45 (s, 6H), 2.49 (s, 6H), 2.65 (s, 3H), 2.72 (s, 3H), 2.81 (s, 3H), 3.18 (s, 3H), 6.7-7.4 (m, 10H). IR (KBr) 2924, 1506, 1458, 1438, 1378, 1122, 1050, 948, 908, 740, 692, 486 cm^{-1}. Anal. Calcd for $C_{53}H_{61}BrN_6P_2Pd$: C, 61.78; H, 5.97; N, 8.16. Found: C, 61.69; H, 6.06; N, 8.07.

3d : ^{1}H-NMR ($CDCl_3$) 0.97 (d, 3H, J=5.2 Hz), 1.35 (d, 3H, J=5.6 Hz), 1.62 (s, 3H), 1.71 (d, 3H, J=6.1 Hz), 1.85 (d, 3H, J=6.3 Hz), 1.95 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 2.12 (s, 3H), 2.20 (s, 3H), 2.28 (s, 6H), 2.31 (s, 9H), 2.32 (s, 3H), 2.46 (s, 3H), 2.72 (s, 3H), 2.85 (s, 3H), 3.01 (s, 3H), 3.10 (s, 3H), 6.63 (br-s, 3H), 7.28 (br-s, 3H), 7.45 (br-s, 2H), 7.68 (br-s, 2H). IR (KBr) 2924, 1458, 1440, 1378, 1196, 1128, 1052, 948, 908, 740, 692 cm^{-1}.

Typical experimental procedure for reaction of 1,2-diisocyano-3,4,5,6-tetramethylbenzene(1b) with trans-bromobis(dimethylphenylphosphine)methylpalladium(II)(2).

A mixture of **1b** and **2** in dry THF was refluxed for 15 min under nitrogen. After cooling to 0°C, (trimethylsilylmethyl)magnesium chloride in ether was added and the mixture was refluxed for 30 min. Extractive workup with chloroform-aqueous buffer solution (pH 7) followed by short column chromatography on silica gel afforded a mixture of **4b**, **4c**. **4d** and **4e**, which were isolated in 20%, 49%, 16% and 2% yields, respectively, by recycling HPLC on polystyrene gel.

Spectral data for quinoxaline oligomers.

4b (n=2) : ^{1}H-NMR ($CDCl_3$) 0.07 (s, 9H), 2.44 (s, 3H), 2.46 (s, 3H), 2.48 (s, 3H), 2.49 (s, 3H), 2.71 (s, 3H), 2.73 (s, 3H), 2.74 (s, 3H), 2.79 (s, 3H), 2.82 (s, 3H). IR (KBr) 2956, 2932, 1464, 1378, 1298, 1248, 1192, 1112, 854 cm^{-1}. MS m/e 470 (M+). Anal. Calcd for $C_{29}H_{38}N_4Si$: C, 74.00; H, 8.14; N, 11.90. Found:

C, 73.76; H, 8.31; N, 11.87.

4c (n=3) : ^{1}H-NMR ($CDCl_3$) 0.14 (s, 9H), 2.12 (s, 3H), 2.14 (s, 3H), 2.20 (s, 3H), 2.21 (s, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 2.52 (s, 6H), 2.68 (s, 3H), 2.72 (s, 3H), 2.81 (s, 3H), 2.85 (s, 3H), 3.02 (s, 3H), 3.06 (s, 2H). IR (KBr) 2932, 1462, 1380, 1284, 1122, 854 cm^{-1}. MS m/e 654 (M+). Anal. Calcd for $C_{41}H_{50}N_6Si$: C, 75.19; H, 7.69; N, 12.83. Found: C, 75.45; H, 7.80; N, 12.81. UV (CH_2Cl_2) 256 nm (ε = 35900), 276 nm (ε = 31800), 354 nm (ε = 18800).

4d (n=4) : ^{1}H-NMR ($CDCl_3$) 0.06 (s, 9H), 1.98 (s, 3H), 2.03 (s, 3H), 2.18 (s, 3H), 2.21 (s, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 2.34 (s, 6H), 2.37 (s, 6H), 2.41 (s, 6H), 2.68 (s, 2H), 2.71 (s, 6H), 2.74 (s, 6H), 2.75 (s, 3H). IR (KBr) 2928, 1566, 1458, 1380, 1276, 1128, 1050, 852, 760, 458 cm^{-1}. MS m/e 839 (M+). Anal. Calcd for $C_{53}H_{62}N_8Si$: C, 75.85; H, 7.45; N, 13.35. Found: C, 75.52; H, 7.66; N, 12.63. UV (CH_2Cl_2) 256 nm (ε = 59200), 281 nm (ε = 55800), 354 nm (ε = 35100)

4e (n=5) : ^{1}H-NMR ($CDCl_3$) 0.15 (s, 9H), 1.93 (s, 6H), 2.09 (s, 6H), 2.12 (s, 6H), 2.16 (s, 6H), 2.21 (s, 3H), 2.22 (s, 3H), 2.25 (s, 3H), 2.26 (s, 3H), 2.34 (s, 3H), 2.36 (s, 3H), 2.41 (s, 3H), 2.43 (s, 3H), 2.74 (s, 3H), 2.76 (s, 3H), 2.80 (s, 3H), 2.83 (s, 3H), 3.05 (s, 3H), 3.07 (s, 2H). IR (KBr) 2928, 1458, 1380, 1130, 1050, 854 cm^{-1}. MS m/e 1023 (M+).

4f (n=6) : ^{1}H-NMR ($CDCl_3$) 0.18 (s, 9H), 1.9-3.2 (m, 77H). IR (KBr) 2932, 1456, 1380, 1134, 1050, 854 cm-1. MS m/e 1207 (M+). Anal. Calcd for $C_{77}H_{86}N_{12}Si$: C, 76.58; H, 7.18; N, 13.92. Found: C, 77.57; H, 7.78; N, 13.74.

4g (n=7) : ^{1}H-NMR ($CDCl_3$) 0.17 (s, 9H), 1.9-3.2 (m, 89H). IR (KBr) 2932, 1458, 1382, 1130, 1052, 854, 820 cm^{-1}. MS m/e 1391 (M+).

4h (n>8) : ^{1}H-NMR ($CDCl_3$) 0.18 (s), 1.9-3.2 (m). IR (KBr) 2932, 2860, 1458, 1382, 1130, 1052 cm^{-1}.

Reactions of quinoxalinylpalladium complex 3c.

A. Reaction with carbon monoxide.

To a EtOH solution (2 ml) of **3c** (6.3 mg, 6.1×10^{-6} mol) in an autoclave was introduced gaseous CO to a pressure of 40 kg/cm^2. The autoclave was heated at 100°C for 70 hrs. Preparative TLC of the cooled reaction mixture on silica gel (n-hexane : ether =

4:1) afforded 5 in 72% yield.

5 : ^{1}H-NMR ($CDCl_3$) 1.06 (t, 3H, J=7.0 Hz), 1.97 (s, 3H), 2.21 (s, 3H), 2.25 (s, 6H), 2.36 (s, 3H), 2.37 (s, 3H), 2.50 (s, 6H), 2.75 (s, 6H), 2.78 (s, 3H), 2.82 (s, 3H), 3.02 (s, 3H), 4.30 (qu, 2H, J=7.0 Hz). IR (KBr) 2932, 1740, 1462, 1380, 1248, 1150 cm^{-1}. MS m/e 640 (M+). Anal. Calcd for $C_{36}H_{40}N_6$: C, 78.14; H, 7.09; N, 14.78. Found: C, 77.12; H, 7.01; N, 14.76.

B. Reaction with sodium borohydride.

To a THF solution (2ml) of **3c** (5.9 mg, $5.7x10^{-6}$ mol) was added 20mg of $NaBH_4$ and the solution was stirred at r.t. for 1.5 hrs. Extractive workup with $CHCl_3$ and water followed by preparative TLC on silica gel (n-hexane : ether = 8:2) afforded 6 in 83% yield.

6 : ^{1}H-NMR ($CDCl_3$) 1.73 (s, 3H), 2.21 (s, 3H), 2.24 (s, 3H), 2.28 (s, 3H), 2.36 (s, 3H), 2.41 (s, 3H), 2.51 (s, 3H), 2.53 (s, 3H), 2.74 (s, 3H), 2.78 (s, 3H), 2.80 (s, 3H), 2.88 (s, 3H), 2.92 (s, 3H), 9.89 (s, 1H). IR (KBr) 2932, 1736, 1456, 1380, 1284, 1194, 1126, 1050, 822, 602 cm^{-1}. MS m/e 568 (M+).

Polymerization of 1,2-diisocyano-3,6-bis(trimethylsilylmethyl)benzene catalyzed by trans-bromobis(dimethylphenylphosphine)methylpalladium(II) complex.

A mixture of **1b** and 2 in dry THF was refluxed for 24 hrs. under nitrogen. (Trimethylsilylmethyl)magnesium chloride in ether was added at r.t. and extractive workup with CH_2Cl_2 and water gave crude polymer. Purification was carried out by HPLC on polystyrene ($CHCl_3$). Yield 65%.

^{1}H-NMR ($CDCl_3$) -0.8-0.2 (m), 1.0-3.2 (m), 6.4-7.5 (m). IR (KBr) 2964, 2904, 1590, 1464, 1416, 1372, 1250, 1160, 1062, 1040, 852, 762, 694 cm^{-1}. Mn=4830 (VPO in $CHCl_3$), Mw/Mn=1.08 (GPC in THF, polystyrene as a standard). UV (CH_2Cl_2) 275 nm (ε = 171000).

Figure 5. Atom Numbering in the Crystal Data of **3b**

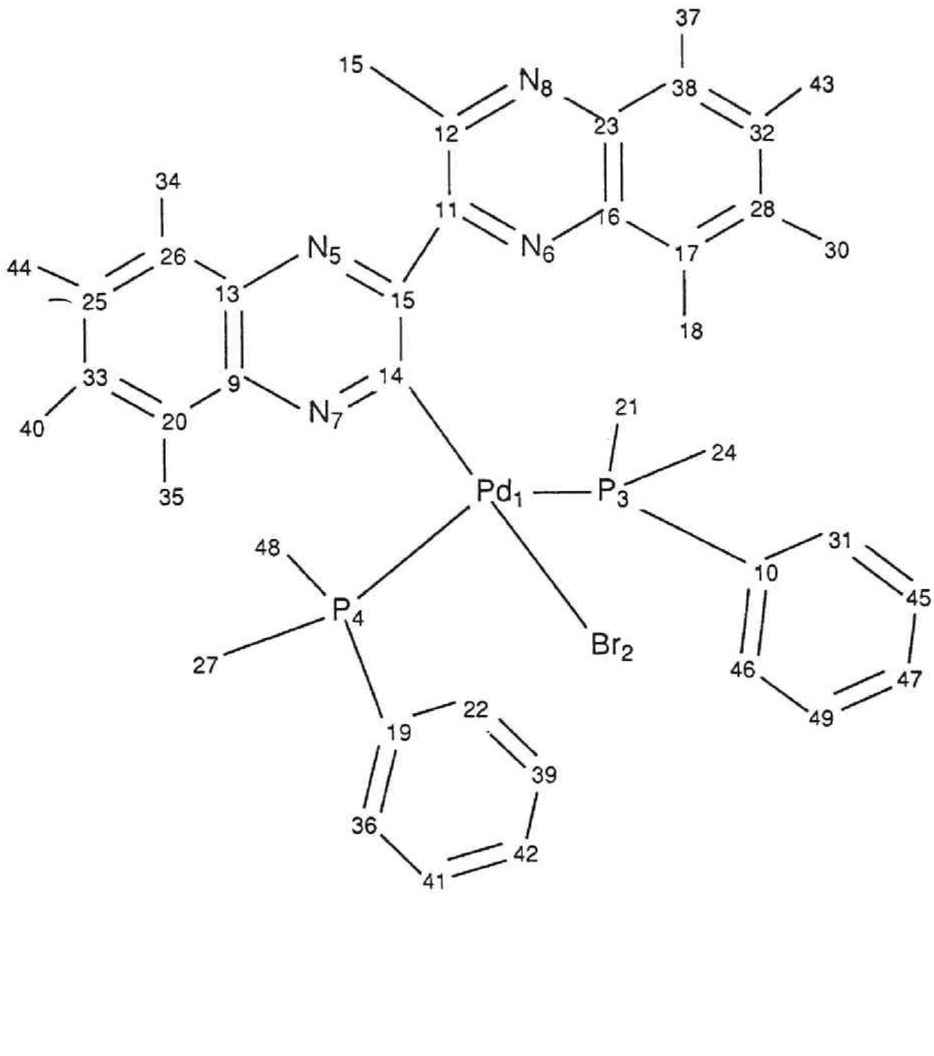


Table 2. Atomic coordinates (x 10^4 ; x 10^3 for H) and equivalent isotropic temperature factors ($Å^2$ x 10) for **3a**

	x	y	z	B_{eq} *
Pd	3128.4(3)	954.7(8)	1520.9(2)	30.6(1)
Br	5131.7(5)	1282.1(8)	1671.1(2)	48.5(2)
P(1)	3287(1)	2155(2)	2261(1)	34.1(4)
P(2)	2783(1)	-155(2)	744(1)	34.8(4)
N(1)	957(3)	2096(5)	1158(1)	35(1)
N(2)	-68(3)	-551(5)	1361(2)	40(2)
C(1)	1527(4)	863(6)	1377(2)	30(2)
C(2)	-162(4)	2089(6)	1035(2)	33(2)
C(3)	-790(4)	3426(7)	799(2)	41(2)
C(4)	-1908(4)	3391(7)	671(2)	41(2)
C(5)	-2420(4)	2043(7)	773(2)	43(2)
C(6)	-1820(4)	730(8)	1006(2)	45(2)
C(7)	-675(4)	749(6)	1138(2)	36(2)
C(8)	996(4)	-490(6)	1481(2)	36(2)
C(9)	-220(5)	4842(8)	698(3)	58(2)
C(10)	-2599(5)	4814(9)	436(3)	62(3)
C(11)	-3658(5)	2031(10)	621(2)	62(3)
C(12)	-2330(5)	-690(9)	1140(3)	62(3)
C(13)	1655(5)	-1933(7)	1727(2)	51(2)
C(14)	2876(6)	4196(7)	2134(2)	54(2)
C(15)	4646(5)	2235(8)	2749(2)	56(2)
C(16)	2455(5)	1367(7)	2578(2)	44(2)
C(17)	2805(6)	10(9)	2867(2)	61(2)
C(18)	2144(8)	-636(12)	3097(3)	94(4)
C(19)	1178(8)	42(15)	3040(3)	110(5)
C(20)	808(8)	1330(13)	2749(4)	103(5)
C(21)	1451(6)	2023(10)	2514(3)	68(3)
C(22)	3287(6)	1000(8)	350(2)	57(2)
C(23)	1360(5)	-494(10)	329(2)	68(3)
C(24)	3433(4)	-2063(6)	796(2)	39(2)
C(25)	4500(5)	-2176(7)	833(2)	49(2)
C(26)	5036(6)	-3629(8)	927(3)	65(3)
C(27)	4525(6)	-4934(9)	979(2)	69(3)
C(28)	3466(7)	-4879(8)	947(3)	70(3)
C(29)	2907(6)	-3434(8)	851(3)	59(3)
H(C9)	-19(5)	579(8)	85(2)	58
H'(C9)	50(5)	475(9)	80(2)	58
H"(C9)	-54(5)	516(8)	38(3)	58
H(C10)	-286(5)	522(9)	64(3)	62
H'(C10)	-324(5)	436(9)	10(3)	62
H"(C10)	-214(5)	539(9)	36(3)	62
H(C11)	-380(5)	188(9)	87(2)	62
H'(C11)	-403(5)	263(9)	31(2)	62
H"(C11)	-395(5)	82(8)	45(3)	62
H(C12)	-279(5)	-48(8)	126(3)	62
H'(C12)	-170(5)	-153(9)	135(3)	62
H"(C12)	-273(6)	-113(8)	90(3)	62
H(C13)	249(5)	-187(8)	179(2)	51
H'(C13)	177(5)	-204(8)	199(2)	51
H"(C13)	137(5)	-267(8)	157(2)	51
H(C14)	221(5)	424(8)	183(2)	54
H'(C14)	284(5)	460(8)	236(2)	54
H"(C14)	339(5)	463(8)	204(2)	54
H(C15)	471(5)	263(8)	306(2)	56
H'(C15)	477(5)	123(8)	289(2)	56
H"(C15)	511(5)	281(8)	260(2)	56
H(C17)	360(5)	-48(8)	293(3)	61
H(C18)	239(7)	-169(11)	334(3)	94
H(C19)	66(7)	-27(12)	317(4)	110
H(C20)	11(7)	182(11)	264(3)	103
H(C21)	109(5)	279(9)	231(3)	68
H(C22)	403(5)	130(8)	52(3)	57

H'(C22)	297(5)	188(9)	27(2)	57
H"(C22)	328(5)	46(9)	9(2)	57
H(C23)	144(6)	-99(9)	5(3)	68
H'(C23)	107(6)	-110(8)	52(3)	68
H"(C23)	121(5)	59(9)	30(3)	68
H(C25)	496(5)	-125(8)	84(2)	49
H(C26)	582(5)	-365(9)	90(3)	65
H(C27)	507(6)	-613(9)	111(3)	69
H(C28)	294(6)	-592(9)	99(3)	70
H(C29)	216(5)	-336(8)	75(2)	59

$$^{*}B_{eq} = 4/3\sum_{i}\sum_{j}\beta_{ij}a_i \cdot a_j$$

Table 3. Anisotropic thermal parameters (Å x 10^3) for **3a**

The temperature factor is of the form :

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}lb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	39.2(2)	38.8(2)	37.3(2)	2.4(2)	13.4(2)	-1.3(2)
Br	52.0(3)	68.5(4)	63.2(4)	1.4(3)	21.6(3)	8.1(3)
P(1)	46(1)	42(1)	40(1)	1(1)	14(1)	-5(1)
P(2)	41(1)	48(1)	40(1)	9(1)	12(1)	-6(1)
N(1)	43(2)	45(3)	42(2)	1(2)	15(2)	-1(2)
N(2)	55(3)	51(3)	46(3)	-1(2)	21(2)	1(2)
C(1)	38(3)	44(3)	33(3)	2(2)	15(2)	-2(2)
C(2)	48(3)	44(3)	36(3)	-3(2)	19(2)	-6(2)
C(3)	54(3)	53(3)	50(3)	0(3)	22(3)	-6(3)
C(4)	52(3)	64(4)	41(3)	13(3)	19(2)	-8(3)
C(5)	43(3)	75(4)	48(3)	8(3)	21(2)	-6(3)
C(6)	53(3)	74(4)	53(3)	-10(3)	29(3)	-6(3)
C(7)	47(3)	49(3)	43(3)	-4(3)	21(2)	-4(3)
C(8)	52(3)	47(3)	38(3)	4(3)	16(2)	-1(3)
C(9)	67(4)	59(4)	92(5)	8(3)	28(4)	16(4)
C(10)	67(4)	83(5)	86(5)	28(4)	32(4)	8(4)
C(11)	51(4)	114(6)	74(4)	6(4)	27(3)	-4(4)
C(12)	58(4)	92(5)	93(5)	-17(4)	37(4)	12(4)
C(13)	81(4)	50(4)	55(4)	4(3)	20(3)	6(3)
C(14)	86(5)	49(4)	63(4)	4(3)	21(3)	0(3)
C(15)	64(4)	79(5)	54(4)	-4(3)	6(3)	-13(3)
C(16)	58(3)	69(4)	40(3)	-4(3)	20(3)	-9(3)
C(17)	92(5)	78(5)	55(4)	-16(4)	21(3)	14(4)
C(18)	155(8)	127(8)	67(5)	-46(6)	33(5)	15(5)
C(19)	147(8)	210(12)	83(6)	-66(9)	67(6)	-11(7)
C(20)	127(7)	176(11)	120(7)	-8(7)	84(6)	-20(7)
C(21)	85(5)	109(6)	80(5)	5(5)	49(4)	4(5)
C(22)	95(5)	66(4)	52(4)	12(4)	27(3)	8(3)
C(23)	61(4)	129(7)	53(4)	7(4)	4(3)	-38(4)
C(24)	64(3)	42(3)	43(3)	6(3)	22(3)	-5(3)
C(25)	64(4)	54(4)	67(4)	16(3)	23(3)	-3(3)
C(26)	86(5)	75(5)	83(5)	36(4)	31(4)	3(4)
C(27)	129(6)	70(5)	64(4)	45(5)	38(4)	4(4)
C(28)	167(7)	44(4)	76(5)	0(4)	70(5)	1(3)
C(29)	94(5)	64(4)	82(5)	-10(4)	54(4)	-13(4)

Table 4. Bond length (Å) and angles (°) for **3a**

Pd - Br	2.529(1)	Pd - P(1)	2.312(2)
Pd - P(2)	2.318(2)	Pd - C(1)	1.996(6)
P(1) - C(14)	1.813(8)	P(1) - C(15)	1.812(7)
P(1) - C(16)	1.810(7)	P(2) - C(22)	1.816(8)
P(2) - C(23)	1.826(9)	P(2) - C(24)	1.814(6)
N(1) - C(1)	1.305(7)	N(1) - C(2)	1.382(7)
N(2) - C(7)	1.373(8)	N(2) - C(8)	1.314(8)
C(1) - C(8)	1.438(8)	C(2) - C(3)	1.419(8)
C(2) - C(7)	1.415(8)	C(3) - C(4)	1.379(8)
C(3) - C(9)	1.507(11)	C(4) - C(5)	1.418(8)
C(4) - C(10)	1.511(11)	C(5) - C(6)	1.385(9)
C(5) - C(11)	1.523(10)	C(6) - C(7)	1.412(9)
C(6) - C(12)	1.504(11)	C(8) - C(13)	1.515(9)
C(16) - C(17)	1.396(10)	C(16) - C(21)	1.385(11)
C(17) - C(18)	1.399(13)	C(18) - C(19)	1.352(17)
C(19) - C(20)	1.354(17)	C(20) - C(21)	1.406(14)
C(24) C(25)	1.376(9)	C(24) - C(29)	1.397(10)
C(25) - C(26)	1.398(11)	C(26) - C(27)	1.337(12)
C(27) - C(28)	1.368(12)	C(28) - C(29)	1.405(13)

Br -Pd -P(1)	94.3(1)	Br -Pd -P(2)	90.9(1)
Br -Pd -C(1)	175.5(2)	P(1) -Pd -P(2)	174.0(1)
P(1) -Pd -C(1)	85.5(2)	P(2) -Pd -C(1)	89.0(2)
Pd -P(1) -C(14)	108.7(3)	Pd -P(1) -C(15)	116.8(2)
Pd -P(1) -C(16)	116.8(2)	C(14)-P(1) -C(15)	104.6(3)
C(14)-P(1) -C(16)	105.3(3)	C(15)-P(1) -C(16)	103.4(3)
Pd -P(2) -C(22)	114.1(3)	Pd -P(2) -C(23)	118.3(3)
Pd -P(2) -C(24)	111.9(2)	C(22)-P(2) -C(23)	101.8(4)
C(22)-P(2) -C(24)	105.0(3)	C(23)-P(2) -C(24)	104.4(3)
C(1) -N(1) -C(2)	118.9(5)	C(7) -N(2) -C(8)	117.8(5)
Pd -C(1) -N(1)	116.0(4)	Pd -C(1) -C(8)	123.5(4)
N(1) -C(1) -C(8)	120.5(5)	N(1) -C(2) -C(3)	119.4(5)
N(1) -C(2) -C(7)	120.1(5)	C(3) -C(2) -C(7)	120.5(5)
C(2) -C(3) -C(4)	118.7(5)	C(2) -C(3) -C(9)	119.3(6)
C(4) -C(3) -C(9)	121.9(6)	C(3) -C(4) -C(5)	120.6(5)
C(3) -C(4) -C(10)	120.3(6)	C(5) -C(4) -C(10)	119.1(6)
C(4) -C(5) -C(6)	121.5(6)	C(4) -C(5) -C(11)	119.4(6)
C(6) -C(5) -C(11)	119.1(6)	C(5) -C(6) -C(7)	118.5(6)
C(5) -C(6) -C(12)	122.9(6)	C(7) -C(6) -C(12)	118.6(6)
N(2) -C(7) -C(2)	120.4(5)	N(2) -C(7) -C(6)	119.4(6)
C(2) -C(7) -C(6)	120.2(5)	N(2) -C(8) -C(1)	122.4(5)
N(2) -C(8) -C(13)	117.2(5)	C(1) -C(8) -C(13)	120.5(5)
P(1) -C(16)-C(17)	119.0(5)	P(1) -C(16)-C(21)	121.4(6)
C(17)-C(16)-C(21)	119.5(7)	C(16)-C(17)-C(18)	119.1(8)
C(17)-C(18)-C(19)	120.5(10)	C(18)-C(19)-C(20)	121.3(12)
C(19)-C(20)-C(21)	120.0(11)	C(16)-C(21)-C(20)	119.5(8)
P(2) -C(24)-C(25)	120.5(5)	P(2) -C(24)-C(29)	120.9(5)
C(25)-C(24)-C(29)	118.2(6)	C(24)-C(25)-C(26)	120.3(6)
C(25)-C(26)-C(27)	121.0(8)	C(26)-C(27)-C(28)	120.8(8)
C(27)-C(28)-C(29)	119.4(8)	C(24)-C(29)-C(28)	120.3(8)

Table 5. Atomic coordinates and equivalent isotropic temperature factors for **3b**

$^{*}B_{eq} = 4/3\Sigma i\Sigma j\beta ijaiaj$.

atom	x	y	z	B (eq)
Pd1	0.22082 (3)	0.36877 (2)	0.26058 (2)	2.66 (1)
Br2	0.08314 (6)	0.52367 (4)	0.24125 (3)	6.85 (2)
P 3	0.05904 (9)	0.26968 (8)	0.32246 (5)	2.90 (3)
P 4	0.3948 (1)	0.47805 (8)	0.21216 (5)	3.26 (3)
N 5	0.4435 (3)	0.0961 (2)	0.2570 (1)	2.50 (8)
N 6	0.1603 (3)	0.1629 (2)	0.1226 (1)	2.42 (8)
N 7	0.4083 (3)	0.2623 (2)	0.3645 (1)	2.73 (8)
N 8	0.3141 (3)	0.1361 (2)	0.0125 (2)	3.20 (9)
C 9	0.4950 (3)	0.1896 (3)	0.3904 (2)	2.53 (9)
C 10	0.0951 (4)	0.3291 (3)	0.4259 (2)	3.5 (1)
C 11	0.2934 (3)	0.1555 (2)	0.1457 (2)	2.34 (9)
C 12	0.3717 (3)	0.1378 (3)	0.0890 (2)	3.0 (1)
C 13	0.5122 (3)	0.1053 (3)	0.3359 (2)	2.55 (9)
C 14	0.3414 (3)	0.2542 (3)	0.2886 (2)	2.51 (9)
C 15	0.3608 (3)	0.1671 (2)	0.2331 (2)	2.32 (9)
C 16	0.0967 (3)	0.1553 (2)	0.0426 (2)	2.43 (9)
C 17	-0.0468 (3)	0.1623 (3)	0.0164 (2)	2.8 (1)
C 18	-0.1268 (4)	0.1726 (4)	0.0774 (2)	4.7 (1)
C 19	0.3376 (4)	0.5036 (3)	0.1086 (2)	3.4 (1)
C 20	0.5662 (3)	0.1976 (3)	0.4728 (2)	3.1 (1)
C 21	0.0515 (5)	0.1165 (4)	0.3246 (3)	4.7 (1)
C 22	0.4316 (4)	0.5780 (3)	0.0766 (2)	4.6 (1)
C 23	0.1769 (3)	0.1462 (3)	-0.0127 (2)	2.68 (9)
C 24	-0.1276 (4)	0.2697 (4)	0.2804 (3)	4.9 (2)
C 25	0.6719 (4)	0.0393 (3)	0.4410 (2)	3.5 (1)
C 26	0.6025 (3)	0.0296 (3)	0.3611 (2)	3.0 (1)
C 27	0.5571 (4)	0.4301 (4)	0.2176 (2)	4.3 (1)
C 28	-0.1068 (4)	0.1614 (3)	-0.0642 (2)	3.1 (1)
C 29	0.5231 (4)	0.1243 (4)	0.1106 (2)	4.5 (1)
C 30	-0.2581 (5)	0.1722 (5)	-0.0946 (3)	5.2 (2)
C 31	0.2157 (4)	0.4148 (4)	0.4609 (2)	4.8 (1)
C 32	-0.0244 (4)	0.1548 (3)	-0.1193 (2)	3.2 (1)
C 33	0.6511 (3)	0.1221 (3)	0.4966 (2)	3.3 (1)
C 34	0.6186 (5)	-0.0559 (4)	0.2994 (3)	4.9 (1)
C 35	0.5409 (5)	0.2852 (4)	0.5304 (2)	4.7 (2)
C 36	0.2031 (5)	0.4502 (3)	0.0616 (2)	4.3 (1)
C 37	0.2084 (6)	0.1441 (5)	-0.1503 (2)	5.5 (2)
C 38	0.1150 (4)	0.1472 (3)	-0.0949 (2)	3.1 (1)
C 39	0.3863 (6)	0.5962 (4)	-0.0027 (3)	6.0 (2)
C 40	0.7234 (5)	0.1267 (4)	0.5849 (2)	5.0 (2)
C 41	0.1594 (5)	0.4688 (4)	-0.0180 (2)	5.3 (2)
C 42	0.2540 (6)	0.5414 (4)	-0.0483 (3)	6.2 (2)
C 43	-0.0958 (5)	0.1562 (4)	-0.2071 (2)	4.7 (1)
C 44	0.7706 (5)	-0.0387 (4)	0.4711 (3)	5.4 (2)
C 45	0.2429 (5)	0.4650 (4)	0.5399 (2)	6.1 (2)
C 46	0.0027 (5)	0.2940 (4)	0.4706 (3)	6.8 (2)
C 47	0.1492 (6)	0.4290 (5)	0.5823 (2)	6.6 (2)
C 48	0.4666 (6)	0.6217 (4)	0.2587 (3)	5.6 (2)
C 49	0.0312 (6)	0.3450 (6)	0.5485 (3)	9.0 (2)
H 44A	0.859 (4)	0.007 (4)	0.503 (2)	5.08 (0)
H 44B	0.746 (5)	-0.076 (4)	0.503 (3)	5.08 (0)
H 40A	0.686 (5)	0.069 (4)	0.604 (2)	4.91 (0)
H 40B	0.713 (5)	0.181 (4)	0.612 (3)	4.91 (0)
H 35A	0.629 (4)	0.334 (3)	0.563 (2)	4.58 (0)
H 35B	0.499 (5)	0.254 (4)	0.560 (2)	4.58 (0)
H 35C	0.498 (4)	0.337 (4)	0.509 (2)	4.58 (0)
H 34A	0.599 (5)	-0.129 (4)	0.312 (2)	4.68 (0)
H 34B	0.546 (4)	-0.084 (4)	0.254 (2)	4.68 (0)
H 34C	0.702 (4)	-0.068 (4)	0.302 (3)	4.68 (0)
H 29A	0.576 (4)	0.175 (4)	0.153 (2)	4.26 (0)
H 29B	0.548 (4)	0.125 (4)	0.072 (2)	4.26 (0)
H 43A	-0.028 (4)	0.157 (4)	-0.236 (2)	4.62 (0)
H 43B	-0.105 (5)	0.219 (4)	-0.209 (3)	4.62 (0)
H 30A	-0.264 (5)	0.236 (4)	-0.113 (3)	5.13 (0)
H 30B	-0.307 (5)	0.171 (4)	-0.062 (3)	5.13 (0)
H 18A	-0.200 (4)	0.108 (3)	0.074 (2)	4.42 (0)
H 18B	-0.168 (5)	0.228 (4)	0.074 (2)	4.42 (0)
H 21A	0.033 (4)	0.085 (3)	0.272 (2)	4.51 (0)
H 24A	-0.182 (4)	0.241 (4)	0.305 (2)	4.73 (0)
H 24B	-0.163 (5)	0.226 (4)	0.235 (2)	4.73 (0)
H 24C	-0.140 (5)	0.340 (4)	0.275 (3)	4.73 (0)
H 31	0.284 (4)	0.447 (3)	0.434 (2)	4.68 (0)
H 46	-0.077 (5)	0.243 (4)	0.448 (3)	6.87 (0)
H 27A	0.624 (4)	0.485 (3)	0.208 (2)	4.15 (0)
H 27B	0.582 (4)	0.408 (4)	0.253 (2)	4.15 (0)
H 27C	0.536 (4)	0.358 (3)	0.180 (2)	4.15 (0)
H 48A	0.393 (5)	0.656 (4)	0.260 (3)	5.47 (0)
H 48B	0.539 (5)	0.666 (4)	0.252 (2)	5.47 (0)
H 48C	0.513 (5)	0.602 (4)	0.316 (2)	5.47 (0)
H 22	0.523 (4)	0.618 (3)	0.108 (2)	4.17 (0)
H 36	0.146 (4)	0.405 (3)	0.082 (2)	4.05 (0)

H 37A	0.180 (5)	0.100 (4)	-0.184 (3)	5.27 (0)
H 37B	0.298 (4)	0.137 (4)	-0.125 (2)	5.27 (0)
H 37C	0.202 (5)	0.204 (4)	-0.180 (3)	5.27 (0)
H 43C	-0.182 (4)	0.098 (3)	-0.222 (2)	4.62 (0)
H 18C	-0.067 (4)	0.168 (4)	0.120 (2)	4.42 (0)
H 40C	0.828 (4)	0.132 (3)	0.596 (2)	4.91 (0)
H 21B	0.149 (4)	0.111 (3)	0.352 (2)	4.51 (0)
H 21C	-0.003 (4)	0.089 (4)	0.348 (2)	4.51 (0)
H 45	0.341 (5)	0.528 (4)	0.564 (2)	6.14 (0)
H 47	0.160 (5)	0.458 (4)	0.632 (3)	6.44 (0)
H 42	0.220 (5)	0.554 (4)	-0.094 (2)	5.50 (0)
H 39	0.442 (5)	0.653 (4)	-0.019 (2)	5.31 (0)
H 41	0.065 (4)	0.423 (4)	-0.045 (2)	5.08 (0)
H 49	-0.033 (6)	0.330 (5)	0.570 (3)	8.83 (0)
H 44C	0.790 (4)	-0.094 (4)	0.428 (2)	5.08 (0)
H 29C	0.524 (4)	0.047 (3)	0.122 (2)	4.25 (0)
H 30C	-0.305 (5)	0.119 (4)	-0.138 (2)	5.13 (0)

Table 6. Anisotropic thermal parameters for **3b**

The temperature factor is of the form :

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}lb^*c^*)].$$

atom	u11	u22	u33	u12	u13	u23
Pd1	0.0377 (2)	0.0356 (2)	0.0254 (1)	0.0141 (1)	0.0112 (2)	0.0070 (1)
Br2	0.1001 (4)	0.0725 (3)	0.0879 (4)	0.0515 (3)	0.0407 (3)	0.0327 (3)
P 3	0.0347 (6)	0.0399 (5)	0.0302 (4)	0.0087 (4)	0.0081 (4)	0.0031 (4)
P 4	0.0494 (6)	0.0368 (5)	0.0316 (6)	0.0055 (5)	0.0148 (5)	0.0034 (4)
N 5	0.029 (2)	0.032 (2)	0.028 (1)	0.006 (1)	0.004 (1)	0.000 (1)
N 6	0.030 (2)	0.034 (1)	0.023 (1)	0.008 (1)	0.005 (1)	0.000 (1)
N 7	0.035 (2)	0.038 (2)	0.025 (1)	0.008 (1)	0.007 (1)	0.002 (1)
N 8	0.035 (2)	0.054 (2)	0.026 (2)	0.010 (1)	0.010 (1)	0.000 (1)
C 9	0.027 (2)	0.037 (2)	0.026 (2)	0.002 (1)	0.006 (1)	0.005 (1)
C 10	0.042 (2)	0.053 (2)	0.031 (2)	0.005 (2)	0.014. (2)	0.004 (2)
C 11	0.028 (2)	0.032 (2)	0.024 (2)	0.005 (1)	0.006 (1)	0.000 (1)
C 12	0.028 (2)	0.049 (2)	0.030 (2)	0.009 (2)	0.008 (2)	0.001 (2)
C 13	0.026 (2)	0.040 (2)	0.026 (2)	0.006 (1)	0.005 (1)	0.008 (1)
C 14	0.030 (2)	0.037 (2)	0.025 (2)	0.005 (1)	0.010 (1)	0.005 (1)
C 15	0.027 (2)	0.035 (2)	0.022 (2)	0.005 (1)	0.005 (1)	0.002 (1)
C 16	0.032 (2)	0.029 (2)	0.026 (2)	0.008 (1)	0.002 (1)	0.001 (1)
C 17	0.031 (2)	0.037 (2)	0.033 (2)	0.010 (2)	0.003 (2)	-0.003 (1)
C 18	0.034 (2)	0.091 (4)	0.046 (2)	0.029 (2)	0.008 (2)	0.003 (2)
C 19	0.056 (2)	0.037 (2)	0.034 (2)	0.017 (2)	0.021 (2)	0.008 (2)
C 20	0.034 (2)	0.049 (2)	0.027 (2)	0.004 (2)	0.005 (2)	0.003 (2)
C 21	0.061 (3)	0.044 (2)	0.065 (3)	0.007 (2)	0.020 (2)	0.007 (2)
C 22	0.066 (3)	0.051 (2)	0.054 (3)	0.021 (2)	0.031 (2)	0.021 (2)
C 23	0.036 (2)	0.034 (2)	0.026 (2)	0.007 (2)	0.007 (2)	-0.002 (1)
C 24	0.035 (2)	0.092 (4)	0.052 (3)	0.014 (3)	0.011 (2)	0.006 (2)
C 25	0.034 (2)	0.048 (2)	0.045 (2)	0.011 (2)	0.008 (2)	0.020 (2)
C 26	0.030 (2)	0.041 (2)	0.038 (2)	0.008 (2)	0.006 (2)	0.011 (2)
C 27	0.044 (2)	0.065 (3)	0.046 (2)	0.005 (2)	0.013 (2)	0.013 (2)
C 28	0.037 (2)	0.036 (2)	0.036 (2)	0.014 (2)	-0.006 (2)	-0.006 (2)
C 29	0.035 (2)	0.092 (3)	0.041 (2)	0.023 (2)	0.014 (2)	0.006 (2)
C 30	0.054 (3)	0.080 (4)	0.052 (3)	0.034 (3)	-0.010 (2)	-0.007 (2)
C 31	0.061 (3)	0.068 (3)	0.041 (2)	-0.004 (2)	0.021 (2)	-0.007 (2)
C 32	0.053 (2)	0.032 (2)	0.025 (2)	0.009 (2)	-0.003 (2)	-0.000 (1)
C 33	0.030 (2)	0.056 (2)	0.030 (2)	0.000 (2)	-0.001 (2)	0.017 (2)
C 34	0.062 (3)	0.052 (3)	0.066 (3)	0.033 (2)	0.005 (2)	0.002 (2)
C 35	0.070 (3)	0.068 (3)	0.028 (2)	0.014 (2)	0.004 (2)	-0.000 (2)
C 36	0.071 (3)	0.044 (2)	0.041 (2)	0.014 (2)	0.020 (2)	0.008 (2)
C 37	0.065 (3)	0.105 (4)	0.028 (2)	0.019 (3)	0.013 (2)	0.004 (2)
C 38	0.044 (2)	0.043 (2)	0.025 (2)	0.006 (2)	0.006 (2)	-0.001 (2)
C 39	0.094 (4)	0.066 (3)	0.070 (3)	0.036 (3)	0.050 (3)	0.038 (3)
C 40	0.056 (3)	0.086 (4)	0.037 (2)	0.013 (3)	-0.001 (2)	0.023 (2)
C 41	0.086 (4)	0.067 (3)	0.041 (2)	0.026 (3)	0.014 (2)	0.004 (2)
C 42	0.106 (4)	0.082 (3)	0.047 (3)	0.054 (3)	0.036 (3)	0.025 (3)
C 43	0.072 (3)	0.062 (3)	0.034 (2)	0.022 (2)	-0.004 (2)	0.006 (2)
C 44	0.058 (3)	0.078 (4)	0.060 (3)	0.032 (3)	0.003 (2)	0.029 (2)
C 45	0.078 (3)	0.091 (4)	0.044 (3)	-0.014 (3)	0.016 (2)	-0.017 (2)
C 46	0.082 (4)	0.109 (4)	0.047 (3)	-0.036 (3)	0.031 (3)	-0.009 (2)
C 47	0.082 (4)	0.113 (4)	0.040 (2)	0.004 (3)	0.022 (3)	-0.015 (3)
C 48	0.087 (4)	0.052 (3)	0.059 (3)	-0.006 (2)	0.027 (3)	-0.014 (2)
C 49	0.108 (5)	0.158 (6)	0.051 (3)	-0.034 (4)	0.052 (3)	-0.013 (3)

atom	atom	distance
Pd1	--C 14	2.005 (3)
Pd1	--P 4	2.307 (1)
Pd1	--Br2	2.5101 (6)
P 3	--C 21	1.807 (4)
P 3	--C 10	1.812 (3)
P 3	--C 24	1.815 (4)
P 4	--C 27	1.806 (5)
P 4	--C 48	1.813 (4)
P 4	--C 19	1.822 (3)
N 5	--C 15	1.315 (4)
N 5	--C 13	1.361 (4)
N 6	--C 11	1.307 (4)
N 6	--C 16	1.368 (3)
N 7	--C 14	1.313 (4)
N 7	--C 9	1.367 (4)
N 8	--C 12	1.312 (4)
N 8	--C 23	1.357 (4)
C 9	--C 13	1.402 (4)
C 9	--C 20	1.421 (4)
C 10	--C 31	1.368 (5)
C 10	--C 46	1.368 (6)
C 11	--C 12	1.437 (5)
C 11	--C 15	1.488 (4)
C 12	--C 29	1.502 (6)
C 13	--C 26	1.417 (5)
C 14	--C 15	1.446 (4)
C 16	--C 17	1.406 (4)
C 16	--C 23	1.412 (5)
Pd1	--N 6	3.160 (2)
Pd1	--P 3	2.321 (1)
C 17	--C 28	1.383 (4)
C 17	--C 18	1.495 (6)
C 19	--C 36	1.370 (5)
C 19	--C 22	1.394 (6)
C 20	--C 33	1.374 (5)
C 20	--C 35	1.500 (6)
C 22	--C 39	1.392 (6)
C 23	--C 38	1.415 (4)
C 25	--C 26	1.377 (4)
C 25	--C 33	1.420 (5)
C 25	--C 44	1.514 (7)
C 26	--C 34	1.492 (6)
C 28	--C 32	1.423 (5)
C 28	--C 30	1.499 (6)
C 31	--C 45	1.401 (6)
C 32	--C 38	1.367 (5)
C 32	--C 43	1.521 (5)
C 33	--C 40	1.520 (5)
C 36	--C 41	1.396 (6)
C 37	--C 38	1.505 (7)
C 39	--C 42	1.349 (7)
C 41	--C 42	1.370 (7)
C 45	--C 47	1.351 (8)
C 46	--C 49	1.387 (7)
C 47	--C 49	1.337 (7)

Table 7. Bond length (Å) and angles (°) for **3b**

atom	atom	atom	angle
C 14	--Pd1	--P 4	90.2 (1)
C 14	--Pd1	--P 3	89.4 (1)
C 14	--Pd1	--Br2	173.54 (8)
C 14	--Pd1	--N 6	66.37 (9)
P 4	--Pd1	--P 3	173.94 (3)
P 4	--Pd1	--Br2	90.05 (3)
P 4	--Pd1	--N 6	90.75 (5)
P 3	--Pd1	--Br2	89.65 (3)
P 3	--Pd1	--N 6	94.64 (5)
C 21	--P 3	--C 10	104.8 (2)
C 21	--P 3	--C 24	102.3 (2)
C 10	--P 3	--C 24	103.4 (2)
C 27	--P 4	--C 48	101.0 (2)
C 27	--P 4	--C 19	103.3 (2)
C 48	--P 4	--C 19	105.0 (2)
C 15	--N 5	--C 13	119.0 (3)
C 11	--N 6	--C 16	118.5 (3)
C 14	--N 7	--C 9	120.4 (3)
C 12	--N 8	--C 23	118.9 (3)
N 7	--C 9	--C 13	120.0 (2)
N 7	--C 9	--C 20	120.3 (3)
C 13	--C 9	--C 20	119.7 (3)
C 31	--C 10	--C 45	117.7 (3)
C 31	--C 10	--P 3	119.9 (3)
C 46	--C 10	--P 3	122.3 (2)
N 6	--C 11	--C 12	121.3 (2)
N 6	--C 11	--C 15	117.3 (3)
C 12	--C 11	--C 15	121.4 (3)
N 8	--C 12	--C 11	120.6 (3)
N 8	--C 12	--C 29	114.8 (3)
C 11	--C 12	--C 29	124.6 (3)
N 5	--C 13	--C 9	120.2 (3)
N 5	--C 13	--C 26	118.7 (3)
C 9	--C 13	--C 26	121.1 (3)
N 7	--C 14	--C 15	118.9 (3)
N 5	--C 15	--C 14	121.6 (2)
N 5	--C 15	--C 11	116.2 (3)
C 14	--C 15	--C 11	122.1 (3)
N 6	--C 16	--C 17	119.4 (3)
N 6	--C 16	--C 23	120.1 . (3)
C 17	--C 16	--C 23	120.5 (3)
C 28	--C 17	--C 16	118.6 (3)
C 28	--C 17	--C 18	123.0 (3)
C 16	--C 17	--C 18	118.4 (3)
C 36	--C 19	--C 22	119.4 (3)
C 21	--P 3	--Pd1	115.8 (2)
C 10	--P 3	--Pd1	112.6 (1)
C 24	--P 3	--Pd1	116.4 (2)
C 27	--P 4	--Pd1	118.6 (2)
C 48	--P 4	--Pd1	111.2 (2)
C 19	--P 4	--Pd1	115.9 (1)
N 7	--C 14	--Pd1	115.2 (2)
C 15	--C 14	--Pd1	125.9 (2)
Br2	--Pd1	--N 6	120.08 (5)
C 36	--C 19	--P 4	120.7 (3)
C 22	--C 19	--P 4	119.9 (2)
C 33	--C 20	--C 9	118.5 (3)
C 33	--C 20	--C 35	122.8 (3)
C 9	--C 20	--C 35	118.6 (3)
C 39	--C 22	--C 19	119.1 (3)
N 8	--C 23	--C 16	120.3 (2)
N 8	--C 23	--C 38	119.3 (3)
C 16	--C 23	--C 38	120.4 (3)
C 26	--C 25	--C 33	120.4 (3)
C 26	--C 25	--C 44	120.7 (3)
C 33	--C 25	--C 44	118.8 (3)
C 25	--C 26	--C 13	118.5 (3)
C 25	--C 26	--C 34	123.3 (3)
C 13	--C 26	--C 34	118.2 (3)
C 17	--C 28	--C 32	120.6 (3)
C 17	--C 28	--C 30	120.5 (4)
C 32	--C 28	--C 30	118.9 (3)
C 10	--C 31	--C 45	120.8 (4)
C 38	--C 32	--C 28	121.5 (3)
C 38	--C 32	--C 43	120.4 (4)
C 28	--C 32	--C 43	118.1 (3)
C 20	--C 33	--C 25	121.7 (3)
C 20	--C 33	--C 40	119.1 (4)
C 25	--C 33	--C 40	119.2 (4)
C 19	--C 36	--C 41	120.8 (4)
C 32	--C 38	--C 23	118.4 (3)
C 32	--C 38	--C 37	123.6 (3)
C 23	--C 38	--C 37	117.9 (3)
C 42	--C 39	--C 22	120.5 (5)
C 42	--C 41	--C 36	118.7 (4)
C 39	--C 42	--C 41	121.4 (4)
C 47	--C 45	--C 31	120.0 (4)
C 10	--C 46	--C 49	120.7 (4)
C 49	--C 47	--C 45	119.5 (4)
C 47	--C 49	--C 46	121.2 (6)

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic temperature factors ($Å^2$ x 10) for **3c**

	x	y	z	B_{eq}*
Pd(1)	1893.1(2)	8896.1(1)	5708.5(2)	39.6(1)
Br(1)	3199.4(3)	9154.9(2)	7007.1(4)	61.7(2)
P(1)	1502(1)	7957(1)	6184(1)	52.0(3)
P(2)	2040(1)	9824(1)	5287(1)	41.8(3)
N(1)	87(2)	8590(1)	5258(3)	42(1)
N(2)	6(2)	8416(1)	3140(2)	41(1)
N(3)	2250(2)	8630(2)	3608(3)	45(1)
N(4)	2290(3)	9040(2)	1619(3)	52(1)
N(5)	542(2)	9433(2)	1733(3)	47(1)
N(6)	-279(3)	8672(2)	111(3)	54(1)
C(1)	802(2)	8674(2)	4799(3)	38(1)
C(2)	-704(3)	8413(2)	4698(3)	43(1)
C(3)	-1477(3)	8302(2)	5195(3)	44(1)
C(4)	-2267(3)	8127(2)	4634(4)	46(1)
C(5)	-2300(3)	8054(2)	3556(3)	46(1)
C(6)	-1549(3)	8141(2)	3044(3)	46(1)
C(7)	-737(3)	8319(2)	3627(3)	41(1)
C(8)	749(3)	8591(2)	3700(3)	41(1)
C(9)	-1403(3)	8380(3)	6362(4)	63(2)
C(10)	-3102(3)	8021(2)	5151(5)	64(2)
C(11)	-3171(3)	7887(3)	2933(5)	66(2)
C(12)	-1582(3)	8071(3)	1888(4)	64(2)
C(13)	1548(3)	8712(2)	3131(3)	41(1)
C(14)	2995(3)	8759(2)	3110(4)	45(1)
C(15)	3758(3)	8670(2)	3624(4)	51(1)
C(16)	4509(3)	8826(2)	3137(4)	55(2)
C(17)	4554(3)	9078(2)	2173(4)	59(2)
C(18)	3810(3)	9138(2)	1639(4)	57(2)
C(19)	3025(3)	8975(2)	2121(4)	49(1)
C(20)	1572(3)	8915(2)	2099(3)	44(1)
C(21)	3708(4)	8395(3)	4645(4)	68(2)
C(22)	5324(4)	8760(3)	3695(6)	78(2)
C(23)	5415(4)	9290(3)	1684(6)	83(2)
C(24)	3803(4)	9368(3)	562(6)	86(3)
C(25)	806(3)	8992(2)	1490(3)	45(1)
C(26)	-175(3)	9495(2)	1173(3)	45(1)
C(27)	-495(3)	9954(2)	1426(3)	50(1)
C(28)	-1255(3)	9985(2)	911(4)	54(2)
C(29)	-1702(3)	9571(2)	144(4)	55(2)
C(30)	-1382(3)	9137(2)	-146(4)	53(2)
C(31)	-590(3)	9107(2)	377(3)	47(1)
C(32)	402(3)	8615(2)	655(4)	52(2)
C(33)	7(4)	10389(2)	2233(4)	65(2)
C(34)	-1621(4)	10473(3)	1151(5)	72(2)
C(35)	-2558(4)	9613(3)	-370(6)	79(2)
C(36)	-1840(4)	8695(3)	-952(5)	73(2)
C(37)	711(4)	8105(3)	397(5)	72(2)
C(38)	2354(5)	7639(3)	6607(6)	85(2)
C(39)	844(6)	7904(3)	7276(5)	94(3)
C(40)	841(4)	7448(2)	5192(5)	67(2)
C(41)	-52(4)	7275(3)	5171(7)	88(3)
C(42)	-537(5)	6949(3)	4292(8)	102(3)
C(43)	-120(5)	6789(3)	3525(7)	102(3)
C(44)	750(6)	6933(3)	3558(7)	106(3)
C(45)	1249(5)	7286(3)	4404(6)	82(2)
C(46)	1083(3)	9958(2)	4651(5)	62(2)
C(47)	2278(4)	10320(2)	6392(4)	61(2)
C(48)	2900(3)	10125(2)	4456(4)	48(1)
C(49)	3649(3)	9961(2)	4532(4)	60(2)
C(50)	4327(4)	10199(2)	3930(5)	66(2)
C(51)	4262(4)	10598(3)	3253(5)	72(2)
C(52)	3530(5)	10767(4)	3175(7)	111(4)
C(53)	2839(4)	10535(4)	3760(6)	92(3)
Pd(1')	3258.6(2)	6130.1(1)	829.5(2)	36.6(1)
Br(1')	1986.9(3)	5863.5(2)	1940.3(4)	58.8(2)
P(1')	3665(1)	7063(1)	1443(1)	48.0(3)
P(2')	3022(1)	5207(1)	258(1)	39.7(3)

N(1')	5078(2)	6389(1)	618(2)	38(1)
N(2')	5080(2)	6709(1)	-1427(2)	39(1)
N(3')	2832(2)	6425(1)	-1302(3)	41(1)
N(4')	2836(2)	6101(2)	-3356(3)	45(1)
N(5')	4520(2)	5691(1)	-3109(2)	39(1)
N(6')	5395(2)	6521(2)	-4399(3)	47(1)
C(1')	4344(2)	6352(2)	92(3)	37(1)
C(2')	5845(2)	6568(2)	152(3)	38(1)
C(3')	6634(3)	6577(2)	714(3)	44(1)
C(4')	7392(3)	6743(2)	204(4)	48(1)
C(5')	7401(3)	6961(2)	-793(4)	48(1)
C(6')	6641(3)	6988(2)	-1315(3)	44(1)
C(7')	5845(3)	6762(2)	-857(3)	39(1)
C(8')	4354(3)	6497(2)	-991(3)	38(1)
C(9')	6625(3)	6399(2)	1806(4)	58(2)
C(10')	8239(3)	6697(3)	747(5)	71(2)
C(11')	8249(3)	7164(3)	-1308(5)	72(2)
C(12')	6625(3)	7254(3)	-2355(4)	65(2)
C(13')	3553(2)	6387(2)	-1687(3)	38(1)
C(14')	2090(3)	6301(2)	-1933(3)	43(1)
C(15')	1308(3)	6343(2)	-1537(4)	50(1)
C(16')	562(3)	6180(2)	-2184(5)	62(2)
C(17')	555(3)	5981(2)	-3216(5)	63(2)
C(18')	1313(3)	5970(2)	-3621(4)	55(2)
C(19')	2082(3)	6124(2)	-2974(3)	46(1)
C(20')	3534(3)	6222(2)	-2742(3)	41(1)
C(21')	1356(4)	6573(3)	-453(5)	76(2)
C(22')	-281(4)	6205(4)	-1771(7)	98(3)
C(23')	-316(4)	5785(3)	-3864(6)	89(3)
C(24')	1356(4)	5781(3)	-4737(5)	83(3)
C(25')	4315(3)	6160(2)	-3251(3)	39(1)
C(26')	5197(3)	5621(2)	-3622(3)	40(1)
C(27')	5423(3)	5109(2)	-3515(3)	43(1)
C(28')	6116(3)	5048(2)	-4035(3)	48(1)
C(29')	6581(3)	5477(2)	-4632(3)	49(1)
C(30')	6362(3)	5981(2)	-4755(3)	51(1)
C(31')	5647(3)	6044(2)	-4251(3)	42(1)
C(32')	4753(3)	6575(2)	-3921(3)	47(1)
C(33')	4910(4)	4656(2)	-2861(4)	58(2)
C(34')	6345(4)	4487(3)	-3968(4)	64(2)
C(35')	7333(4)	5388(3)	-5196(5)	75(2)
C(36')	6865(4)	6468(3)	-5371(5)	76(2)
C(37')	4478(4)	7114(2)	-4086(5)	66(2)
C(38')	2824(5)	7362(3)	1846(7)	91(3)
C(39')	4390(5)	7108(3)	2584(4)	80(2)
C(40')	4253(4)	7584(2)	591(4)	59(2)
C(41')	5168(4)	7744(2)	659(5)	69(2)
C(42')	5622(5)	8101(3)	-74(7)	94(3)
C(43')	5158(6)	8288(3)	-834(7)	106(3)
C(44')	4294(6)	8154(3)	-929(6)	98(3)
C(45')	3827(5)	7787(3)	-218(5)	83(2)
C(46')	3926(3)	5049(2)	-325(5)	62(2)
C(47')	2786(4)	4691(2)	1272(4)	62(2)
C(48')	2099(3)	4961(2)	-696(3)	42(1)
C(49')	1272(3)	4867(2)	-366(4)	56(2)
C(50')	551(3)	4689(3)	-1067(5)	66(2)
C(51')	645(4)	4613(2)	-2110(4)	64(2)
C(52')	1468(4)	4707(2)	-2433(4)	63(2)
C(53')	2198(3)	4884(2)	-1740(4)	52(1)

*$B_{eq} = 4/3\sum_i\sum_j \beta_{ij} a_i \cdot a_j$

Table 9. Anisotropic thermal parameters (Å x 10^3) for **3c**

The temperature factor is of the form :

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}lb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	48.9(2)	45.1(2)	52.9(2)	9.9(1)	-4.3(1)	3.0(1)
Br(1)	70.4(3)	82.1(3)	79.1(3)	23.0(3)	-15.5(2)	-6.0(3)
P(1)	76(1)	49(1)	69(1)	13(1)	-2(1)	12(1)
P(2)	48(1)	46(1)	63(1)	12(1)	1(1)	4(1)
N(1)	51(2)	51(2)	50(2)	5(2)	-5(1)	1(1)
N(2)	47(2)	51(2)	52(2)	10(2)	-3(1)	-2(2)
N(3)	50(2)	56(2)	61(2)	14(2)	2(2)	-4(2)
N(4)	61(2)	75(3)	67(2)	26(2)	14(2)	7(2)
N(5)	59(2)	65(2)	52(2)	16(2)	3(2)	3(2)
N(6)	73(3)	77(3)	58(2)	24(2)	5(2)	-2(2)
C(1)	42(2)	43(2)	56(2)	6(2)	0(2)	3(2)
C(2)	56(2)	47(2)	55(2)	9(2)	1(2)	5(2)
C(3)	55(2)	48(2)	62(3)	9(2)	8(2)	9(2)
C(4)	51(2)	47(2)	73(3)	9(2)	7(2)	3(2)
C(5)	58(3)	47(2)	67(3)	12(2)	-3(2)	-3(2)
C(6)	50(2)	59(3)	60(3)	9(2)	-2(2)	-5(2)
C(7)	51(2)	45(2)	53(2)	8(2)	0(2)	-4(2)
C(8)	53(2)	47(2)	53(2)	13(2)	4(2)	1(2)
C(9)	67(3)	106(4)	55(3)	9(3)	14(2)	5(3)
C(10)	53(3)	90(4)	93(4)	8(3)	14(2)	10(3)
C(11)	49(3)	100(4)	97(4)	18(3)	-8(3)	-14(3)
C(12)	60(3)	113(4)	58(3)	10(3)	-3(2)	-9(3)
C(13)	51(2)	50(2)	53(2)	15(2)	-1(2)	-5(2)
C(14)	54(2)	50(2)	69(3)	18(2)	-2(2)	-9(2)
C(15)	56(3)	59(3)	81(3)	23(2)	-4(2)	-19(2)
C(16)	55(3)	60(3)	94(4)	23(2)	-3(2)	-25(2)
C(17)	57(3)	67(3)	100(4)	18(2)	10(3)	-18(3)
C(18)	67(3)	70(3)	84(3)	27(3)	14(2)	5(3)
C(19)	55(3)	63(3)	73(3)	20(2)	9(2)	-1(2)
C(20)	56(3)	62(3)	51(2)	19(2)	3(2)	-3(2)
C(21)	86(4)	102(4)	83(4)	50(3)	-8(3)	2(3)
C(22)	64(3)	116(5)	124(5)	41(3)	-12(3)	-23(4)
C(23)	61(3)	124(5)	128(5)	22(3)	28(3)	-13(4)
C(24)	97(5)	138(6)	113(5)	54(4)	48(4)	48(4)
C(25)	53(2)	66(3)	53(2)	16(2)	10(2)	3(2)
C(26)	60(3)	65(3)	48(2)	22(2)	10(2)	11(2)
C(27)	67(3)	68(3)	55(3)	20(2)	4(2)	8(2)
C(28)	66(3)	76(3)	68(3)	24(2)	14(2)	20(2)
C(29)	53(3)	80(3)	72(3)	15(2)	6(2)	14(2)
C(30)	64(3)	81(3)	55(3)	19(2)	6(2)	8(2)
C(31)	56(3)	73(3)	50(2)	17(2)	0(2)	5(2)
C(32)	67(3)	78(3)	58(3)	33(2)	3(2)	-4(2)
C(33)	97(4)	82(4)	70(3)	31(3)	-5(3)	-6(3)
C(34)	101(4)	102(4)	89(4)	59(4)	9(3)	11(3)
C(35)	78(4)	106(5)	117(5)	34(3)	-22(3)	11(4)
C(36)	85(4)	106(5)	80(4)	24(3)	-15(3)	-13(3)
C(37)	95(4)	95(4)	90(4)	43(3)	-7(3)	-22(3)
C(38)	112(5)	72(4)	137(6)	33(3)	-34(4)	17(4)
C(39)	168(7)	100(5)	93(4)	30(5)	59(5)	35(4)
C(40)	93(4)	47(3)	109(4)	17(3)	-3(3)	10(3)
C(41)	75(4)	60(4)	186(7)	5(3)	-7(4)	-7(4)
C(42)	109(5)	90(5)	177(8)	20(4)	-22(5)	-13(5)
C(43)	119(6)	96(5)	158(7)	19(4)	-20(5)	-9(5)
C(44)	169(8)	101(5)	123(6)	31(5)	-21(6)	-28(5)
C(45)	123(5)	67(4)	112(5)	16(3)	8(4)	-17(3)
C(46)	60(3)	73(3)	107(4)	25(3)	-2(3)	22(3)
C(47)	91(4)	56(3)	79(3)	13(3)	12(3)	-10(2)
C(48)	62(3)	52(3)	68(3)	16(2)	4(2)	1(2)
C(49)	64(3)	75(3)	87(3)	19(3)	10(3)	9(3)
C(50)	72(3)	79(4)	97(4)	16(3)	23(3)	-2(3)
C(51)	81(4)	112(5)	75(3)	16(3)	19(3)	20(3)
C(52)	100(5)	192(9)	141(7)	48(5)	37(5)	98(7)
C(53)	89(4)	152(7)	127(5)	54(4)	38(4)	80(5)

Pd(1')	41.5(2)	48.0(2)	46.7(2)	7.7(1)	7.2(1)	-3.7(1)
Br(1')	61.6(3)	89.4(4)	71.3(3)	16.7(2)	19.0(2)	2.4(3)
P(1')	62(1)	55(1)	60(1)	9(1)	8(1)	-15(1)
P(2')	44(1)	46(1)	59(1)	10(1)	5(1)	-2(1)
N(1')	41(2)	52(2)	48(2)	9(1)	0(1)	0(1)
N(2')	44(2)	52(2)	49(2)	10(1)	8(1)	-2(1)
N(3')	49(2)	50(2)	55(2)	15(2)	5(1)	2(2)
N(4')	58(2)	61(2)	50(2)	22(2)	-7(2)	-8(2)
N(5')	51(2)	55(2)	40(2)	14(2)	4(1)	-1(1)
N(6')	70(2)	63(2)	47(2)	22(2)	14(2)	7(2)
C(1')	46(2)	41(2)	48(2)	6(2)	9(2)	-1(2)
C(2')	43(2)	47(2)	51(2)	9(2)	1(2)	-2(2)
C(3')	51(2)	50(2)	64(3)	13(2)	1(2)	0(2)
C(4')	49(2)	54(3)	77(3)	12(2)	-1(2)	3(2)
C(5')	49(2)	53(3)	76(3)	8(2)	14(2)	-3(2)
C(6')	50(2)	62(3)	49(2)	7(2)	5(2)	-2(2)
C(7')	47(2)	47(2)	50(2)	9(2)	8(2)	-1(2)
C(8')	46(2)	44(2)	51(2)	11(2)	3(2)	-8(2)
C(9')	62(3)	82(3)	68(3)	11(2)	-9(2)	15(3)
C(10')	45(3)	99(4)	124(5)	22(3)	-11(3)	12(4)
C(11')	53(3)	102(4)	113(5)	12(3)	25(3)	15(3)
C(12')	59(3)	111(4)	63(3)	-2(3)	10(2)	15(3)
C(13')	43(2)	46(2)	55(2)	9(2)	5(2)	4(2)
C(14')	46(2)	48(2)	68(3)	15(2)	1(2)	4(2)
C(15')	47(2)	67(3)	82(3)	21(2)	14(2)	17(2)
C(16')	53(3)	72(3)	116(4)	24(2)	12(3)	26(3)
C(17')	62(3)	62(3)	111(4)	16(2)	-23(3)	3(3)
C(18')	62(3)	57(3)	90(3)	25(2)	-19(2)	-11(2)
C(19')	57(3)	49(2)	66(3)	18(2)	-9(2)	-2(2)
C(20')	58(2)	50(2)	47(2)	16(2)	0(2)	0(2)
C(21')	79(4)	139(6)	89(4)	55(4)	24(3)	9(4)
C(22')	60(4)	184(8)	141(6)	50(4)	23(4)	38(6)
C(23')	67(4)	121(6)	138(6)	16(4)	-30(4)	-11(4)
C(24')	98(4)	130(6)	93(4)	55(4)	-40(3)	-41(4)
C(25')	52(2)	57(2)	41(2)	17(2)	0(2)	-1(2)
C(26')	54(2)	57(2)	38(2)	14(2)	-2(2)	-1(2)
C(27')	59(3)	57(3)	46(2)	19(2)	0(2)	-3(2)
C(28')	63(3)	74(3)	48(2)	28(2)	-8(2)	-12(2)
C(29')	54(3)	75(3)	56(3)	16(2)	3(2)	-11(2)
C(30')	69(3)	69(3)	54(3)	17(2)	12(2)	-4(2)
C(31')	54(2)	62(3)	44(2)	14(2)	2(2)	-1(2)
C(32')	71(3)	57(3)	51(2)	22(2)	-1(2)	4(2)
C(33')	92(4)	67(3)	69(3)	30(3)	15(3)	10(2)
C(34')	94(4)	94(4)	70(3)	58(3)	1(3)	-8(3)
C(35')	81(4)	106(5)	105(4)	35(3)	36(3)	-13(4)
C(36')	105(5)	96(4)	91(4)	21(3)	51(4)	14(3)
C(37')	104(4)	65(3)	98(4)	45(3)	26(3)	23(3)
C(38')	102(5)	87(4)	163(7)	32(4)	44(5)	-42(4)
C(39')	118(5)	100(5)	62(3)	1(4)	-20(3)	-16(3)
C(40')	90(4)	58(3)	72(3)	17(3)	0(3)	-11(2)
C(41')	81(4)	66(3)	103(4)	-3(3)	22(3)	-5(3)
C(42')	113(5)	95(5)	141(6)	6(4)	40(5)	7(4)
C(43')	166(8)	99(5)	116(6)	5(5)	8(5)	12(4)
C(44')	161(7)	90(5)	109(5)	21(5)	-20(5)	14(4)
C(45')	120(5)	76(4)	104(5)	14(4)	-17(4)	17(3)
C(46')	54(3)	77(3)	111(4)	26(2)	15(3)	-11(3)
C(47')	79(3)	62(3)	90(4)	17(3)	3(3)	22(3)
C(48')	53(2)	49(2)	57(2)	12(2)	4(2)	-3(2)
C(49')	54(3)	79(3)	77(3)	16(2)	4(2)	-8(3)
C(50')	63(3)	89(4)	90(4)	15(3)	-5(3)	-21(3)
C(51')	83(4)	76(4)	79(3)	20(3)	-10(3)	-10(3)
C(52')	87(4)	82(4)	67(3)	19(3)	5(3)	-5(3)
C(53')	71(3)	57(3)	67(3)	15(2)	3(2)	-6(2)

Table 10. Bond length (Å) and angles (°) for **3c**

	A	B*
Pd(1) Br(1)	2.534(1)	2.536(1)
Pd(1) P(1)	2.329(2)	2.321(2)
Pd(1) P(2)	2.314(2)	2.306(2)
Pd(1) - N(3)	2.942(5)	2.966(4)
Pd(1) - C(1)	1.987(5)	2.002(5)
P(1) C(38)	1.831(8)	1.829(9)
P(1) C(39)	1.821(10)	1.809(8)
P(1) - C(40)	1.838(7)	1.811(7)
P(2) - C(46)	1.821(7)	1.829(7)
P(2) - C(47)	1.824(7)	1.832(7)
P(2) - C(48)	1.817(5)	1.827(5)
N(1) C(1)	1.305(6)	1.307(6)
N(1) - C(2)	1.377(6)	1.379(6)
N(2) C(7)	1.361(6)	1.369(6)
N(2) C(8)	1.316(6)	1.314(6)
N(3) C(13)	1.324(7)	1.329(6)
N(3) - C(14)	1.368(7)	1.361(6)
N(4) C(19)	1.368(7)	1.366(7)
N(4) - C(20)	1.318(7)	1.294(7)
N(5) - C(25)	1.322(7)	1.306(6)
N(5) - C(26)	1.374(7)	1.374(6)
N(6) - C(31)	1.362(7)	1.366(7)
N(6) - C(32)	1.311(7)	1.286(7)
C(1) - C(8)	1.437(7)	1.462(7)
C(2) - C(3)	1.408(7)	1.420(7)
C(2) - C(7)	1.407(7)	1.406(7)
C(3) - C(4)	1.376(7)	1.396(7)
C(3) C(9)	1.523(9)	1.496(7)
C(4) - C(5)	1.410(7)	1.413(7)
C(4) - C(10)	1.509(8)	1.532(9)
C(5) - C(6)	1.392(7)	1.382(7)
C(5) - C(11)	1.519(9)	1.526(9)
C(6) - C(7)	1.418(7)	1.425(7)
C(6) - C(12)	1.510(9)	1.517(9)
C(8) - C(13)	1.493(7)	1.483(7)
C(13) - C(20)	1.442(7)	1.425(7)
C(14) - C(15)	1.437(7)	1.430(7)
C(14) - C(19)	1.401(7)	1.418(7)
C(15) - C(16)	1.369(7)	1.377(8)
C(15) - C(21)	1.500(9)	1.504(9)
C(16) - C(17)	1.408(7)	1.424(9)
C(16) C(22)	1.512(9)	1.519(12)
C(17) - C(18)	1.394(7)	1.376(8)
C(17) - C(23)	1.528(9)	1.536(10)
C(18) - C(19)	1.413(7)	1.404(7)
C(18) - C(24)	1.523(9)	1.534(9)
C(20) - C(25)	1.484(7)	1.513(7)
C(25) - C(32)	1.414(7)	1.418(7)
C(26) - C(27)	1.420(7)	1.421(7)
C(26) - C(31)	1.396(7)	1.402(7)
C(27) C(28)	1.381(7)	1.394(7)
C(27) - C(33)	1.505(8)	1.504(8)
C(28) C(29)	1.418(7)	1.394(7)
C(28) - C(34)	1.527(9)	1.537(9)
C(29) - C(30)	1.378(7)	1.398(7)
C(29) - C(35)	1.527(9)	1.532(9)
C(30) - C(31)	1.430(7)	1.415(7)
C(30) C(36)	1.495(9)	1.520(9)
C(32) C(37)	1.526(9)	1.535(8)
C(40) - C(41)	1.381(11)	1.414(9)
C(40) - C(45)	1.374(10)	1.396(10)
C(41) - C(42)	1.435(14)	1.407(11)
C(42) - C(43)	1.360(14)	1.366(13)
C(43) - C(44)	1.346(13)	1.336(14)
C(44) - C(45)	1.438(13)	1.407(13)
C(48) C(49)	1.382(7)	1.391(7)
C(48) - C(53)	1.389(11)	1.398(7)
C(49) - C(50)	1.389(8)	1.389(9)
C(50) - C(51)	1.354(10)	1.395(10)
C(51) - C(52)	1.363(12)	1.381(9)
C(52) - C(53)	1.387(14)	1.393(8)

Br(1)-Pd(1)-P(1)	92.0(1)	92.0(1)
Br(1)-Pd(1)-P(2)	93.9(1)	92.4(1)
Br(1)-Pd(1)-N(3)	115.1(1)	114.8(1)
Br(1)-Pd(1)-C(1)	174.7(1)	173.9(1)
P(1) -Pd(1)-P(2)	170.1(1)	173.3(1)
P(1) -Pd(1)-N(3)	94.2(1)	93.5(1)
P(1) -Pd(1)-C(1)	85.5(2)	85.7(2)
P(2) -Pd(1)-N(3)	90.4(1)	89.1(1)
P(2) -Pd(1)-C(1)	88.0(1)	89.4(1)
N(3) -Pd(1)-C(1)	69.8(2)	71.0(2)
Pd(1)-P(1) -C(38)	118.9(3)	118.5(3)
Pd(1)-P(1) -C(39)	107.6(3)	107.0(3)
Pd(1)-P(1) -C(40)	114.9(2)	116.0(2)
C(38)-P(1) -C(39)	104.8(4)	105.0(4)
C(38)-P(1) -C(40)	103.3(3)	103.3(4)
C(39)-P(1) -C(40)	106.2(4)	105.8(4)
Pd(1)-P(2) -C(46)	115.8(2)	115.9(2)
Pd(1)-P(2) -C(47)	114.1(2)	114.1(2)
Pd(1)-P(2) -C(48)	115.0(2)	113.4(2)
C(46)-P(2) -C(47)	101.9(3)	102.7(3)
C(46)-P(2) -C(48)	104.6(3)	105.2(3)
C(47)-P(2) -C(48)	103.9(3)	104.2(3)
C(1) -N(1) -C(2)	120.3(4)	120.0(4)
C(7) -N(2) -C(8)	118.2(4)	118.3(4)
Pd(1)-N(3) -C(13)	96.9(3)	96.8(3)
Pd(1)-N(3) -C(14)	132.3(3)	134.0(3)
C(13)-N(3) -C(14)	118.4(5)	118.6(4)
C(19)-N(4) -C(20)	118.6(5)	118.7(5)
C(25)-N(5) -C(26)	117.2(5)	117.0(4)
C(31)-N(6) -C(32)	117.8(5)	117.9(5)
Pd(1)-C(1) -N(1)	116.0(4)	118.1(3)
Pd(1)-C(1) -C(8)	125.1(4)	123.0(4)
N(1) -C(1) -C(8)	118.9(4)	118.9(4)
N(1) -C(2) -C(3)	120.5(4)	119.5(4)
N(1) -C(2) -C(7)	119.6(4)	119.9(4)
C(3) -C(2) -C(7)	119.9(4)	120.5(4)
C(2) -C(3) -C(4)	120.4(5)	117.7(5)
C(2) -C(3) -C(9)	117.7(5)	119.7(4)
C(4) -C(3) -C(9)	121.9(5)	122.6(5)
C(3) -C(4) -C(5)	119.7(5)	121.7(5)
C(3) -C(4) -C(10)	121.1(5)	119.1(5)
C(5) -C(4) -C(10)	119.2(5)	119.2(5)
C(4) -C(5) -C(6)	121.4(5)	120.4(5)
C(4) -C(5) -C(11)	119.6(5)	120.3(5)
C(6) -C(5) -C(11)	119.0(5)	119.3(5)
C(5) -C(6) -C(7)	118.6(4)	118.9(5)
C(5) -C(6) -C(12)	121.5(5)	122.3(5)
C(7) -C(6) -C(12)	119.8(5)	118.8(5)
N(2) -C(7) -C(2)	120.5(4)	120.3(4)
N(2) -C(7) -C(6)	119.6(4)	119.3(4)
C(2) -C(7) -C(6)	119.9(4)	120.3(4)
N(2) -C(8) -C(1)	122.6(4)	122.0(4)
N(2) -C(8) -C(13)	116.4(4)	115.3(4)
C(1) -C(8) -C(13)	121.0(4)	122.6(4)
N(3) -C(13)-C(8)	117.8(4)	118.8(4)
N(3) -C(13)-C(20)	120.1(5)	119.7(4)
C(8) -C(13)-C(20)	122.1(4)	121.5(4)
N(3) -C(14)-C(15)	118.6(5)	119.6(4)
N(3) -C(14)-C(19)	121.4(5)	120.7(4)
C(15)-C(14)-C(19)	120.0(5)	119.7(4)
C(14)-C(15)-C(16)	117.9(5)	117.6(5)
C(14)-C(15)-C(21)	120.0(5)	118.1(5)
C(16)-C(15)-C(21)	122.1(5)	124.3(5)
C(15)-C(16)-C(17)	122.1(5)	122.2(6)
C(15)-C(16)-C(22)	118.2(5)	118.5(6)
C(17)-C(16)-C(22)	119.5(5)	119.3(6)
C(16)-C(17)-C(18)	120.6(5)	120.6(6)
C(16)-C(17)-C(23)	121.1(5)	118.3(6)

C(18)-C(17)-C(23)	118.4(5)	121.1(6)
C(17)-C(18)-C(19)	118.2(5)	118.5(5)
C(17)-C(18)-C(24)	123.2(5)	123.2(5)
C(19)-C(18)-C(24)	118.6(5)	118.3(5)
N(4) -C(19)-C(14)	119.9(5)	119.4(5)
N(4) -C(19)-C(18)	119.2(5)	119.2(5)
C(14)-C(19)-C(18)	120.9(5)	121.3(5)
N(4) -C(20)-C(13)	121.5(5)	122.8(5)
N(4) -C(20)-C(25)	114.8(4)	113.4(4)
C(13)-C(20)-C(25)	123.6(4)	123.8(4)
N(5) -C(25)-C(20)	117.7(5)	117.1(4)
N(5) -C(25)-C(32)	121.9(5)	122.0(4)
C(20)-C(25)-C(32)	120.3(4)	120.7(4)
N(5) -C(26)-C(27)	119.1(5)	118.8(4)
N(5) -C(26)-C(31)	120.4(5)	120.5(4)
C(27)-C(26)-C(31)	120.5(5)	120.7(4)
C(26)-C(27)-C(28)	118.3(5)	117.9(4)
C(26)-C(27)-C(33)	119.1(5)	119.5(5)
C(28)-C(27)-C(33)	122.6(5)	122.7(5)
C(27)-C(28)-C(29)	120.9(5)	121.3(5)
C(27)-C(28)-C(34)	120.2(5)	118.7(5)
C(29)-C(28)-C(34)	118.9(5)	120.0(5)
C(28)-C(29)-C(30)	121.7(5)	121.6(5)
C(28)-C(29)-C(35)	118.6(5)	119.3(5)
C(30)-C(29)-C(35)	119.7(5)	119.0(5)
C(29)-C(30)-C(31)	117.6(5)	117.8(4)
C(29)-C(30)-C(36)	122.8(5)	123.6(5)
C(31)-C(30)-C(36)	119.6(5)	118.6(5)
N(6) -C(31)-C(26)	121.2(5)	120.5(5)
N(6) -C(31)-C(30)	118.0(5)	118.8(5)
C(26)-C(31)-C(30)	120.8(5)	120.6(5)
N(6) -C(32)-C(25)	121.4(5)	122.0(5)
N(6) -C(32)-C(37)	117.5(5)	117.6(5)
C(25)-C(32)-C(37)	121.0(5)	120.4(5)
P(1) -C(40)-C(41)	121.3(6)	119.9(5)
P(1) -C(40)-C(45)	118.3(5)	121.6(5)
C(41)-C(40)-C(45)	120.0(7)	118.1(6)
C(40)-C(41)-C(42)	118.6(8)	119.9(6)
C(41)-C(42)-C(43)	120.3(9)	118.4(8)
C(42)-C(43)-C(44)	121.6(9)	124.1(9)
C(43)-C(44)-C(45)	119.0(9)	118.3(9)
C(40)-C(45)-C(44)	120.3(7)	121.1(7)
P(2) -C(48)-C(49)	120.0(4)	118.1(4)
P(2) -C(48)-C(53)	121.6(5)	122.4(4)
C(49)-C(48)-C(53)	118.4(6)	119.4(5)
C(48)-C(49)-C(50)	121.1(5)	120.1(5)
C(49)-C(50)-C(51)	120.1(6)	120.7(6)
C(50)-C(51)-C(52)	119.5(7)	118.9(6)
C(51)-C(52)-C(53)	121.8(9)	121.2(6)
C(48)-C(53)-C(52)	119.1(8)	119.7(5)

* The two independent molecules in an asymmetric unit were named by A and B.

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic temperature factors ($Å^2$ x 10) for **3d**

$^*B_{eq} = 4/3 \Sigma i \Sigma j \beta ij ai aj$.

	x	y	z	Beq
Pd1	0.14810(1)	0.11445(2)	0.05152(1)	3.86(1)
Br1	0.11912(3)	0.22640(4)	-0.01502(3)	6.93(3)
P1	0.16206(5)	0.02012(7)	0.00741(4)	4.24(5)
P2	0.13505(5)	0.20332(7)	0.09945(5)	4.45(5)
N1	0.1176(1)	0.0002(2)	0.0950(1)	4.1(1)
N2	0.2147(1)	-0.0717(2)	0.1704(1)	3.7(1)
N3	0.2665(1)	0.0863(2)	0.1396(1)	3.6(1)
N4	0.3469(1)	-0.0296(2)	0.1736(1)	4.4(2)
N5	0.2700(2)	-0.1924(2)	0.1401(1)	4.6(2)
N6	0.3507(2)	-0.2494(2)	0.2387(2)	4.7(2)
N7	0.3591(2)	-0.0586(2)	0.2836(2)	4.8(2)
N8	0.4688(2)	-0.0727(3)	0.3397(2)	6.1(2)
C1	0.1600(2)	0.0249(2)	0.1001(2)	3.4(2)
C2	0.1212(2)	-0.0584(3)	0.1275(2)	4.1(2)
C3	0.0751(2)	-0.0819(3)	0.1228(2)	4.8(2)
C4	0.0796(2)	-0.1420(4)	0.1552(2)	5.6(2)
C5	0.1286(2)	-0.1800(3)	0.1930(2)	5.7(2)
C6	0.1740(2)	-0.1558(3)	0.1988(2)	4.8(2)
C7	0.1697(2)	-0.0945(3)	0.1649(2)	4.0(2)
C8	0.2104(2)	-0.0140(2)	0.1395(1)	3.5(2)
C9	0.0240(2)	-0.0364(4)	0.0839(2)	6.6(3)
C10	0.0298(3)	-0.1661(5)	0.1512(3)	8.9(4)
C11	0.1315(3)	-0.2471(5)	0.2279(3)	8.5(4)
C12	0.2289(2)	-0.1931(4)	0.2394(2)	6.8(3)
C13	0.2607(2)	0.0085(2)	0.1478(1)	3.4(2)
C14	0.3127(2)	0.1090(2)	0.1477(2)	3.9(2)
C15	0.3195(2)	0.1928(3)	0.1387(2)	4.6(2)
C16	0.3663(2)	0.2151(3)	0.1476(2)	5.1(2)
C17	0.4065(2)	0.1547(4)	0.1630(2)	5.9(2)
C18	0.3999(2)	0.0726(3)	0.1706(2)	5.4(2)
C19	0.3530(1)	0.0511(3)	0.1645(2)	4.2(2)
C20	0.3026(2)	-0.0507(2)	0.1658(2)	3.8(2)
C21	0.2743(3)	0.2518(3)	0.1198(3)	6.4(3)
C22	0.3747(3)	0.3045(4)	0.1387(3)	7.7(4)
C23	0.4552(3)	0.1824(5)	0.1680(3)	9.0(4)
C24	0.4385(3)	0.0037(5)	0.1830(3)	8.4(4)
C25	0.3026(2)	-0.1404(3)	0.1777(2)	3.9(2)
C26	0.2771(2)	-0.2745(3)	0.1515(2)	5.2(2)
C27	0.2434(3)	-0.3328(4)	0.1115(2)	7.4(3)
C28	0.2511(4)	-0.4161(4)	0.1229(3)	8.9(5)
C29	0.2935(3)	-0.4446(3)	0.1736(3)	7.6(4)
C30	0.3261(3)	-0.3907(3)	0.2117(3)	6.4(3)
C31	0.3178(2)	-0.3031(3)	0.2007(2)	5.1(3)
C32	0.3438(2)	-0.1695(3)	0.2280(2)	4.2(2)
C33	0.2005(4)	-0.2994(5)	0.0573(3)	10.4(5)
C34	0.2150(6)	-0.4804(5)	0.0807(4)	14.8(8)
C35	0.3010(5)	-0.5383(4)	0.1838(4)	11.3(7)
C36	0.372(3)	-0.4190(4)	0.2646(3)	8.5(4)
C37	0.3807(2)	-0.1130(3)	0.2713(2)	4.4(2)
C38	0.3924(2)	-0.0092(3)	0.3257(2)	5.2(2)
C39	0.3700(3)	0.0507(4)	0.3389(3)	6.8(3)
C40	0.4036(3)	0.0971(4)	0.3830(3)	7.9(4)
C41	0.4592(3)	0.0861(5)	0.4135(3)	9.0(4)
C42	0.4812(3)	0.0296(5)	0.3999(3)	8.2(3)
C43	0.4475(2)	-0.0178(4)	0.3548(2)	5.8(2)
C44	0.4364(2)	-0.1189(3)	0.2987(2)	5.4(2)
C45	0.3108(3)	0.0595(5)	0.3054(3)	9.9(4)
C46	0.3808(4)	0.1636(6)	0.3990(4)	11.4(6)
C47	0.4949(5)	0.1378(8)	0.4631(5)	14.2(7)
C48	0.5413(3)	0.0131(8)	0.4329(4)	12.8(5)
C49	0.4601(3)	-0.1771(4)	0.2808(3)	7.3(3)
C50	0.1129(2)	0.0255(4)	-0.0629(2)	6.6(2)
C51	0.1609(3)	-0.0893(3)	0.0209(2)	5.9(3)
C52	0.2249(2)	0.0346(3)	0.0181(2)	4.8(2)

C53	0.2358(2)	0.1120(4)	0.0074(2)	6.0(3)
C54	0.2834(3)	0.1280(4)	0.0158(3)	7.0(3)
C55	0.3204(3)	0.0684(5)	0.0346(3)	7.6(3)
C56	0.3114(3)	-0.0093(5)	0.0462(3)	8.0(3)
C57	0.2627(3)	-0.0266(4)	0.0370(2)	6.5(3)
C58	0.1728(3)	0.1771(4)	0.1670(2)	6.8(3)
C59	0.1508(3)	0.3139(3)	0.1005(3)	7.1(3)
C60	0.0666(2)	0.2064(3)	0.0767(2)	5.1(2)
C61	0.0285(2)	0.1657(3)	0.0326(2)	5.8(2)
C62	-0.0244(2)	0.1701(4)	0.0125(3)	7.1(3)
C63	-0.0393(2)	0.2169(4)	0.0384(3)	7.4(3)
C64	-0.0013(3)	0.2580(6)	0.0825(3)	9.5(4)
C65	0.0519(3)	0.2525(6)	0.1024(3)	9.0(4)

Table 12. Anisotropic thermal parameters (Å x 10^3) for **3d**

The temperature factor is of the form :

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}lb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
PD	0.0461(2)	0.0505(2)	0.0503(2)	-0.0030(1)	0.0290(2)	0.0071(1)
Br1	0.0915(4)	0.0876(4)	0.0922(4)	0.0160(3)	0.0593(4)	0.0335(3)
P1	0.0536(6)	0.0590(6)	0.0480(6)	-0.0096(5)	0.0302(6)	-0.0006(5)
P2	0.0501(6)	0.0533(6)	0.0606(7)	-0.0066(5)	0.0304(6)	-0.0055(5)
N1	0.047(2)	0.059(2)	0.048(2)	-0.010(2)	0.028(2)	-0.004(2)
N2	0.047(2)	0.049(2)	0.045(2)	-0.010(1)	0.027(2)	-0.001(1)
N3	0.045(2)	0.046(2)	0.044(2)	-0.009(1)	0.025(2)	-0.002(1)
N4	0.052(2)	0.058(2)	0.060(2)	-0.003(2)	0.036(2)	0.009(2)
N5	0.073(2)	0.047(2)	0.056(2)	-0.007(2)	0.039(2)	-0.002(2)
N6	0.070(2)	0.046(2)	0.065(2)	0.005(2)	0.043(2)	0.007(2)
N7	0.058(2)	0.054(2)	0.058(2)	-0.003(2)	0.028(2)	0.002(2)
N8	0.055(2)	0.104(3)	0.071(3)	-0.013(2)	0.036(2)	-0.002(2)
C1	0.043(2)	0.045(2)	0.043(2)	-0.008(2)	0.026(2)	-0.000(2)
C2	0.051(2)	0.056(2)	0.045(2)	-0.015(2)	0.027(2)	-0.006(2)
C3	0.053(3)	0.079(3)	0.056(3)	-0.018(2)	0.034(2)	-0.004(2)
C4	0.057(3)	0.091(3)	0.064(3)	-0.026(3)	0.036(3)	-0.002(3)
C5	0.076(3)	0.081(3)	0.069(3)	-0.020(3)	0.049(3)	0.007(3)
C6	0.060(3)	0.066(3)	0.057(3)	-0.009(2)	0.035(2)	0.011(2)
C7	0.050(2)	0.053(2)	0.048(2)	-0.013(2)	0.029(2)	0.000(2)
C8	0.047(2)	0.044(2)	0.038(2)	-0.009(2)	0.024(2)	-0.003(2)
C9	0.052(3)	0.117(5)	0.077(4)	-0.011(3)	0.036(3)	0.008(3)
C10	0.081(4)	0.161(7)	0.113(5)	-0.032(4)	0.066(4)	0.023(5)
C11	0.104(5)	0.117(5)	0.116(6)	-0.010(4)	0.074(5)	0.044(4)
C12	0.081(4)	0.093(4)	0.077(4)	0.003(3)	0.044(3)	0.037(3)
C13	0.044(2)	0.042(2)	0.042(2)	-0.010(2)	0.025(2)	-0.002(2)
C14	0.051(2)	0.051(2)	0.042(2)	-0.013(2)	0.026(2)	-0.004(2)
C15	0.068(3)	0.052(2)	0.056(3)	-0.016(2)	0.039(2)	-0.007(2)
C16	0.073(3)	0.066(3)	0.057(3)	-0.033(2)	0.041(3)	-0.009(2)
C17	0.058(3)	0.102(4)	0.068(3)	-0.024(3)	0.039(3)	0.007(3)
C18	0.051(3)	0.085(3)	0.070(3)	-0.005(2)	0.036(2)	0.016(3)
C19	0.048(2)	0.060(2)	0.050(2)	-0.009(2)	0.028(2)	0.003(2)
C20	0.050(2)	0.049(2)	0.046(2)	-0.005(2)	0.029(2)	0.001(2)
C21	0.094(4)	0.048(3)	0.109(5)	-0.003(3)	0.065(4)	0.005(3)
C22	0.121(5)	0.066(3)	0.123(5)	-0.031(3)	0.082(5)	-0.003(3)
C23	0.080(4)	0.133(6)	0.142(7)	-0.030(4)	0.074(5)	0.017(5)
C24	0.076(4)	0.125(5)	0.153(7)	0.025(4)	0.079(5)	0.051(5)
C25	0.055(2)	0.048(2)	0.054(2)	-0.002(2)	0.037(2)	0.002(2)
C26	0.095(4)	0.052(2)	0.059(3)	-0.007(2)	0.051(3)	-0.001(2)
C27	0.140(6)	0.061(3)	0.069(4)	-0.020(3)	0.057(4)	-0.010(3)
C28	0.205(8)	0.051(3)	0.090(4)	-0.036(4)	0.093(5)	-0.017(3)
C29	0.159(6)	0.043(3)	0.105(5)	-0.003(3)	0.089(5)	-0.003(3)
C30	0.123(5)	0.048(3)	0.095(4)	0.009(3)	0.077(4)	0.012(3)
C31	0.093(4)	0.045(2)	0.078(3)	0.007(2)	0.063(3)	0.005(2)
C32	0.055(2)	0.052(2)	0.060(3)	0.002(2)	0.039(2)	0.008(2)
C33	0.182(8)	0.082(4)	0.062(4)	-0.036(5)	0.037(5)	-0.011(3)
C34	0.32(2)	0.070(4)	0.096(6)	-0.055(6)	0.081(8)	-0.031(4)
C35	0.25(1)	0.043(3)	0.159(8)	0.003(5)	0.137(8)	0.000(4)
C36	0.142(6)	0.071(4)	0.111(5)	0.032(4)	0.076(5)	0.032(4)
C37	0.062(3)	0.055(2)	0.055(3)	-0.003(2)	0.038(2)	0.007(2)
C38	0.062(3)	0.065(3)	0.064(3)	-0.013(2)	0.035(3)	-0.002(2)
C39	0.088(4)	0.076(3)	0.092(4)	-0.011(3)	0.052(4)	-0.019(3)
C40	0.109(5)	0.094(4)	0.092(5)	-0.022(4)	0.058(4)	-0.028(4)

C41	0.112(5)	0.133(6)	0.103(5)	-0.056(5)	0.068(5)	-0.059(5)
C42	0.068(4)	0.136(6)	0.095(5)	-0.047(4)	0.042(4)	-0.033(4)
C43	0.068(3)	0.074(3)	0.070(3)	-0.021(3)	0.043(3)	-0.011(3)
C44	0.060(3)	0.078(3)	0.069(3)	-0.003(2)	0.040(3)	0.009(2)
C45	0.086(5)	0.117(5)	0.122(6)	0.019(4)	0.037(4)	-0.040(5)
C46	0.159(8)	0.119(6)	0.131(7)	-0.014(6)	0.073(6)	-0.063(6)
C47	0.137(8)	0.23(1)	0.160(9)	-0.092(8)	0.083(7)	-0.126(9)
C48	0.060(4)	0.26(1)	0.129(7)	-0.061(6)	0.039(5)	-0.086(8)
C49	0.076(4)	0.101(4)	0.120(5)	0.003(3)	0.069(4)	-0.003(4)
C50	0.063(3)	0.119(5)	0.046(3)	-0.014(3)	0.020(2)	0.002(3)
C51	0.100(4)	0.056(3)	0.077(3)	-0.021(3)	0.057(3)	-0.011(2)
C52	0.054(3)	0.078(3)	0.050(3)	-0.001(2)	0.032(2)	-0.002(2)
C53	0.072(39	0.088(4)	0.080(4)	-0.021(3)	0.052(3)	-0.004(3)
C54	0.084(4)	0.112(5)	0.092(4)	-0.030(3)	0.064(4)	-0.025(3)
C55	0.071(4)	0.150(6)	0.077(4)	-0.022(4)	0.049(3)	-0.023(4)
C56	0.074(4)	0.147(6)	0.086(4)	0.018(4)	0.049(4)	0.003(4)
C57	0.079(4)	0.100(4)	0.072(3)	0.006(3)	0.047(3)	-0.003(3)
C58	0.085(4)	0.092(4)	0.052(3)	0.002(3)	0.025(3)	-0.012(3)
C59	0.088(4)	0.052(3)	0.130(5)	-0.012(3)	0.065(4)	-0.006(3)
C60	0.057(3)	0.065(3)	0.072(3)	-0.006(2)	0.039(3)	-0.011(2)
C61	0.055(3)	0.079(3)	0.066(3)	-0.003(2)	0.027(3)	-0.010(3)
C62	0.062(3)	0.095(4)	0.099(5)	-0.008(3)	0.041(3)	-0.016(3)
C63	0.064(3)	0.089(4)	0.121(5)	-0.012(3)	0.052(4)	-0.024(4)
C64	0.073(4)	0.169(7)	0.128(6)	-0.020(4)	0.065(4)	-0.057(6)
C65	0.065(4)	0.160(7)	0.116(6)	-0.022(4)	0.055(4)	-0.064(5)

Table 13. Bond length (Å) and angles (°) for **3d**

PD1	BR1	2.526(1)	PD1	P1	2.304(2)
PD1	P2	2.325(2)	PD1	C1	1.999(5)
P1	C50	1.839(5)	P1	C51	1.820(6)
P1	C52	1.812(7)	P2	C58	1.809(6)
P2	C59	1.843(6)	P2	C60	1.817(6)
N1	C1	1.308(7)	N1	C2	1.369(7)
N2	C7	1.372(7)	N2	C8	1.314(6)
N3	C13	1.315(5)	N3	C14	1.365(7)
N4	C19	1.370(6)	N4	C20	1.308(7)
N5	C25	1.321(5)	N5	C26	1.353(6)
N6	C31	1.345(6)	N6	C32	1.315(6)
N7	C37	1.309(8)	N7	C38	1.372(6)
N8	C43	1.37(1)	N8	C44	1.318(7)
C1	C8	1.455(5)	C2	C3	1.421(9)
C2	C7	1.387(5)	C3	C4	1.373(9)
C3	C9	1.513(7)	C4	C5	1.414(7)
C4	C10	1.55(1)	C5	C6	1.38(1)
C5	C11	1.53(1)	C6	C7	1.424(8)
C6	C12	1.538(7)	C8	C13	1.488(7)
C13	C20	1.441(6)	C14	C15	1.423(6)
C14	C19	1.398(7)	C15	C16	1.373(9)
C15	C21	1.505(8)	C16	C17	1.430(8)
C16	C22	1.522(9)	C17	C18	1.383(9)
C17	C23	1.51(1)	C18	C19	1.415(9)
C18	C24	1.51(1)	C20	C25	1.495(6)
C25	C32	1.425(6)	C26	C27	1.430(7)
C26	C31	1.398(6)	C27	C28	1.373(8)
C27	C33	1.535(8)	C28	C29	1.439(9)
C28	C34	1.54(1)	C29	C30	1.348(8)
C29	C35	1.532(8)	C30	C31	1.439(6)
C30	C36	1.51(3)	C32	C37	1.483(6)
C37	C44	1.420(8)	C38	C39	1.41(1)
C38	C43	1.402(8)	C39	C40	1.384(9)
C39	C45	1.50(1)	C40	C41	1.42(1)
C40	C46	1.54(2)	C41	C42	1.37(1)
C41	C47	1.54(1)	C42	C43	1.411(9)
C42	C48	1.54(1)	C44	C49	1.52(1)
C52	C53	1.391(9)	C52	C57	1.377(8)
C53	C54	1.38(1)	C54	C55	1.34(1)
C55	C56	1.38(1)	C56	C57	1.41(1)
C60	C61	1.365(6)	C60	C65	1.39(1)
C61	C62	1.381(9)	C62	C63	1.40(1)
C63	C64	1.37(1)	C64	C65	1.40(1)

BR1	PD1	P1	92.56(4)
BR1	PD1	C1	171.7(1)
P1	PD1	C1	90.0(2)
PD1	P1	C50	114.0(2)
PD1	P1	C52	113.1(2)
C50	P1	C52	104.1(3)
PD1	P2	C58	114.6(2)
PD1	P2	C60	112.9(2)
C58	P2	C60	104.9(4)
C1	N1	C2	120.4(3)
C13	N3	C14	118.6(4)
C25	N5	C26	117.2(3)
C37	N7	C38	117.6(4)
PD1	C1	N1	115.2(2)
N1	C1	C8	118.5(4)
N1	C2	C7	120.0(5)
C2	C3	C4	118.4(4)
C4	C3	C9	123.3(6)
C3	C4	C10	118.7(5)
C4	C5	C6	120.2(6)
C6	C5	C11	120.1(5)
C5	C6	C12	123.4(5)
N2	C7	C2	121.1(5)
C2	C7	C6	120.6(5)
N2	C8	C13	114.9(3)
N3	C13	C8	117.3(4)
C8	C13	C20	122.3(4)
N3	C14	C19	120.9(4)
C14	C15	C16	118.7(5)
C16	C15	C21	124.0(5)
C15	C16	C22	119.7(5)
C16	C17	C18	121.0(6)
C18	C17	C23	120.9(6)
C17	C18	C24	124.5(7)
N4	C19	C14	120.2(5)
C14	C19	C18	121.6(5)
N4	C20	C13	121.5(4)
C13	C20	C25	126.8(5)
N5	C25	C32	121.4(4)
N5	C26	C27	118.8(4)
C27	C26	C31	119.8(4)
C26	C27	C33	118.4(5)
C27	C28	C29	120.9(5)
C29	C28	C34	119.2(5)
C28	C29	C35	118.6(5)
C29	C30	C31	118.6(5)
C31	C30	C36	119.1(7)
N6	C31	C30	118.4(4)
N6	C32	C25	121.1(4)
C25	C32	C37	122.9(4)
N7	C37	C44	121.9(4)
N7	C38	C39	118.4(5)
C39	C38	C43	120.7(5)
C38	C39	C45	118.7(6)
C39	C40	C41	121.1(9)
C41	C40	C46	118.9(7)
C40	C41	C47	119(1)
C41	C42	C43	118.8(6)
C43	C42	C48	118.5(8)
N8	C43	C42	119.5(6)
N8	C44	C37	121.0(6)
C37	C44	C49	120.8(5)
P1	C52	C57	123.4(5)
C52	C53	C54	121.4(6)
C54	C55	C56	120.3(8)
C52	C57	C56	119.8(7)
P2	C60	C65	121.0(4)
C60	C61	C62	121.9(7)
C62	C63	C64	119.2(7)
C60	C65	C64	119.9(7)

BR1	PD1	P2	90.85(5)
P1	PD1	P2	176.57(5)
P2	PD1	C1	86.5(2)
PD1	P1	C51	116.7(3)
C50	P1	C51	102.8(3)
C51	P1	C52	104.9(3)
PD1	P2	C59	116.9(4)
C58	P2	C59	103.2(3)
C59	P2	C60	102.9(3)
C7	N2	C8	117.6(3)
C19	N4	C20	118.4(4)
C31	N6	C32	118.1(4)
C43	N8	C44	118.3(5)
PD1	C1	C8	126.3(4)
N1	C2	C3	119.6(4)
C3	C2	C7	120.4(5)
C2	C3	C9	118.2(5)
C3	C4	C5	121.7(6)
C5	C4	C10	119.6(6)
C4	C5	C11	119.7(7)
C5	C6	C7	118.7(4)
C7	C6	C12	117.9(6)
N2	C7	C6	118.3(4)
N2	C8	C1	122.3(5)
C1	C8	C13	122.8(4)
N3	C13	C20	120.4(4)
N3	C14	C15	119.3(4)
C15	C14	C19	119.8(5)
C14	C15	C21	117.3(6)
C15	C16	C17	121.0(5)
C17	C16	C22	119.3(6)
C16	C17	C23	118.0(6)
C17	C18	C19	117.7(5)
C19	C18	C24	117.7(6)
N4	C19	C18	118.1(4)
N4	C20	C13	121.5(4)
N4	C20	C25	111.6(4)
N5	C25	C20	119.6(4)
C20	C25	C32	118.2(3)
N5	C26	C31	121.4(4)
C26	C27	C28	118.7(5)
C28	C27	C33	122.9(5)
C27	C28	C34	119.9(6)
C28	C29	C30	121.3(5)
C30	C29	C35	120.1(6)
C29	C30	C36	122.3(6)
N6	C31	C26	120.8(4)
C26	C31	C30	120.8(4)
N6	C32	C37	116.0(4)
N7	C37	C32	116.3(5)
C32	C37	C44	121.8(5)
N7	C38	C43	120.9(6)
C38	C39	C40	118.1(6)
C40	C39	C45	123.2(8)
C39	C40	C46	120.0(7)
C40	C41	C42	120.8(7)
C42	C41	C47	120.1(8)
C41	C42	C48	122.7(7)
N8	C43	C38	120.1(5)
C38	C43	C42	120.3(7)
N8	C44	C49	118.2(5)
P1	C52	C53	118.4(4)
C53	C52	C57	118.3(6)
C53	C54	C55	120.2(7)
C55	C56	C57	119.9(7)
P2	C60	C61	120.0(6)
C61	C60	C65	119.0(6)
C61	C62	C63	119.2(5)
C63	C64	C65	121(1)

Table 14. Summary of Crystal Data, Intensity Collection, and Least-squares Processing for **3a**, **3b**, **3c** and **3d**

compound	**3a**	**3b**	**3c**	**3d**
formula	C29H37N2P2BrPd	C41H49N4P2Br1Pd	C53H61N6P2BrPd	C65H73N8P2BrPd
formula weight	661.9	846.1	1030.4	1214.6
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	P21/c	P-1	P-1	C2/c
a, Å	13.221(2)	9.943(2)	16.178(3)	31.567(9)
b, Å	8.449(1)	11.873(3)	24.714(5)	16.095(3)
c, Å	28.985(5)	17.483(3)	13.037(1)	32.466(9)
α, deg		93.92(2)	90.81(1)	
β, deg	112.57(3)	104.67(1)	94.08(1)	126.83
γ, deg	-	102.38(2)	106.77(2)	-
V, $Å^3$	3007.4(9)	1933.8(7)	4975(2)	13202(6)
Z	4	2	4	8
ρcalcd, g cm-3	1.462	1.45	1.376	1.222
μ, cm-1	80.2 (Cu Kα)	15.41 (Mo Kα)	50.8 (Cu Kα)	47.4 (Cu Kα)
diffractometer	Rigaku AFC-5R	Mac Science MXC18	Rigaku AFC-5R	Rigaku AFC-5R
2θmax, deg	110	55	110	120
No. of unique reflections	3773	8917	12486	9780
No. of reflections used for refinement	3186	6668	11556	8409
R	0.036	0.038	0.048	0.057
Rw	0.046	0.054	0.072	0.085
S	1.124	1.82	1.208	1.13

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4) (Biquinoxalinyl)-, (terquinoxalinyl)- and (quaterquinoxalinyl)palladium complexes (**3b**, **3c** and **3d**) were isolated by TLC (silica gel) from the reaction mixture of **1a** and **2** (**1a**/**2** are 2, 3 and 4, respectively) followed by recrystallization from dichloromethane-hexane.

5) Produced oligomers were isolated after conversion to **4c-f** by the reaction with [(trimethylsilyl)methyl]magnesium chloride (reflux in THF for 15 min).

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Chapter 3

Living Polymerization of 1,2-Diisocyanoarenes Promoted by (Quinoxalinyl)nickel Complexes

Abstract

A controlled living polymerization was achieved by use of 3,6-bis[(trimethylsilyl)methyl]-1,2-diisocyanobenzene (**1b**) and (quinoxalinyl)nickel complex having Me_3P ligands (**5**). An initiating nickel(II) catalyst (**5**) was produced by the reaction of **1b** with trans-$(Me_3P)_2Cl$(o-tolyl)Ni(II). Oligomerization of **1b** induced by **5** with varying feeding ratio (**1b**/**5**) gave poly(2,3-quinoxaline) in good yield after the quenching with MeMgBr. The higher poly(2,3-quinoxaline) was produced with the higher feeding ratio (**1b**/**5**). The molecular weight distribution of the resultant polymer was quite narrow and close to a monodisperse distribution (Mw/Mn=1.05-1.10).

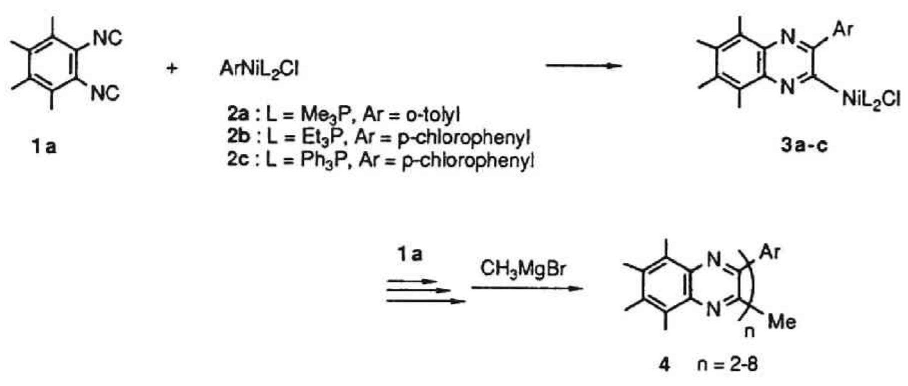
Introduction

Poly(quinoxaline) has acquired significant interests in view of heat-resistant polymer and is generally prepared by the reaction of bis(o-diamines) with bis(glyoxals).[1] In chapter 2, the author described a new living polymerization of 1,2-diisocyanoarenes catalyzed by trans-$(Me_2PhP)_2Br(Me)Pd(II)$ giving a new type of conjugated polymer, poly(2,3-quinoxaline), in which oligomeric (2,3-quinoxalinyl)palladium(II) complexes are involved as the propagating species.[2] On the other hand, successful polymerization of isocyanides forming poly(N-substituted iminomethylene) so far reported has mostly been achieved by nickel(II) catalyst.[3] However, use of organonickel(II) complexes [$(Me_2PhP)_2X(R)Ni$, R-: Me_3SiCH_2-, o-tolyl-] in the polymerization of 1,2-diisocyanoarenes resulted in a formation of only a trace amount of poly(2,3-quinoxaline) with unidentified tarry materials. In this chapter, the author describes that (quinoxalinyl)nickel(II) complexes having suitable phosphine ligands successively promote the living polymerization of 3,6-bis[(trimethylsilyl)methyl]-1,2-diisocyanobenzene to afford poly(2,3-quinoxaline) of an extremely sharp distribution of molecular weight.

Results and Discussion.

When an excess of trans-$(Me_3P)_2Cl$(o-tolyl)Ni(II) (**2a**), generated in situ from trans-$(Me_3P)_2Cl_2Ni$(II) and (o-tolyl)MgCl, was reacted with 1,2-diisocyano-3,4,5,6-tetramethylbenzene (**1a**) at 0°C in benzene, the desired (quinoxalinyl)nickel complex (**3a**) was produced in 36% yield by successive insertion of ortho isocyano groups into Ni-C bond. Then, the isolated nickel complex (3a) having Me_3P as ligands was treated with 3-fold excess of **1a** to give a mixture of oligo(2,3-quinoxaline) (4) of up to the hexamer in 50% total yield after a termination with MeMgBr. The similar result was also obtained with arylnickel complex (2b) having Et_3P as ligands.

Scheme 1



In contrast, the reaction of trans $(Ph_3P)_2Cl$(p-chlorophenyl)Ni(II) (2c) with **1a** did not give the corresponding **3c**, but a trace amount of oligomeric **4** together with unidentified tarry products. Remarked here is an observation that Ph_3P ligand of **2c** was liberated up to 54% from the nickel(II) complex during the reaction. It is likely that the ligand substitution of Ph_3P on nickel by isocyano groups of **1a** may cause the intractable polymerization. Indeed, $Ni(acac)_2$ catalyzed polymerization of

1,2-diisocyanoarenes in the absence of phosphine ligand, in which two or more isocyanogroups of **1a** should be involved on coordination sphere of the nickel, produced the similar intractable tarry materials.

A controlled living polymerization was achieved by use of 3,6-bis[(trimethylsilyl)methyl]-1,2-diisocyanobenzene (**1b**) and (quinoxalinyl)nickel complex having Me_3P ligands (**5**). An initiating nickel(II) catalyst (**5**) was produced by the reaction of **1b** with **2a** and was so stable to allow isolation by TLC (39%) and full characterization (IR, ^1H and ^{13}C NMR, combustion analysis).

Scheme 2

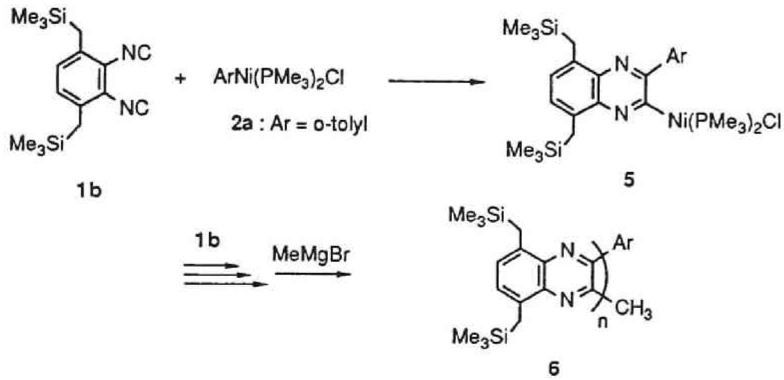


Table 1. Living Polymerization of 1b Catalyzed by 5.

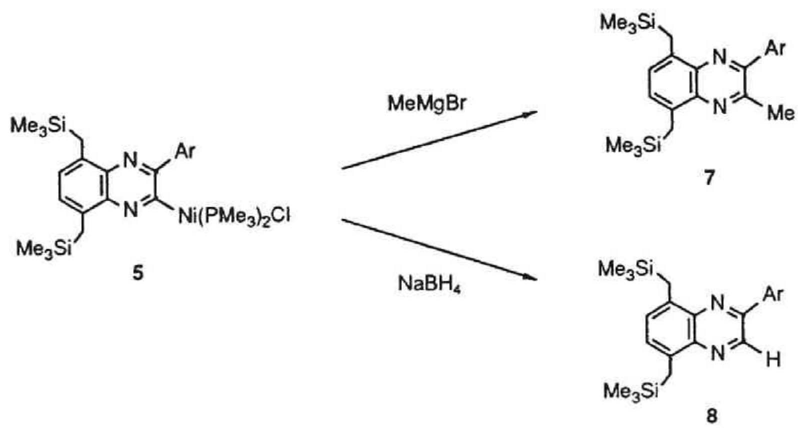
Entry	1b/5	Yield %	Mn(calc.)[a]	Mn(obsd.)[b]	Mw / Mn[c]
1	2	76 [6 (n=3) 70%, 6 (n=4) 6%][d]		-	-
2	7	82	2630	3010	1.05
3	15	94	4880	4890	1.10

a) Calculated from monomer to initiator ratio.
b) Determined by VPO.
c) Determined by GPC.
d) Yield of isolation by HPLC.

Polymerization of **1b** induced by **5** with varying feeding ratio (**1b**/**5**) was carried out in THF at room temperature, and poly(2,3-quinoxaline) (**6**) was obtained in good yield after the quenching with MeMgBr (Table I). The higher poly(2,3-quinoxaline) was produced with the higher feeding ratio (**1b**/**5**). In addition, the molecular weight distribution (polydispersity) of the resultant polymer which was determined by using polystyrene as internal standard in measuring GPC profile was quite narrow and close to a monodisperse distribution (Mw/Mn= 1.05-1.10) (Figure 1). The sterically bulky (trimethylsilyl)methyl substituents on the neighboring quinoxaline ring may stabilize the propagating $(Me_3P)_2Cl$(quinoxalinyl)Ni(II) complex, which can be assumed to be of a square pyramidal structure based on the X-ray crystal study of analogous palladium(II) complex,[2] and make the living polymerization of **1b** feasible.[4]

Finally, substitutions of Ni moiety of **5** were examined. MeMgBr reacted with **5** to give **7** in the same manner as the termination of polymerization described above. Hydrogen was introduced by the reaction with $NaBH_4$.

Scheme 3



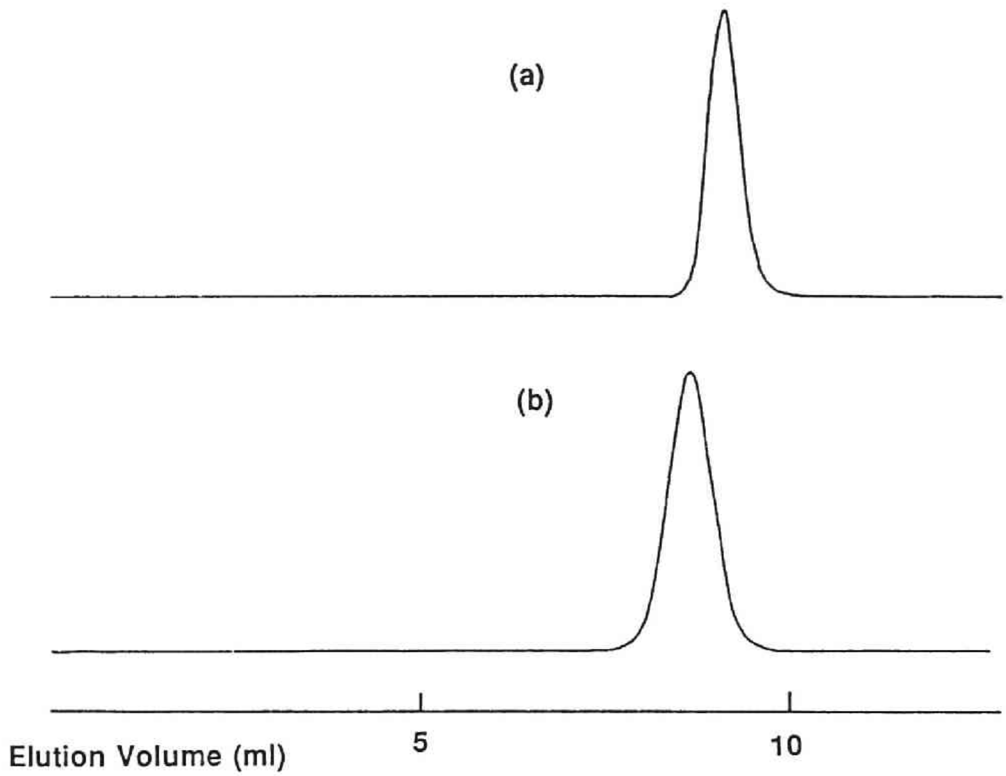


Figure 1. GPC curves of polyquinoxaline (**6**) ;
(a) feeding ratio = 7, (b) feeding ratio = 15

Experimental Section.

General. ^{1}H-NMR and ^{13}C-NMR spectra were measured with Varian VXR-200 and Gemini-200 spectrometer in $CDCl_3$. Chemical shifts are reported in δ ppm. Infrared spectra were measured with a Hitachi 270-30 spectrometer. Data are given in cm^{-1}. Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. The molecular weights of polymers were measured by a Corona 117 vapor pressure osmometer in chloroform at 40°C. Gel permeation chromatographic analysis (GPC) were carried out on a Toyo-Soda HLC-8020 (Toyo-Soda G3000) by using THF as a eluent and polystyrene as a standard. Recycling HPLC purification was performed with JAI LC-908 equipped with JAIGEL-1H and 2H columns ($CHCl_3$).

Materials. All solvents were dried over appropriate desiccants and distilled under nitrogen. Preparation 1,2-diisocyano-3,4,5,6-tetramethylbenzene(**1a**) and 1,2-diisocyano-3,6-bis(trimethylsilylmethyl)benzene(**1b**) are described in chapter 1 and 2, respectively. trans-$(Me_3P)_2Cl_2Ni(II)$.[5] trans-$(Et_3P)_2ClArNi(II)$ and trans-$(Ph_3P)_2ClArNi(II)$ (Ar=p-chlorophenyl)[6] were prepared according to the literature method.

Preparation of aryl-monoquinoxaline-Ni(II) complexes.

trans$(Me_3P)_2Cl$(Ar-Q)Ni(II)(3a).

To a solution of $(Me_3P)_2NiCl_2$ in THF, excess of o-tolylmagnesium chloride was added at 0°C and the mixture was stirred for 10 min at 0°C. Extractive workup with CH_2Cl_2 and water gave crude $(Me_3P)_2ClArNi(II)$. Then, to the solution of the crude Ni(II) complex, **1a** was added at 0°C. After evaporation of the solvent, preparative TLC on silica gel (n-hexane : ether = 1:1) afforded **3a** in 36% yield.

^{1}H-NMR ($CDCl_3$) 0.89 (t, 18H, J=3.9 Hz), 2.40 (s, 3H), 2.44 (s,3H), 2.54 (s, 3H), 2.70 (s, 3H), 2.85 (s, 3H), 7.3-7.7 (m, 4H).

3b (28%) and **5** (39%) were prepared in a similar procedures.

trans$(Et_3P)_2Cl$(Ar-Q)Ni(II) (3b).

^{1}H-NMR ($CDCl_3$) 0.99 (qui, 12H, J=7.7 Hz), 1.26 (m, 8H), 2.42

(s, 3H), 2.45 (s, 3H), 2.77 (s, 3H), 2.83 (s, 3H), 7.61 (d, 4H, J= 8.76 Hz), 10.06 (d, 4H, J= 8.50 Hz). IR (KBr) 2972, 2940, 1500, 1456, 1300, 1258, 1204, 1130, 1118, 1094, 1036, 838, 770, 736, 522 cm^{-1}.

trans$(Me_3P)_2$Cl(Ar-Si-Q)Ni(II) (5).

mp 178 C (dec). ^{1}H-NMR ($CDCl_3$) -0.19 (s, 9H), 0.04 (s, 9H), 0.89 (t, 18H, J= 3.9 Hz), 2.67 (s, 2H), 2.75 (s, 2H), 7.05 (d, 1H, J= 7.4 Hz), 7.17 (d, 2H, J= 7.4 Hz), 7.3-7.7 (m, 4H); ^{13}C-NMR ($CDCl_3$) -1.43, -0.80, 12.41 (t, J= 13.9 Hz), 20.55, 20.68, 22.11, 124.75, 125.88, 127.00, 128.09 (t, J= 3.4 Hz), 128.80, 131.96, 133.59, 135.04, 136.45, 137.85, 139.58, 139.76, 153.04. IR (KBr) 2964, 2900, 1508, 1248, 1158, 952, 848, 734 cm^{-1}. Anal. Calcd for $C_{29}H_{49}ClN_2NiP_2Si_2$: C, 54.60; H, 7.74; N, 4.39. Found: C,54.61; H, 7.90; N, 4.44.

Oligomerization and polymerization 1,2-diisocyano-3,6-bis(trimethylsilylmethyl)benzene (1b) catalyzed by mono-quinoxalinyl-Ni(II) complex (5).

Typical Procedure.

A mixture of 1b and **5** in dry THF was refluxed for 10 hrs under nitrogen. Methylmagnesium bromide in ether was added at r.t. and extractive workup with CH_2Cl_2 and water gave crude polymer. Purification was carried out by HPLC on polystyrene ($CHCl_3$).

Quinoxaline trimer(6, n=3). ^{1}H-NMR ($CDCl_3$) -0.41 (s, 9H), -0.23 (s, 9H), -0.19 (s, 9H), -0.10 (s, 18H), 0.00 (s, 9H), 1.56 (s, 2H), 1.70 (s, 2H), 1.95 (s, 3H), 2.49 (s, 2H), 2.56 8s, 2H), 2.65 8s, 3H), 2.69 (s, 2H), 2.71 (s, 2H), 6.8-7.4 (m, 10H). IR (KBr) 2964, 2904, 1582, 1472, 1374, 1248, 1160, 1052, 846, 756, 694, 644 cm^{-1}. MS m/e 1007 (M+).

Quinoxaline tetramer(6, n=4). ^{1}H-NMR ($CDCl_3$) -0.41 (s, 9H), -0.30 (s, 18H), -0.25 (s, 9H), -0.24 (s, 18H), -0.14 (s, 9H), -0.03 (s, 9H), 1.9-2.9 (m, 22H), 6.9-7.4(m, 12H). IR (KBr) 2964, 2904, 1582, 1468, 1406, 1248, 1160, 1050, 848, 758, 694, 642 cm^{-1}. MS m/e 1307 (M+).

Quinoxaline Polymer (6, 1b/5=7). ^{1}H-NMR ($CDCl_3$) -1.0-0.2 (br-m), 1.0-3.2 (br-m), 6.7-7.5 (br-m). IR (KBr) 2964, 2904, 1590, 1464, 1418, 1374, 1250, 1162, 1066, 1042, 852, 694, 638, 484 cm^{-1}.

Quinoxaline Polymer (6, 1b/5=15). ^1H-NMR ($CDCl_3$) -1.0-0.2 (br-m), 1.0-3.2 (br-m), 6.4-7.5 (br-m). IR (KBr) 2964, 2904, 1590, 1464, 1416, 1250, 1160, 1062, 1040, 850, 694 cm^{-1}.

Reactions of quinoxalinyl-Ni(II) complex (5).

Reaction with MeMgBr.

To a benzene solution (3 mL) of **5** (33 mg, $5.14x10^{-5}$ mol) was added a large excess of CH_3MgBr (ether solution). The mixture was stirred at r.t. for 30 min, then, excess of CH_3MgBr was quenched with water. Extractive workup with CH_2Cl_2 and water followed by preparative TLC on silica gel (n-hexane : ether = 8:3) afforded **7** in 78% yield.

7 : ^1H-NMR ($CDCl_3$) -0.11 (s, 9H), -0.03 (s, 9H), 2.12 (s, 3H), 2.48 (s, 3H), 2.69 (s, 2H), 2.74 (s, 2H), 7.2-7.4 (m, 6H). IR (neat) 2964, 2904, 1584, 1472, 1340, 1248, 1196, 1164, 1058, 1042, 848, 694 cm^{-1}. MS m/e 406 (M+).

Reaction with $NaBH_4$.

A THF solution (3 mL) of **5** (21 mg, $3.32x10^{-5}$ mol) and a large excess of $NaBH_4$ was stirred at r.t. for 10 min. Extractive workup with CH_2Cl_2 and water followed by preparative TLC on silica gel (n-hexane : ether = 5:1) afforded **8** in 67% yield.

8 : ^1H-NMR ($CDCl_3$) -0.09 (s, 9H), -0.05 (s, 9H), 2.74 (s, 2H), 2.76 (s, 2H), 3.52 (s, 3H), 7.3-7.7 (m, 6H), 8.92 (s, 1H). IR (neat) 2964, 2904, 1738, 1594, 1552, 1470, 1406, 1356, 1312, 1248, 1162, 1038, 848, 760, 730, 694, 636 cm^{-1}. MS m/e 392 (M+).

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Chapter 4

A Screw Sense Selective Polymerization of 1,2-Diisocyanoarenes--- Synthesis of Optically Active Poly(2,3-quinoxaline)

Abstract

The two diastereomerically pure trans-bromobis[bis((S)-2-methylbutyl)phenylphosphine]quinque[2,3-(5,8-di-p-tolyl)quinoxalinyl]palladium(II) [(-)-**6**] and [(+)-**6**], which have the opposite sense of helicity, were prepared by oligomerization of 3,6-di-p-tolyl-1,2-diisocyanobenzene catalyzed with trans-bromobis[bis((S)-2-methylbutyl)phenylphosphine]methylpalladium(II) followed by GPC and HPLC separation. The chiral palladium(II) complexes [(-)-**6**] and [(+)-**6**] induced a screw-sense selective polymerization of 3,6-dimethyl-4,5-bis(propyloxymethyl)-1,2-diisocyanobenzene to afford optically active poly[2,3-(5,8-dimethyl-6,7-bis(propyloxymethyl))quinoxaline]s [(+)-**9**] and [(-)-**9**] (M. W. = ca. 10000), respectively, after removal of the chiral palladium(II) moiety. CD spectra of [(+)-**9**] and [(-)-**9**] indicated that they have the opposite sense helical structures.

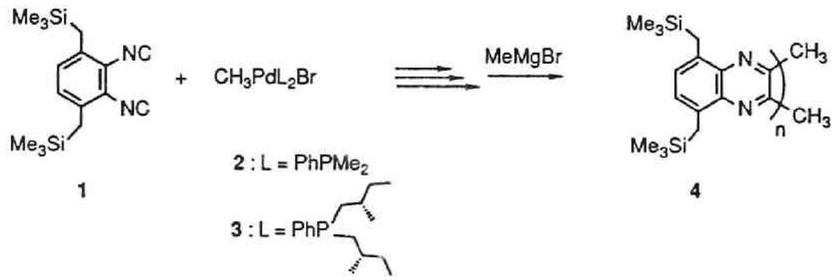
Introduction.

In chapter 2, the author described a new living polymerization of 1,2-diisocyanoarenes catalyzed by trans-bromobis(phosphine)methylpalladium(II) to give poly(2,3-quinoxaline) with narrow molecular weight distribution. Noteworthy was that some reactive propagating trans-bromobis(phosphine)oligo(2,3-quinoxalinyl)palladium(II) complexes were isolated and fully characterized. The X-ray crystal structure revealed that quinque[2,3-(5,8-bis(trimethylsilylmethyl)quinoxaline] (4, n=5) which was obtained by quenching the corresponding oligo(2,3-quinoxalinyl)palladium(II) complex with methylmagnesium bromide, exists in helical structure.(Figure 1) This finding suggested that quinoxaline polymer also took a helical conformation and prompted the author to undertake a synthesis of optically active poly(2,3-quinoxaline) whose chirality is derived from the helical structure.[1]

Results and Discussion.

Some attempts for the screw sense selective polymerization of 1,2-diisocyanoarenes (1) have been carried out by means of chiral trans-bromomethylpalladium(II) complexes (3) having optically active bis((S)-2-methylbutyl)phenylphosphine ligands, resulting in the formation of poly(2,3-quinoxaline) with probably low degree of optical activities {$[\alpha]_D$ = +7.2°($CHCl_3$, c = 1.2)} after the removal of the chiral palladium(II) moiety by quenching with methylmagnesium bromide.(Scheme 1) The specific rotations of 4 were, however, lost gradually on dissolving in solution even at room temperature.

Scheme 1



Molecular modeling studies on the structure of poly(quinoxaline) suggested that the introduction of sterically bulky substituents in 1,2-diisocyanoarene monomer might stabilize the helical conformation of poly(2,3-quinoxaline). Indeed, oligomerization of 3,6-di-p-tolyl-1,2-diisocyanobenzene (5, 0.32 mmol) was catalyzed by trans-bromobis[bis((S)-2-methylbutyl)phenylphosphine]methylpalladium(II) (3, 0.08mmol) in THF (5 mL) at 25°C for 12 hrs to afford quantitatively a mixture of trans-bromobis[bis((S)-2-methylbutyl)phenylphosphine]oligo [2,3-(5,8-di-p-tolylquinoxalinyl)]palladium(II), which was subjected to GPC (polystyrene : $CHCl_3$) to give trans-bromobis[bis((S)-2-methylbutyl)phenylphosphine]quinque(5,8-di-p-

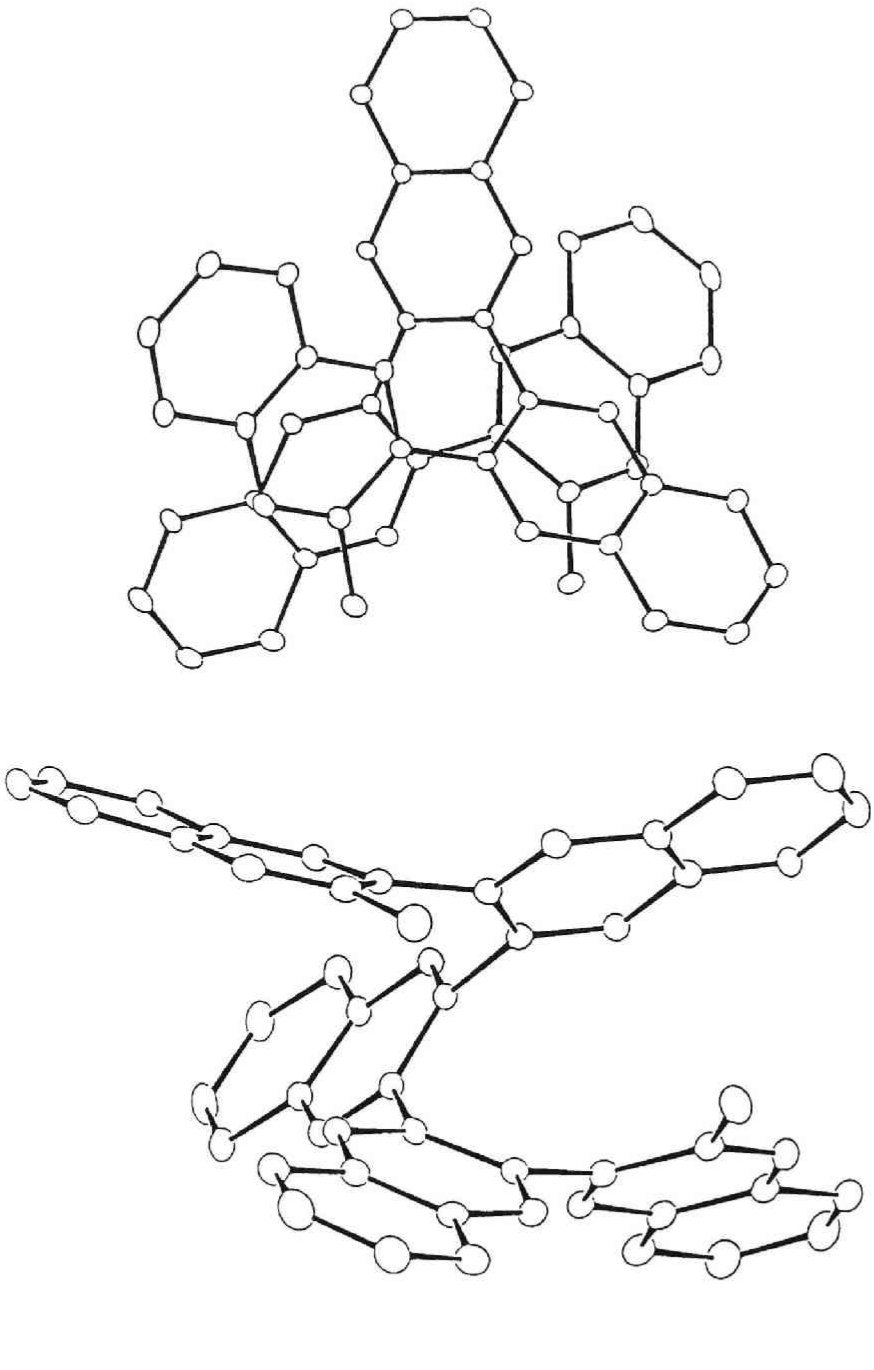


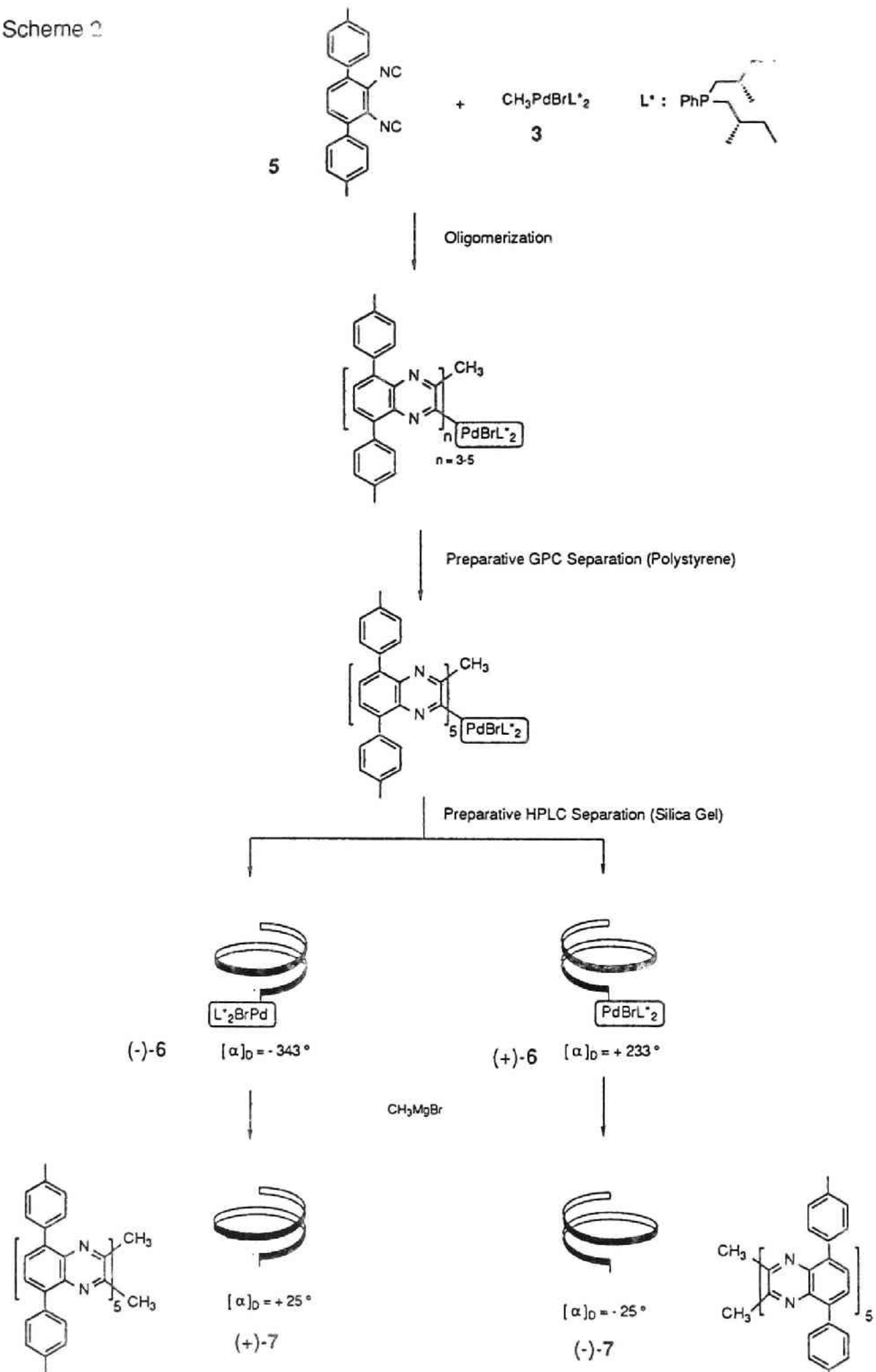
Figure 1. Structure of **4** (n = 5).

tolyl-2,3-quinoxalinyl)palladium(II) (6). Subsequent preparative HPLC on silica gel of **6** thus isolated permitted the separation of its two helical diastereomers [(-)-**6**] and [(+)-**6**] in a ratio of 3:4, which were conformationally stable in solution.(Scheme 2) CD spectra of [(-)-6] and [(+)-6] were nearly mirror image with large cotton effects being indicative of the opposite sense helicity.(Figure 2) Removal of the chiral palladium(II) phosphine moiety from [(-)-**6**] and [(+)-**6**] gave optically active [(+)-7] and [(+)-7] respectively, whose CD spectra exhibited very weak cotton effect.

It was now found that the two diastereomerically pure palladium(II) complexes [(-)-**6**] and [(+)-**6**] induced a screw sense selective polymerization of 3,6-dimethyl-4,5-bis(propyloxymethyl)1,2-diisocyanobenzene (**8**) to give optically active poly(quinoxaline)s [(+)-**9**] and [(-)-**9**], respectively, after removal of the chiral palladium(II) moiety, whose optical rotations were almost same with opposite sign.(Scheme 3) CD spectra of [(+)-**9**] and [(+)-**9**], which were perfect mirror image with large cotton effects, indicate that they have the opposite sense helical structures.(Figure 3) The CD splitting (240 nm and 290 nm) were assigned to helical chromophore of **9** by quantum-mechanical calculations, of the helical poly(2,3-quinoxaline). Furthermore, it was determined that [(+)-**9**] had right-handed helical structure from the pattern of the splitting. (Details of the theoretical assignment of the left- and right-handed helicities to the optically active poly(quinoxaline)s is described in chapter 5.

Just after the polymerization finished, five quinoxaline units from the initiator regulated the helical sense and conformation of the whole polymer. However, allowed to stand at r.t. in solution, the chiral polyquinoxaline gradually lost their optical activity. This phenomenon may be ascribed to the fluctuation of the helical structure derived from **8**. Accordingly, in order to obtain rigid helical polyquinoxaline, all the monomeric units should have bulky substituents like o-tolyl group. Indeed, polymerization of 10 initiated by [(+)-6] and [(+)-6] gave optically active polyquinoxalines [(+)-11] and [(+)-11], whose CD spectra never changed when they heated in solution.(Scheme 4, Figure 4)

Scheme 2


NC
NC
5
+
CH3PdBrL*2
3
L* : PhP
Oligomerization
CH3
N
N
PdBrL*2
n = 3-5
Preparative GPC Separation (Polystyrene)
PdBrL*2
Preparative HPLC Separation (Silica Gel)
L*2BrPd
(-)-6
[α]D = - 343°
(+)-6
[α]D = + 233°
CH3MgBr
[α]D = + 25°
(+)-7
[α]D = - 25°
(-)-7

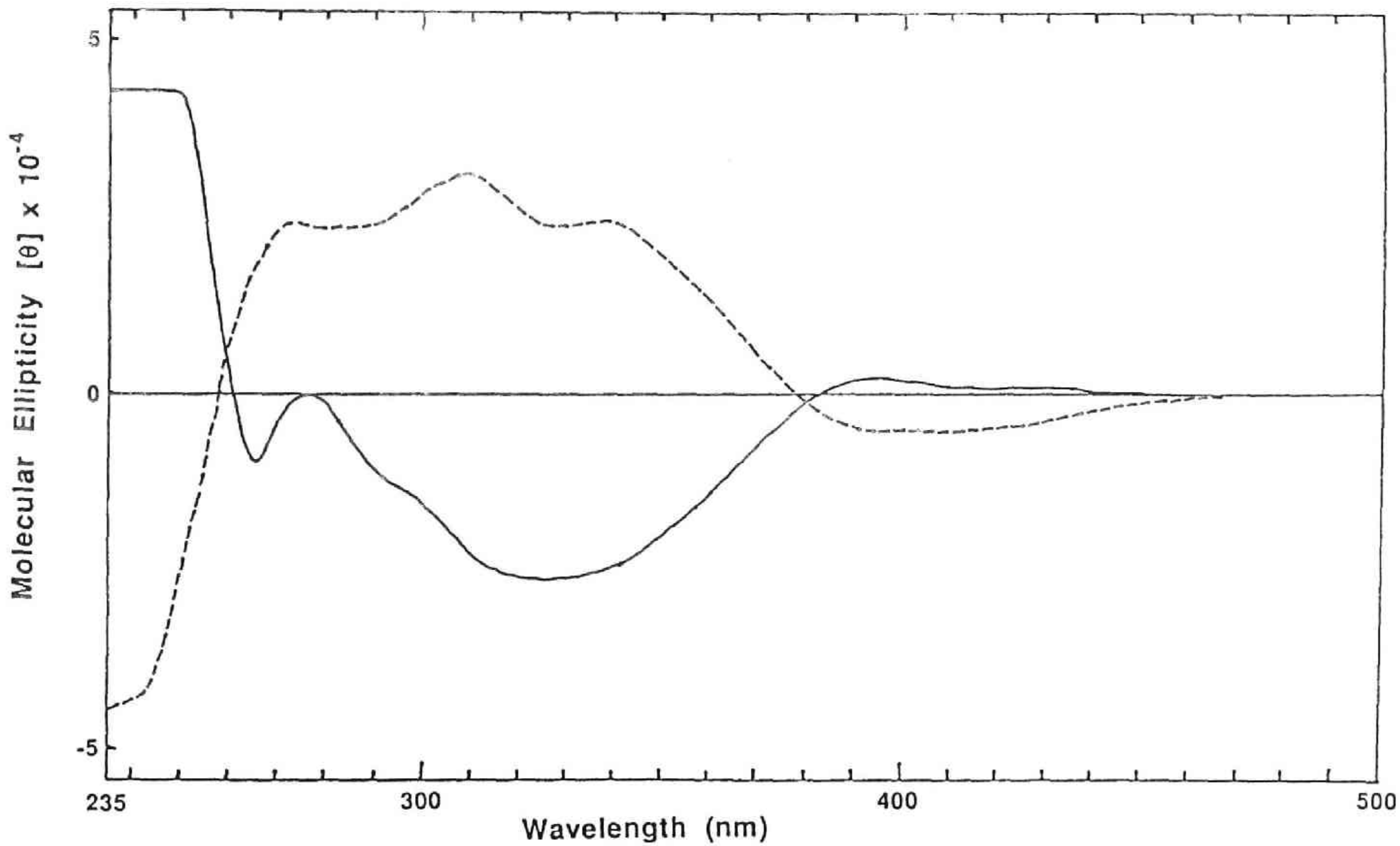
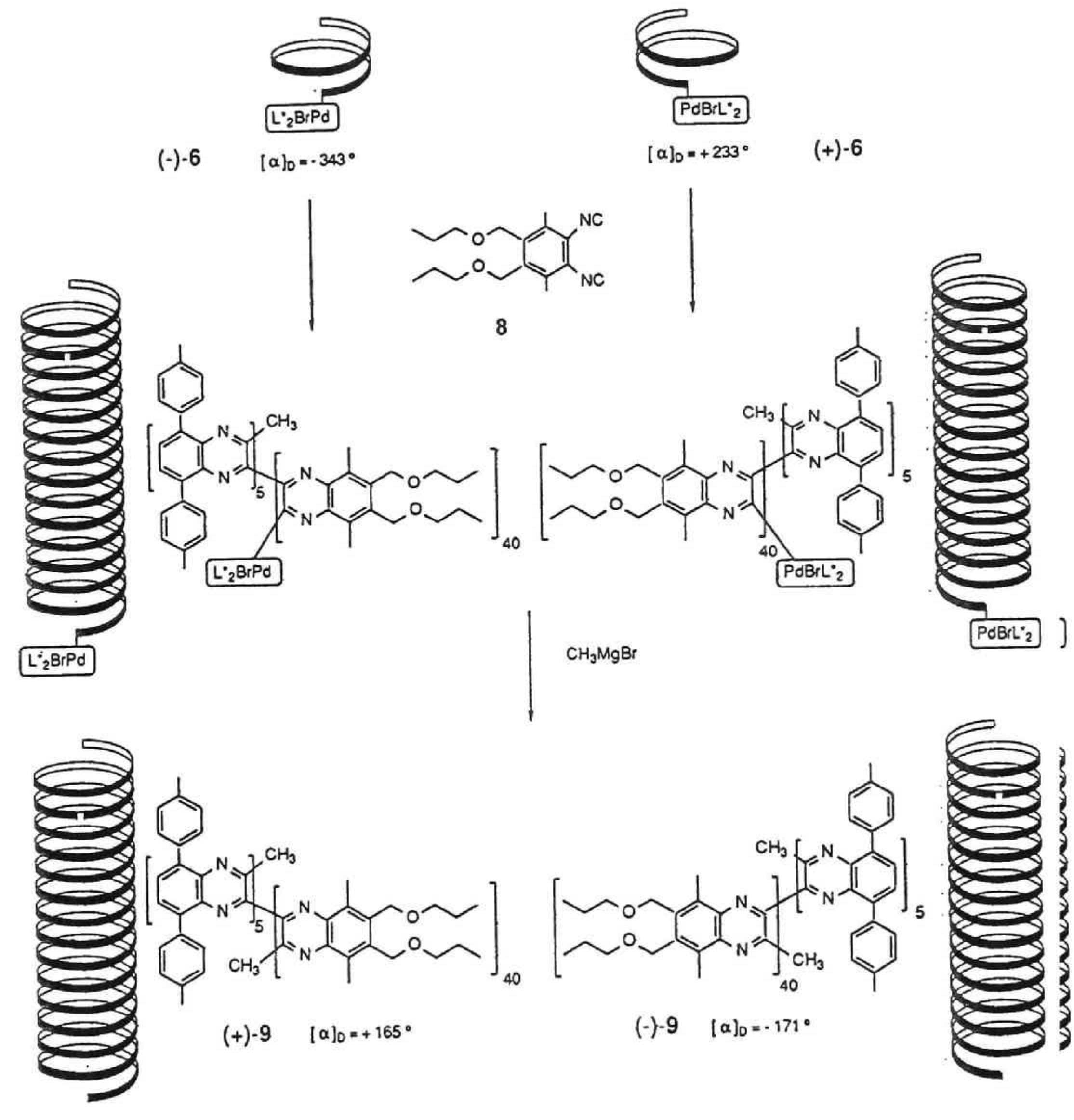


Figure 2. CD spectra of (-)-**6** (——) and (+)-**6** (-----).

Scheme 3


L*2BrPd
PdBrL*2
(-)-6
[α]D = - 343°
[α]D = + 233°
(+)-6
NC
NC
8
CH3
N
5
40
CH3MgBr
(+)-9
[α]D = + 165°
(-)-9
[α]D = - 171°

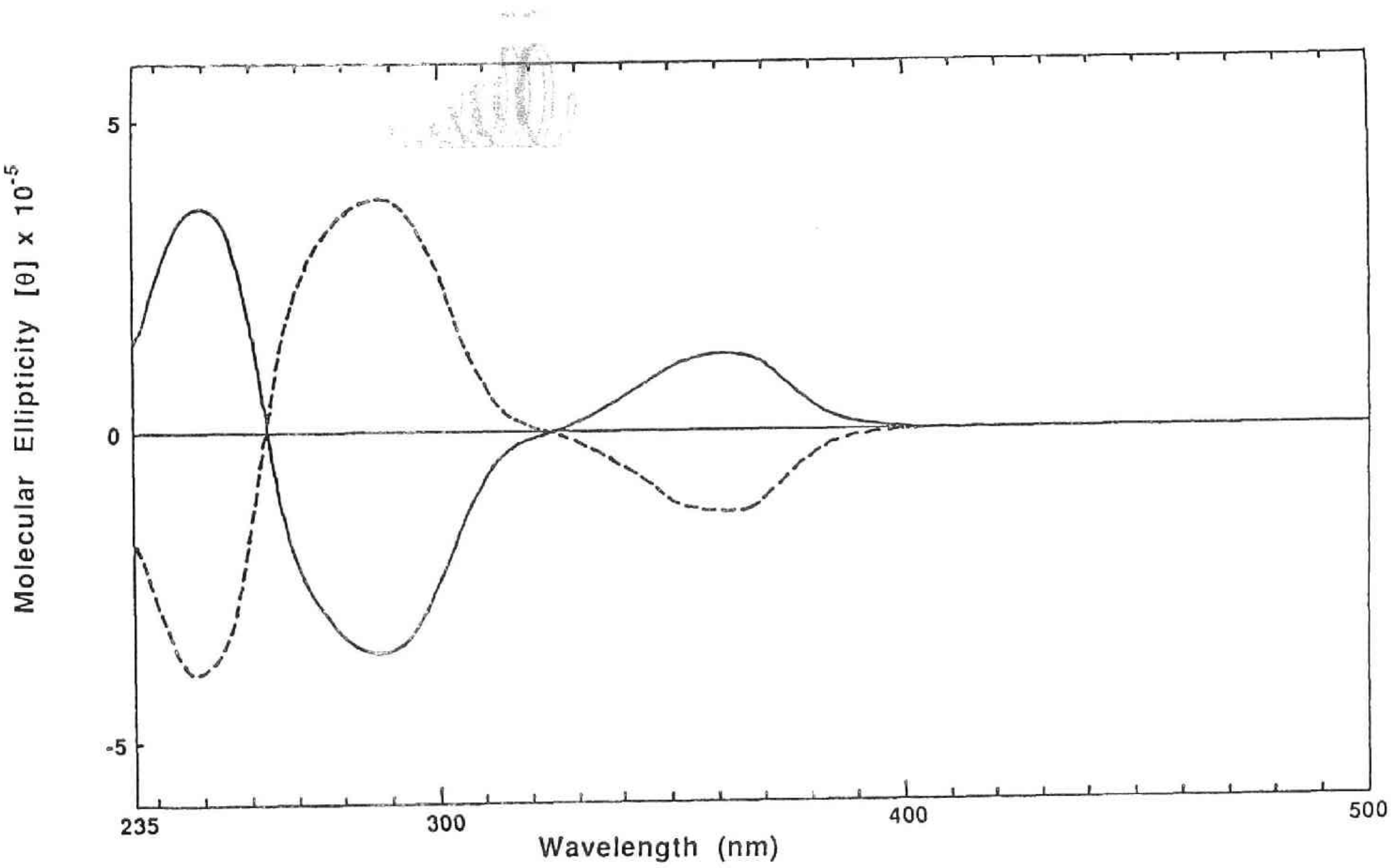
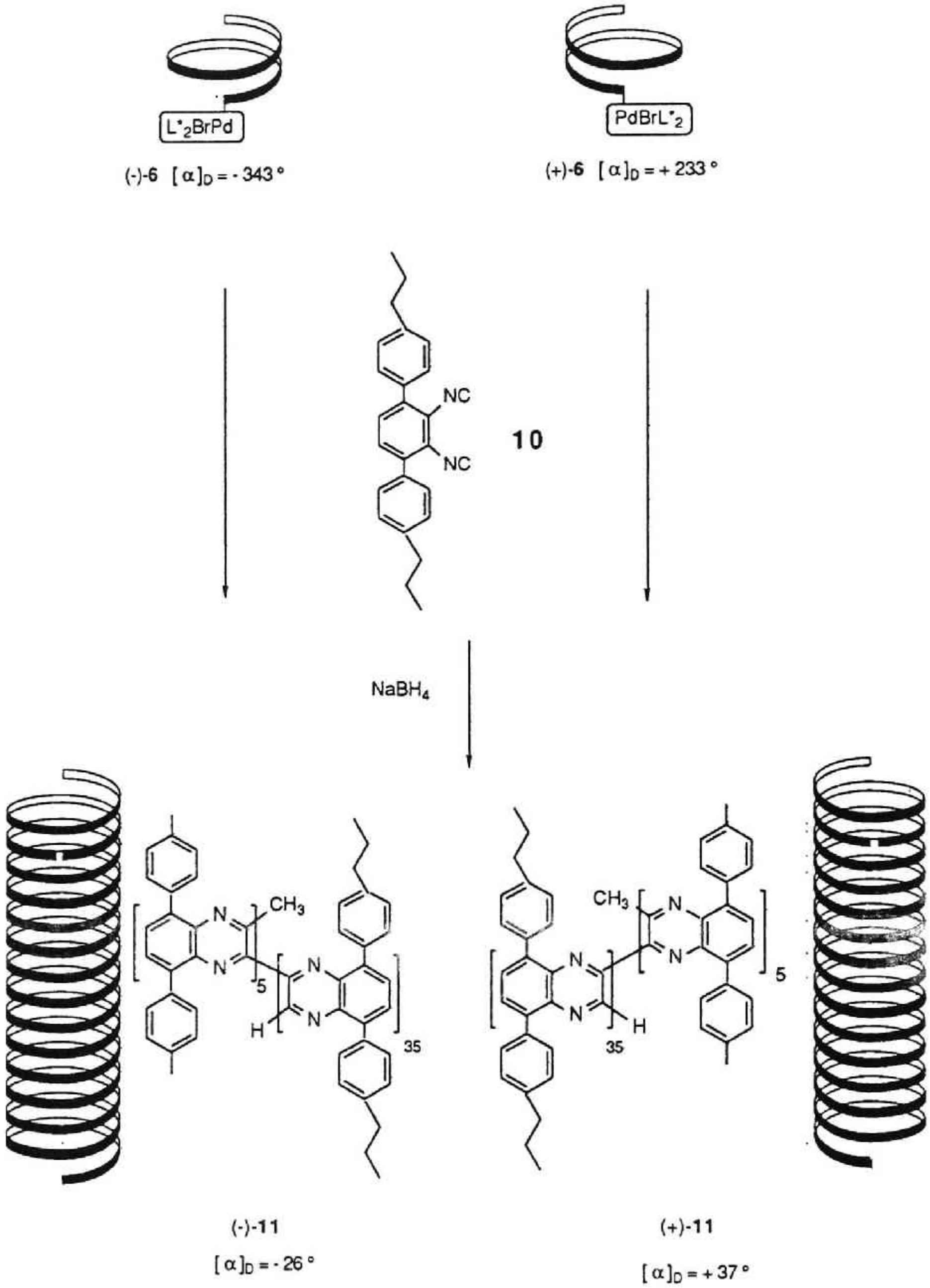


Figure 3. CD spectra of (+)-9 (——) and (-)-9 (----).

Scheme 4


L*2BrPd
(-)-6 [α]D = - 343 °
PdBrL*2
(+)-6 [α]D = + 233 °
NC
NC
10
NaBH4
CH3
N
N
5
H
35
(-)-11
[α]D = - 26 °
(+)-11
[α]D = + 37 °

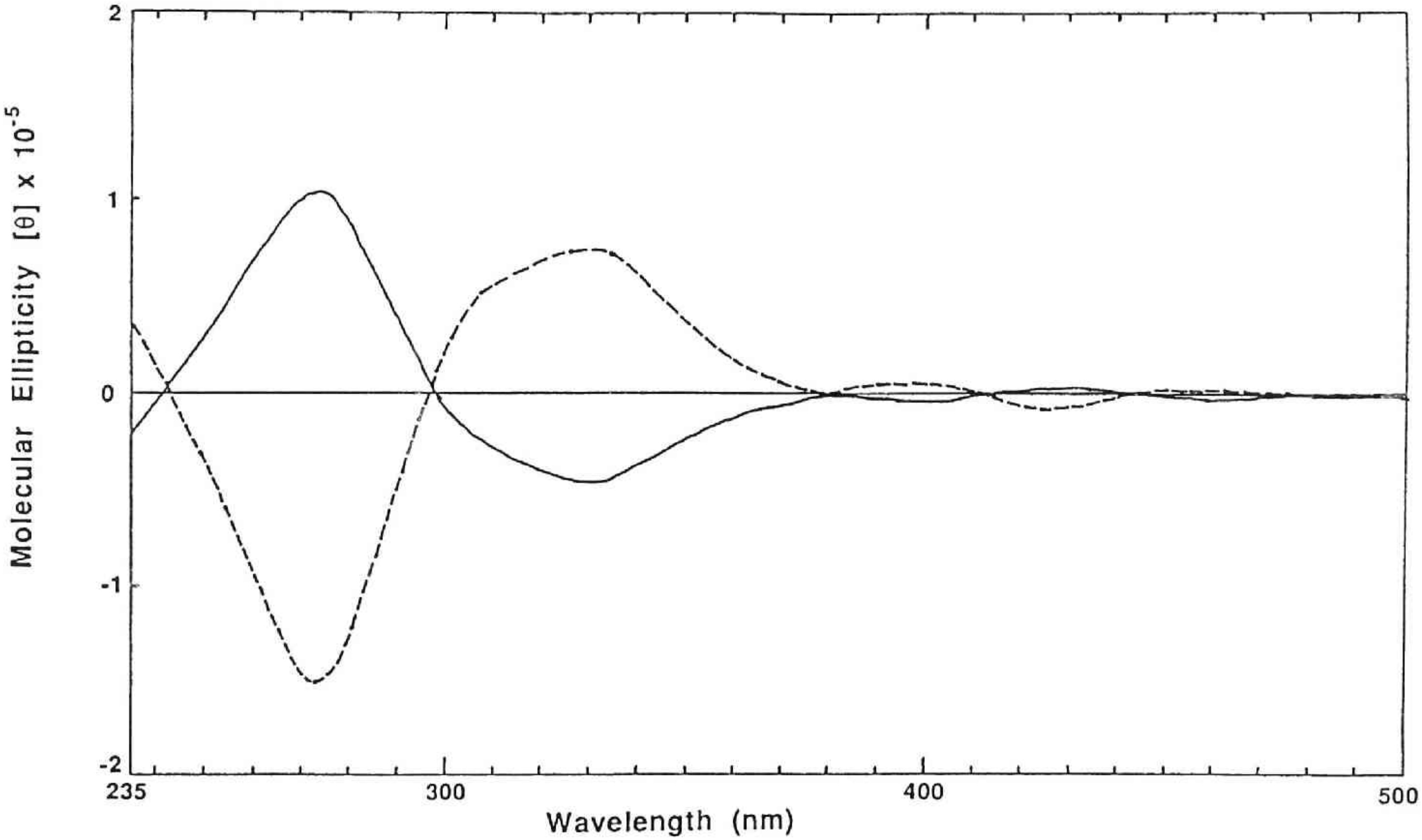


Figure 4. CD spectra of (-)-**11** (——) and (+)-**11** (----).

Experimental Section.

General. ^{1}H-NMR spectra were measured with a Varian VXR-200 and Gemini-200 spectrometer in $CDCl_3$. Chemical shifts are reported in δ ppm. Infrared spectra were measured with a Hitachi 270-30 spectrometer. Data are given in cm^{-1}. UV spectra were recorded with a Hitachi U-3410. CD spectra were measured with JASCO J-600. The molecular weights of polymers were measured by a Corona 117 vapor pressure osmometer in chloroform in 40°C. Recycling HPLC purification was performed with a JAI LC-908 equipped with JAIGEL-1H and -2H columns. High-performance liquid chromatography (HPLC) was done using a 20 mm x 25 cm YMC SH-043-5 column.

Materials. All solvents were dried over appropriate desiccant and distilled under nitrogen. (S)-2-Methylbutyl alcohol and 3-propylbromobenzene are commercially available. Preparation of 3,6-dimethyl-4,5-bis(propyloxymethyl)-1,2-diisocyanobenzene (**8**) is described in chapter 6.

Preparation of Penta(TMS)quinoxaline.(4, n=5)

A THF solution (3 mL) of **1** (31 mg, 1.74×10^{-5} mol) and **2a** (8.3 mg, 1.03×10^{-4} mol) was heated at reflux for 15 hrs under nitrogen. A large excess of CH_3MgBr (ether solution) was added and the mixture was heated at reflux for 1 hr. After excess of CH_3MgBr was quenched with water, preparative TLC on silica gel (n-hexane : ether = 5:1) following extractive workup with CH_2Cl_2 afforded mixture of quinoxaline oligomers. Quinoxaline pentamer (4, n=5, 32% yield) was isolated by Preparative GPC on polystyrene.

^{1}H-NMR ($CDCl_3$ at 50 C) -0.47 (s, 18H), -0.34 (s, 18H). -0.25 (s, 18H), -0.19 (s, 18H), -0.15 (s, 18H), 1.8-3.5 (br-m, 26H), 6.93 (d, 4H, J=7.4 Hz), 7.14 (d, 4H, J=7.4 Hz), 7.11 (s, 2H), 7.27 (d, 4H, J=7.4 Hz), 7.34 (d, 4H, J=7.4 Hz). IR (KBr) 2964, 2904, 1582, 1470, 1374, 1250, 1160, 1066, 1050, 996, 848, 694, 644 cm^{-1}.

Crystal data : $C_{82}H_{126}N_{10}Si_{10}$, M=1532.80, monoclinic, space group P21/a, a=25.287(8) Å, b=24.423(8) Å, c=15.842(7) Å, α=89.98(2), β=93.52(3), γ=90.00(2), V=9766(3)$Å^3$, Z=4,

$Dc=1.04 g/cm^3$, λ(Cu Kα)=1.54178 , μ =15.00cm^{-1}.

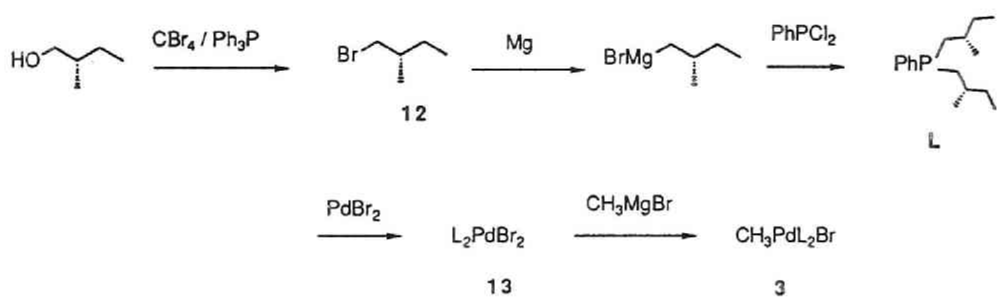
Intensity data were measured on a Mac Science MXC[3] diffractometer using ω-2θ scan technique and 13681 unique reflections within 3<2θ <130 were collected. Structure was solved by the direct method[a] and refined anisotropically by the full-matrix least-squares to R = 0.068, Rw = 0.080, and S = 1.64 for 8462 reflections. The thermal parameter of each hydrogen atom was assumed to be isotropic and equal to that of the bonded atom.

a) i) Furusaki, A. Acta Crystallogr. **1979**, A35, 220. ii) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN-78 ; A System Computer Program for Automatic Solution of Crystal Structures from X-ray Diffraction Data, University of York, and Louvain 1978.

Preparation of optically active phosphine complexes.(3)

Pd-complex (**3**) was prepared following the scheme below.

Scheme 5



(S)-2-Methyl-1-bromobutane.(12)

To a ether solution (80 mL) of (S)-2-methylbutanol (4.4 mL, 40 mmol) and CBr_4 (20 g, 60 mmol) was added PPh_3 (17 g, 64 mmol) at r.t. The reaction mixture was heated at reflux for 1 hr. The cooled reaction mixture was passed through a column of silica gel. The filtrate was condensed, and distillation of the residue gave **12** in 60% yield, bp 117°C / 760 mmHg.

^{1}H-NMR ($CDCl_3$) 0.91 (t, 3H, J=7.5 Hz), 1.01 (d, 3H, J=6.6 Hz), 1.1-1.8 (m, 3H), 3.3-3.5 (m, 2H). IR (neat) 3028, 2972, 2940, 2884, 1462, 1380, 1232, 1146, 656 cm^{-1}.

trans-Dibromo-bis[bis((S)-2-methylbutyl)phenylphophine]palladium(II).(13)

To a ether solution of (S)-2-methylbutylmagnesium bromide which was prepared by the reaction of **12** (3 mL, 24 mmol) and Mg (0.6 g, 24 mmol) in dry ether was added dichlorophenylphosphine (1 mL, 7.7 mmol) at 0°C. The reaction mixture was heated at reflux for 1 hr then treated with deoxygenated saturated NH_4Cl aq. (20 mL) at 0°C. Organic layer was extracted with ether and the extract was dried with $MgSO_4$. Removal of the ether gave crude bis((S)-2-methylbutyl)phosphine as a colorless liquid. The reaction of the phosphine and $PdBr_2$ in CH_2Cl_2 afforded **13** after preparative TLC on silica gel (n-hexane : ether = 4:1).

^{1}H-NMR ($CDCl_3$) 0.7-2.5 (m, 44H), 7.3-7.8 (m, 10H). IR (KBr) 2968, 2932, 2884, 1462, 1438, 1404, 1380, 1106, 1078, 846, 802, 738, 694, 500 cm^{-1}. Anal. Calcd for $C_{32}H_{54}P_2Br_2Pd$; C, 50.11; H, 7.10. Found. C, 50.26; H, 7.17.

trans-Bromo-bis[bis((S)-2-methylbutyl)phenylphosphine]methylpalladium(II).(3)

To a benzene solution (3 mL) of **13** (56 mg, 7.3×10^{-5} mol) was added a large excess of CH_3MgBr (ether solution) at 0°C, and the mixture was stirred at 0°C for 30 min. Extractive workup gave **3** in 86% yield.

^{1}H-NMR (CDCl3) 0.01 (t, 3H, J=4.6 Hz), 0.8-2.4 (m, 44H),7.3-7.7 (m, 10H).

Screw sense selective polymerization of 1,2-diisocyanoarene catalyzed by optically active phosphine methylpalladium(II) complexes.

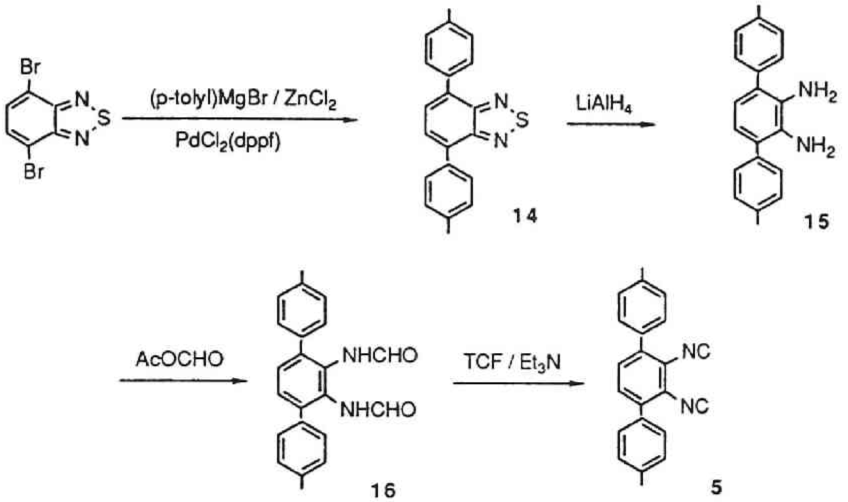
A solution of **3** (8.3 mg, 1.2×10^{-5} mol) and **1** (43.5 mg, 1.5×10^{-4} mol) was heated at reflux for 18 hrs. Then, a large excess of CH_3MgBr (ether solution) was added to the cooled mixture and it was stirred at r.t. for 15 min. Extractive workup with CH_2Cl_2 and water, followed by preparative GPC gave **4** in 60% yield.

4 : ^{1}H-NMR ($CDCl_3$) -1.0-0.3 (m), 1.0-2.7 (m), 6.4-7.5 (m). IR (KBr) 2964, 2904, 1582, 1464, 1414, 1250, 1162, 1066, 1042, 850, 694 cm^{-1}.

Preparation of 3,6-di-p-tolyl-1,2-diisocyanoarene.

3,6-di-p-tolyl-1,2-diisocyanoarene was prepared following the scheme below.

Scheme 6



Preparation of 4,7-di-p-tolyl-2,1,3-benzothiadiazol.(14)

To a suspension (150 mL) of p-tolylzinc chloride (80 mmol) in THF and ether, which was prepared from p-tolylMgBr and $ZnCl_2$, was added a THF solution (120 mL) of 4,7-dibromo-1,2,3-benzothiadiazol (8g, 27 mmol) and $PdCl_2$dppf (0.5g, 0.68 mmol). The mixture was stirred at r.t. for 4 hrs, then excess of p-tolylZnCl was quenched with water. Extractive workup with ether and water followed by washing with n-hexane afforded **14** as light green solid in 50% yield.

^{1}H-NMR ($CDCl_3$) 2.47 (s, 6H), 7.38 (d, 4H, J= 8.14 Hz), 7.76 (s, 2H), 7.88 (d, 4H, J= 8.24 Hz). IR (KBr) 3032, 2924, 1614, 1554, 1518, 1482, 1346, 1192, 892, 852, 814, 536, 516 cm^{-1}.

Preparation of 1,2-diamino-3,6-di-p-tolylbenzene.(15)

To a THF solution (100 mL) of 14 (4.7 g, 15 mmol), was added $LiAlH_4$ (1.1 g, 29 mmol) at 0°C. After excess of $LiAlH_4$ was quenched with H_2O, extractive workup with CH_2Cl_2 and water afforded **15** in 90% yield.

^{1}H-NMR ($CDCl_3$) 2.45 (s, 6H), 6.81 (s, 2H), 7.31 (d, 4H, J=8.06 Hz), 7.42 (d, 4H, J= 8.14 Hz). IR (KBr) 3416, 3032, 2924, 1608, 1524, 1484, 1440, 1400, 1310, 1210, 1112, 1016, 826, 800, 654 cm^{-1}.

Preparation of 1,2-diformamido-3,6-di-p-tolylbenzene.(16) To a CH_2Cl_2 solution (50 mL) of **15** (3.9 g, 13.5 mmol), acetylformate (3.7 g, 42 mmol) was added dropwise at 0°C. The mixture was stirred overnight gradually warming up to r.t. The mixture was filtrated and the residual solid was washed with MeOH. Drying in vacuo afforded **16** in 90% yield.

IR (KBr) 3222, 3032, 2988, 2928, 2876, 1660, 1514, 1470, 1384, 1314, 1238, 1166, 1114, 1020, 916, 812, 710, 506 cm^{-1}.

Preparation of 1,2-diisocyano-3,6-di-p-tolylbenzene.(5)

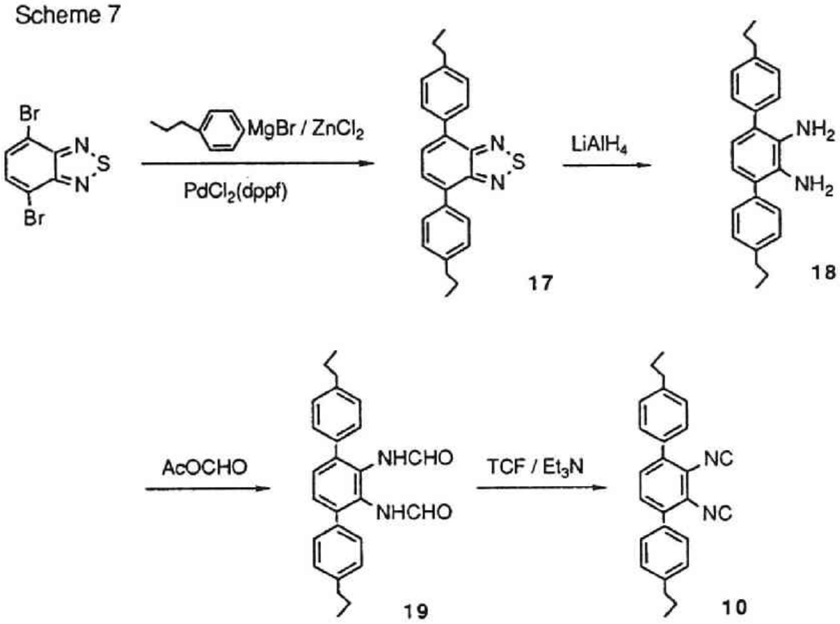
A CH_2Cl_2 suspension (5 mL) of **16** (0.82 g, 2.38 mmol) and Et_3N (5 mL) was cooled to -78°C. Trichloromethylchloroformate (1.5 mL, 12.4 mmol) in CH_2Cl_2 (15 mL) was added dropwise at -78°C and the mixture was stirred at -78°C for 10 hrs. After gradually warmed up to -30°C, 10% Na_2CO_3 aq. was added dropwise. Extractive workup with CH_2Cl_2 and 10% Na_2CO_3 aq. followed by recrystallization from diisopropylether gave **5** in 60% yield.

^{1}H-NMR ($CDCl_3$) 2.45 (s, 6H), 7.34 (d, 4H, J= 8.06 Hz), 7.46 (d, 4H, J= 8.06 Hz), 7.51 (s, 2H). IR (KBr) 3036, 2924, 2120, 1612, 1482, 1386, 1188, 1020, 860, 814, 500 cm^{-1}. Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08. Found C, 85.44; H, 5.08; N, 8.91.

Preparation of 3,6-di-(3-n-propylphenyl)-1,2-diisocyanobenzene.(10)

3,6-di-(4-n-propylphenyl)-1,2-diisocyanobenzene was prepared in the same manner as that of 5 following the scheme below.

Scheme 7



4,7-di-(4-n-propylphenyl)-2,1,3-benzothiadiazol.(17)

^{1}H-NMR ($CDCl_3$) 1.01 t, 6H, J= 6.0 Hz), 1.74 (sex, 4H, J= 8.0 Hz), 2.69 (t, 4H, J= 6.0 Hz), 7.37 d, 4H, J= 8.14 Hz), 7.76 (s, 2H), 7.89 (d, 4H, J= 8.22 Hz).

3,6-di-(4-n-propylphenyl)-1,2-diaminobenzene.(18)

^{1}H-NMR ($CDCl_3$) 1.09 (t, 6H, J= 7.36 Hz), 1.80 (sex, 4H, J= 7.60 Hz), 2.74 (t, 4H, J= 8.06 Hz), 3.63 (br-s, 4H), 6.87 (s, 2H), 7.36 (d, 4H, J= 8.28 Hz), 7.49 (d, 4H, J= 8.18 Hz).

3,6-di-(4-n-propylphenyl)-1,2-diformamidobenzene.(19)

IR (KBr) 3272, 2968, 2940, 2876, 1698, 1668, 1516, 1466, 1390, 1252, 1166, 802 cm^{-1}.

3,6-di-(4-n-propylphenyl)-1,2-diisocyanobenzene.(10)

^{1}H-NMR ($CDCl_3$) 1.01 (t, 6H, J= 7.38 Hz), 1.72 (sex, 4H, J= 7.62 Hz), 7.34 (d, 4H, J= 8.34 Hz), 7.48 (d, 4H, J= 8.32 Hz), 7.52 (s, 2H). IR (KBr) 2968, 2940, 2880, 2124, 1482, 832, 830 cm^{-1}. Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found C, 85.58; H, 6.56; N, 7.75.

Oligomerization of **5** catalyzed by **3**.

Penta-quinoxalinyl-palladium complex(-).(-)-**6** IR (KBr) 2928, 1518, 1454, 982, 810 cm-1.

Penta-quinoxalinyl-palladium complex(+).(+)-**6** IR (KBr) 2932, 1518, 1458, 982, 810 cm-1.

^{1}H-NMR spectra for both isomers are shown in Figure 6 and 7.

Me-PENTA-Me.(**7**)

(-)- or (+)-**6** was reacted with a large excess of CH_3MgBr in THF at r.t. Extractive workup with $CHCl_3$ and water gave (-)- or (+)-**7**.

^{1}H-NMR ($CDCl_3$) 1.30 (s, 6H), 1.35 (s, 6H), 2.46 (s, 6H), 2.49 (s, 6H), 2.53 (s, 6H), 2.84 (s, 6H), 5.92 (d, 4H, J= 7.7 Hz), 6.13 (d, 4H, J= 7.9 Hz), 6.25 (d, 4H, J= 8.0 Hz), 6.35 (d, 4H, J= 8.3 Hz), 6.78 (d, 4H, J= 7.9 Hz), 7.14 (d, 4H, J= 7.9 Hz), 7.24 (d, 2H J= 1.3 Hz), 7.26 (d, 2H, J= 1.3 Hz), 7.30 (d, 4H, J= 8.0 Hz), 7.40 (s, 2H), 7.41 (d, 4H, J= 7.5 Hz), 7.43 (d, 2H, J= 7.4 Hz), 7.58 (d, 4H, J= 8.0 Hz), 7.69 (d, 2H, J= 7.4 Hz), 7.82 (d, 4H, J= 8.1 Hz). IR (KBr) 2928, 1518, 1456, 1130, 982, 810 cm^{-1}. MS m/e 1573 (M+).

Polymerization of 1,2-diisocyanobenzenes (**5** and **10**) catalyzed by pentaquinoxalinylpalladium complexes ((-)-**6** and (+)-**6**).

Polymerization of **5** by (-)-**6**.

A THF solution (6 mL) of (-)-6 (4.9 mg, $2.2x10^{-6}$ mol) and 5 (31 mg. $1.0x10^{-4}$ mol) was stirred at r.t. for 35 hrs. Then, a large excess of CH_3MgBr was added and the mixture was stirred at r.t. for 1 hr. Extractive workup with $CHCl_3$ and water followed by preparative GPC afforded (+)-**9** in 79% yield.

^{1}H-NMR ($CDCl_3$) 0.79 (t, J=7.1 Hz), 1.57 (br-s), 2.34 (br-s), 3.46 (br-s), 4.59 (br-s), 6.0-8.0 (br-m). IR (KBr) 2972, 2940, 2880, 1460, 1360, 1096, 1042 cm^{-1}. UV (CH_2Cl_2) 287nm (ε=905000), 349nm (ε=345000). VPO ($CHCl_3$) Mn=11200.

(-)-**9** (82%) was prepared in a similar procedure from (+)-**6** (4.9 mg, $2.2x10^{-6}$ mol) and **5** (30.5 mg, $1.0x10^{-4}$ mol).

^{1}H-NMR ($CDCl_3$) 0.89 (t, J=7.3 Hz), 1.56 (br-s), 2.34 (br-s), 3.45 (br-s), 4.60 (br-s), 6.0-8.0 (br-m). IR (KBr) 2972, 2940, 2880, 1464, 1360, 1096, 1042 cm^{-1}. UV (CH_2Cl_2) 288nm (ε=912000), 349nm (ε=339000). VPO ($CHCl_3$) Mn=10000.

Polymerization of **10** by (-)-**6**.

A THF solution (6 mL) of (-)-**6** (6.8 mg, 3.0×10^{-6} mol) and **10** (38 mg, 1.0×10^{-4} mol) was heated at reflux for 3 days. Then, EtOH (1.5 mL) and $NaBH_4$ (30 mg) was added and the mixture was stirred at r.t. for 1 hr. Extractive workup with $CHCl_3$ and water followed by preparative GPC afforded (-)-**11** in 74% yield.

^{1}H-NMR ($CDCl_3$) 0.5-1.0 (br-s), 1.0-1.5 (br-s), 1.6-2.2 (br-s), 5.5-8.0 (br-m). IR (KBr) 3032, 2968, 2940, 2880, 1520, 1466, 1262, 1096, 1046, 1020, 978, 802 cm^{-1}. VPO ($CHCl_3$) Mn= 7150. UV (CH_2Cl_2) 267 nm (ε = 720000).

(+)-11 was (71%) was prepared in a similar procedure from (+)-**6** (6.7 mg, 3.5×10^{-6} mol) and **10** (38 mg, 1.0×10^{-4} mol).

^{1}H-NMR ($CDCl_3$) 0.5-1.0 (br-s), 1.0-1.5 (br-s), 1.6-2.2 (br-s), 5.5-8.0 (br-m). IR (KBr) 3032, 2968, 2936, 2876, 1518, 1462, 1262, 1126, 1046, 978, 802 cm^{-1}. VPO ($CDCl_3$) Mn=8230. UV (CH_2Cl_2) 266 nm (ε = 787000).

References and Notes.

1) Examples of optically active helical polymers ; Poly(triaryl methacrylate) : Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. J. Am. Chem. Soc. **1979**, 101, 4763. Okamoto, Y.; Mohri, H.; Nakano, T; Hatada, K. J. Am. Chem. Soc. **1989**, 111, 5952. : Polyisocyanide : Nolte, R. J. M.; van Beijnen, A. J. M.; Drenth, W. J. Am. Chem. Soc. **1974**. 96. 5932. Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. J. Chem. Soc., Chem. Commun. **1986**, 1789. J. Am. Chem. Soc. **1988**, 110, 6818. : Polychloral : Corley, L. S.; Vogl, O. Polym. Bull. 1980, 3, 211. Ute, K.; Hirose, K.; Kashimoto, H.; Hatada, K.; Vogl, O.; J. Am. Chem. Soc. **1991**, 113, 6305. : Poly-b-pyrroles : Magnus, P.; Danikiewicz, W.; Katoh, T.; Huffman, J. C.; Folting, K. J. Am. Chem. Soc. **1990**, 112, 2465.

Figure 5. Atom Numbering in the Crystal Data of **4** (n=5)

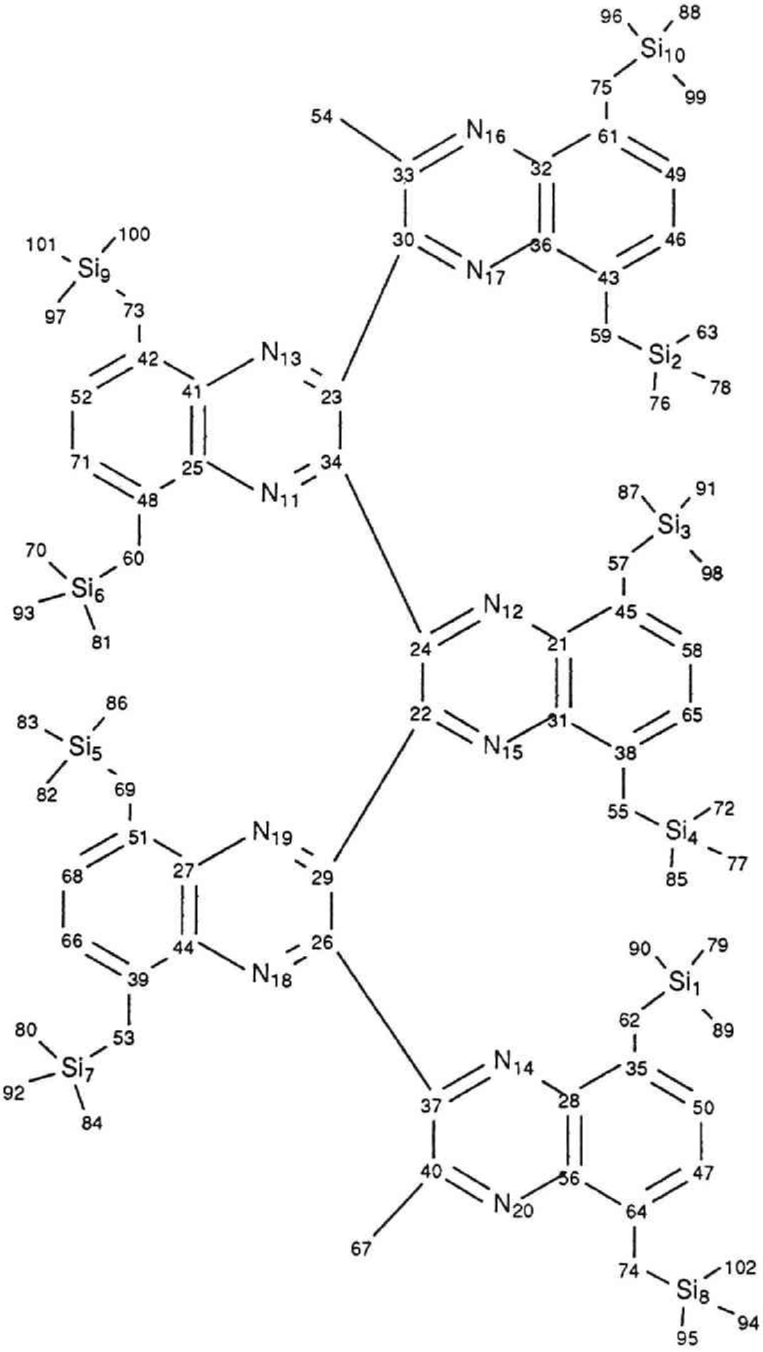


Table 1. Atomic coordinates (x 10^4) and equivalent isotropic temperature factors ($Å^2$x10) for **4** (n = 5).

*B_{eq} = 4/3ΣiΣjβijaiaj.

atom	x	y	z	B(eq)
Si1	0.42084 (6)	0.86497 (6)	0.94007 (9)	6.31 (4)
Si2	0.03194 (5)	0.80520 (6)	0.77360 (8)	5.93 (4)
Si3	0.17590 (6)	0.86733 (6)	1.10494 (9)	7.06 (5)
Si4	0.25704 (6)	0.97924 (5)	0.65230 (8)	6.05 (4)
Si5	0.30589 (7)	0.83523 (7)	0.42230 (9)	7.68 (5)
Si6	0.16765 (6)	0.64922 (6)	1.11688 (9)	6.61 (4)
Si7	0.39361 (7)	0.53383 (6)	0.5848 (1)	7.79 (5)
Si8	0.43681 (7)	0.58630 (8)	1.1520 (1)	9.52 (7)
Si9	0.07799 (8)	0.51529 (8)	0.7154 (1)	9.18 (7)
Si10	0.04118 (9)	0.7101 (1)	0.3684 (1)	11.58 (9)
N 11	0.2143 (1)	0.6782 (1)	0.8968 (2)	4.3 (1)
N 12	0.1999 (1)	0.7962 (1)	0.8786 (2)	4.00 (9)
N 13	0.1758 (1)	0.6263 (1)	0.7481 (2)	4.7 (1)
N 14	0.3422 (1)	0.7406 (1)	0.8894 (2)	4.2 (1)
N 15	0.2719 (1)	0.8371 (1)	0.7664 (2)	4.05 (9)
N 16	0.1512 (1)	0.7158 (2)	0.5231 (2)	5.2 (1)
N 17	0.1446 (1)	0.7563 (1)	0.6867 (2)	4.01 (9)
N 18	0.3530 (1)	0.6742 (1)	0.7008 (2)	4.5 (1)
N 19	0.2847 (1)	0.7560 (1)	0.6340 (2)	4.3 (1)
N 20	0.3480 (1)	0.6363 (2)	0.9603 (2)	5.3 (1)
C 21	0.2109 (2)	0.8506 (2)	0.8763 (2)	4.1 (1)
C 22	0.2613 (2)	0.7848 (2)	0.7711 (2)	3.8 (1)
C 23	0.1864 (2)	0.6793 (2)	0.7498 (2)	4.1 (1)
C 24	0.2235 (1)	0.7643 (2)	0.8262 (2)	3.5 (1)
C 25	0.2009 (2)	0.6235 (2)	0.8972 (3)	4.7 (1)
C 26	0.3258 (2)	0.7057 (2)	0.7507 (2)	3.9 (1)
C 27	0.3121 (2)	0.7231 (2)	0.5815 (3)	4.6 (1)
C 28	0.3544 (2)	0.7344 (2)	0.9739 (3)	4.7 (1)
C 29	0.2916 (2)	0.7476 (2)	0.7160 (2)	3.8 (1)
C 30	0.1685 (2)	0.7098 (2)	0.6722 (2)	4.0 (1)
C 31	0.2464 (2)	0.8719 (2)	0.8175 (2)	4.2 (1)
C 32	0.1243 (2)	0.7629 (2)	0.5372 (3)	4.6 (1)
C 33	0.1732 (2)	0.6893 (2)	0.5885 (3)	4.7 (1)
C 34	0.2076 (1)	0.7050 (2)	0.8250 (2)	3.8 (1)
C 35	0.3629 (2)	0.7816 (2)	1.0254 (3)	5.3 (1)
C 36	0.1220 (2)	0.7840 (2)	0.6195 (2)	4.3 (1)
C 37	0.3352 (2)	0.6966 (2)	0.8428 (2)	4.2 (1)
C 38	0.2563 (2)	0.9290 (2)	0.8120 (3)	4.8 (1)
C 39	0.3766 (2)	0.6484 (2)	0.5624 (3)	5.4 (1)
C 40	0.3371 (2)	0.6427 (2)	0.8792 (3)	4.8 (1)
C 41	0.1832 (2)	0.5975 (2)	0.8221 (3)	4.9 (1)
C 42	0.1709 (2)	0.5400 (2)	0.8195 (3)	6.0 (2)
C 43	0.0929 (2)	0.8325 (2)	0.6357 (3)	4.7 (1)
C 44	0.3470 (2)	0.6823 (2)	0.6157 (3)	4.4 (1)
C 45	0.1838 (2)	0.8872 (2)	0.9302 (3)	4.9 (1)
C 46	0.0702 (2)	0.8580 (2)	0.5659 (4)	6.0 (2)
C 47	0.3766 (2)	0.7203 (3)	1.1451 (4)	7.4 (2)
C 48	0.2066 (2)	0.5948 (2)	0.9752 (3)	5.3 (1)
C 49	0.0725 (2)	0.8376 (2)	0.4839 (4)	6.4 (2)
C 50	0.3749 (2)	0.7728 (3)	1.1098 (3)	6.7 (2)
C 51	0.3037 (2)	0.7298 (2)	0.4925 (3)	5.4 (1)
C 52	0.1772 (2)	0.5136 (2)	0.8958 (4)	6.9 (2)
C 53	0.4147 (2)	0.6068 (2)	0.5992 (4)	6.4 (2)
C 54	0.2035 (2)	0.6378 (2)	0.5694 (4)	6.4 (2)
C 55	0.2929 (2)	0.9518 (2)	0.7500 (3)	5.8 (2)
C 56	0.3567 (2)	0.6812 (2)	1.0094 (3)	5.2 (1)
C 57	0.1478 (2)	0.8660 (2)	0.9944 (3)	6.1 (2)
C 58	0.1944 (2)	0.9419 (2)	0.9221 (3)	6.0 (2)
C 59	0.0838 (2)	0.8492 (2)	0.7238 (3)	5.5 (2)
C 60	0.2232 (2)	0.6223 (2)	1.0555 (3)	6.0 (2)
C 61	0.0977 (2)	0.7895 (2)	0.4666 (3)	5.8 (2)
C 62	0.3603 (2)	0.8375 (2)	0.9884 (3)	5.6 (2)
C 63	-0.0092 (2)	0.7708 (3)	0.6894 (4)	6.9 (2)
C 64	0.3682 (2)	0.6739 (2)	1.0984 (3)	6.1 (2)
C 65	0.2292 (2)	0.9620 (2)	0.8643 (3)	6.0 (2)
C 66	0.3670 (2)	0.6562 (2)	0.4773 (3)	6.5 (2)
C 67	0.3261 (3)	0.5920 (2)	0.8286 (4)	7.0 (2)
C 68	0.3311 (2)	0.6951 (2)	0.4433 (3)	6.9 (2)
C 69	0.2686 (2)	0.7736 (2)	0.4554 (3)	6.5 (2)
C 70	0.1276 (3)	0.6973 (3)	1.0497 (4)	7.6 (2)
C 71	0.1936 (2)	0.5397 (2)	0.9707 (4)	6.7 (2)
C 72	0.2129 (3)	0.9246 (3)	0.6081 (4)	7.4 (2)
C 73	0.1517 (2)	0.5133 (2)	0.7396 (4)	6.9 (2)
C 74	0.3702 (2)	0.6174 (3)	1.1367 (4)	7.5 (2)
C 75	0.0946 (2)	0.7634 (3)	0.3815 (3)	7.6 (2)
C 76	0.0639 (3)	0.7514 (4)	0.8428 (5)	9.3 (2)
C 77	0.2183 (3)	1.0409 (3)	0.6784 (4)	8.8 (2)

C 78	-0.0094 (4)	0.8510 (4)	0.8357 (5)	10.3 (3)
C 79	0.4272 (3)	0.8357 (3)	0.8342 (4)	9.3 (2)
C 80	0.4106 (4)	0.5105 (4)	0.4778 (6)	11.7 (3)
C 81	0.1246 (4)	0.5916 (3)	1.1473 (5)	9.9 (3)
C 82	0.3510 (3)	0.8568 (3)	0.5127 (5)	10.1 (3)
C 83	0.2588 (5)	0.8908 (5)	0.3893 (6)	12.5 (4)
C 84	0.3216 (3)	0.5285 (3)	0.5971 (5)	9.2 (2)
C 85	0.3080 (3)	0.9997 (4)	0.5775 (5)	9.8 (3)
C 86	0.3454 (4)	0.8187 (4)	0.3292 (5)	10.6 (3)
C 87	0.1281 (4)	0.8361 (3)	1.1751 (5)	10.4 (3)
C 88	0.0198 (5)	0.7037 (4)	0.2565 (7)	12.8 (4)
C 89	0.4129 (4)	0.9409 (3)	0.9304 (5)	9.9 (3)
C 90	0.4818 (3)	0.8504 (4)	1.0089 (6)	11.1 (3)
C 91	0.2371 (3)	0.8240 (5)	1.1064 (6)	12.8 (4)
C 92	0.4294 (5)	0.4911 (4)	0.6670 (8)	14.6 (4)
C 93	0.1972 (4)	0.6827 (4)	1.2132 (4)	10.4 (3)
C 94	0.4295 (4)	0.5150 (3)	1.1947 (6)	12.6 (4)
C 95	0.4730 (4)	0.6257 (5)	1.2438 (9)	16.8 (4)
C 96	0.0675 (6)	0.6415 (4)	0.4047 (9)	26.2 (7)
C 97	0.0656 (6)	0.4859 (8)	0.6069 (9)	17.9 (7)
C 98	0.1867 (6)	0.9393 (4)	1.1399 (5)	17.0 (5)
C 99	-0.0135 (7)	0.728 (1)	0.432 (1)	34 (1)
C 100	0.0530 (4)	0.5850 (5)	0.722 (1)	19.9 (6)
C 101	0.0485 (5)	0.4678 (9)	0.788 (1)	24.8 (9)
C 102	0.4653 (8)	0.582 (1)	1.051 (1)	37 (1)

Table 2. Anisotropic thermal parameters (Å x 10^3) for **4** (n = 5).

The temperature factor is of the form :

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}lb^*c^*)].$$

atom	u11	u22	u33	u12	u13	u23
Si1	0.072 (1)	0.0770 (9)	0.090 (1)	0.0106 (8)	0.0061 (7)	-0.0114 (8)
Si2	0.0610 (6)	0.0946 (9)	0.0698 (9)	0.0090 (8)	0.0076 (6)	0.0066 (8)
Si3	0.104 (1)	0.090 (1)	0.0750 (9)	-0.0158 (9)	0.0278 (8)	-0.0009 (8)
Si4	0.097 (1)	0.0628 (9)	0.0700 (9)	-0.0061 (8)	0.0076 (7)	0.0107 (7)
Si5	0.125 (1)	0.095 (1)	0.0732 (9)	0.0230 (9)	0.0338 (9)	0.0134 (8)
Si6	0.096 (1)	0.0686 (9)	0.085 (1)	-0.0002 (8)	0.0024 (8)	0.0174 (8)
Si7	0.096 (1)	0.0713 (9)	0.128 (1)	0.0211 (9)	-0.012 (1)	-0.0244 (9)
Si8	0.084 (1)	0.136 (2)	0.141 (2)	0.015 (1)	0.008 (1)	0.062 (1)
Si9	0.110 (1)	0.109 (2)	0.130 (2)	-0.029 (1)	0.014 (1)	-0.033 (1)
Si10	0.132 (2)	0.229 (3)	0.077 (1)	-0.073 (2)	-0.010 (1)	-0.010 (1)
N 11	0.051 (2)	0.049 (2)	0.064 (2)	0.003 (2)	0.004 (2)	0.008 (2)
N 12	0.056 (2)	0.039 (2)	0.056 (2)	-0.002 (2)	0.003 (2)	0.000 (2)
N 13	0.057 (2)	0.047 (2)	0.074 (2)	0.000 (2)	0.007 (2)	-0.002 (2)
N 14	0.048 (2)	0.060 (2)	0.053 (2)	0.005 (2)	0.001 (2)	0.004 (2)
N 15	0.053 (2)	0.043 (2)	0.058 (2)	-0.002 (2)	-0.000 (2)	0.005 (2)
N 16	0.055 (2)	0.083 (3)	0.058 (2)	-0.012 (2)	0.006 (2)	-0.004 (2)
N 17	0.051 (2)	0.049 (2)	0.053 (2)	-0.006 (2)	0.006 (2)	0.002 (2)
N 18	0.049 (2)	0.055 (2)	0.068 (2)	0.005 (2)	0.003 (2)	-0.004 (2)
N 19	0.057 (2)	0.054 (2)	0.053 (2)	0.001 (2)	0.007 (2)	0.001 (2)
N 20	0.062 (2)	0.067 (3)	0.073 (3)	0.008 (2)	-0.001 (2)	0.016 (2)
C 21	0.059 (2)	0.046 (3)	0.051 (2)	0.002 (2)	-0.003 (2)	0.004 (2)
C 22	0.050 (2)	0.043 (2)	0.050 (2)	-0.002 (2)	-0.000 (2)	0.001 (2)
C 23	0.046 (2)	0.044 (3)	0.067 (3)	0.000 (2)	0.004 (2)	-0.003 (2)

C 24	0.045 (2)	0.036 (2)	0.050 (2)	0.001 (2)	-0.001 (2)	0.002 (2)
C 25	0.056 (2)	0.045 (3)	0.078 (3)	0.000 (2)	0.004 (2)	0.004 (2)
C 26	0.047 (2)	0.044 (2)	0.058 (2)	-0.002 (2)	0.000 (2)	-0.002 (2)
C 27	0.056 (2)	0.058 (3)	0.060 (3)	-0.006 (2)	0.006 (2)	-0.002 (2)
C 28	0.049 (2)	0.076 (3)	0.055 (3)	0.011 (2)	0.003 (2)	0.005 (2)
C 29	0.052 (2)	0.043 (2)	0.052 (2)	-0.004 (2)	0.007 (2)	0.001 (2)
C 30	0.047 (2)	0.050 (3)	0.054 (2)	-0.005 (2)	0.002 (2)	-0.004 (2)
C 31	0.059 (2)	0.044 (3)	0.056 (2)	-0.004 (2)	-0.007 (2)	0.002 (2)
C 32	0.047 (2)	0.071 (3)	0.058 (3)	-0.012 (2)	0.007 (2)	0.008 (2)
C 33	0.054 (2)	0.062 (3)	0.061 (3)	-0.012 (2)	0.003 (2)	-0.009 (2)
C 34	0.043 (2)	0.048 (3)	0.054 (2)	0.006 (2)	0.006 (2)	0.002 (2)
C 35	0.062 (3)	0.078 (4)	0.060 (3)	0.013 (2)	0.004 (2)	-0.003 (3)
C 36	0.050 (2)	0.060 (3)	0.054 (3)	-0.012 (2)	0.004 (2)	0.007 (2)
C 37	0.046 (2)	0.050 (3)	0.061 (3)	0.005 (2)	0.003 (2)	0.000 (2)
C 38	0.082 (3)	0.043 (3)	0.057 (3)	-0.006 (2)	-0.012 (2)	-0.000 (2)
C 39	0.067 (3)	0.063 (3)	0.077 (3)	-0.002 (2)	0.014 (2)	-0.016 (2)
C 40	0.051 (2)	0.060 (3)	0.072 (3)	0.006 (2)	-0.002 (2)	0.004 (2)
C 41	0.060 (3)	0.042 (3)	0.084 (3)	-0.000 (2)	0.010 (2)	0.004 (2)
C 42	0.074 (3)	0.056 (3)	0.098 (4)	-0.001 (2)	0.014 (3)	-0..000 (3)
C 43	0.052 (2)	0.053 (3)	0.073 (3)	-0.005 (2)	0.004 (2)	0.013 (2)
C 44	0.048 (2)	0.056 (3)	0.064 (3)	-0.005 (2)	0.007 (2)	-0.007 (2)
C 45	0.075 (3)	0.050 (3)	0.062 (3)	0.008 (2)	0.003 (2)	-0.002 (2)
C 46	0.063 (4)	0.070 (4)	0.097 (4)	-0.007 (3)	0.008 (3)	0.026 (3)
C 47	0.096 (4)	0.127 (6)	0.056 (3)	0.020 (4)	0.003 (3)	0.014 (4)
C 48	0.062 (3)	0.055 (3)	0.084 (3)	0.003 (2)	0.004 (2)	0.024 (2)
C 49	0.074 (4)	0.091 (4)	0.079 (4)	-0.010 (3)	0.003 (3)	0.038 (3)
C 50	0.094 (4)	0.104 (5)	0.058 (3)	0.017 (3)	0.002 (3)	-0.007 (3)
C 51	0.072 (3)	0.072 (3)	0.060 (3)	-0.000 (3)	0.010 (2)	-0.004 (2)
C 52	0.098 (4)	0.046 (3)	0.116 (5)	-0.002 (3)	0.015 (4)	0.008 (3)
C 53	0.058 (3)	0.078 (4)	0.105 (4)	0.006 (3)	0.004 (3)	-0.029 (3)
C 54	0.097 (4)	0.070 (4)	0.076 (4)	0.013 (3)	0.013 (3)	-0.017 (3)
C 55	0.083 (4)	0.052 (3)	0.084 (4)	-0.026 (3)	-0.001 (3)	0.010 (2)
C 56	0.051 (2)	0.086 (4)	0.061 (3)	0.007 (2)	0.001 (2)	0.017 (3)
C 57	0.079 (4)	0.060 (3)	0.093 (4)	0.010 (3)	0.023 (3)	-0.006 (3)
C 58	0.110 (4)	0.055 (3)	0.062 (3)	0.016 (3)	-0.001 (3)	-0.005 (2)
C 59	0.064 (3)	0.050 (3)	0.093 (4)	0.011 (2)	0.009 (3)	0.002 (3)
C 60	0.073 (4)	0.075 (4)	0.079 (4)	-0.004 (3)	-0.013 (3)	0.028 (3)
C 61	0.062 (3)	0.098 (4)	0.062 (3)	-0.016 (3)	0.007 (2)	0.019 (3)
C 62	0.067 (3)	0.077 (4)	0.068 (3)	0.008 (3)	0.001 (2)	-0.020 (3)
C 63	0.078 (4)	0.103 (5)	0.080 (4)	-0.006 (3)	0.011 (3)	0.016 (3)
C 64	0.064 (3)	0.101 (4)	0.066 (3)	0.011 (3)	0.004 (2)	0.022 (3)
C 65	0.125 (4)	0.041 (3)	0.060 (3)	-0.004 (3)	-0.009 (3)	0.000 (2)
C 66	0.098 (4)	0.075 (4)	0.076 (4)	0.003 (3)	0.024 (3)	-0.018 (3)
C 67	0.109 (5)	0.061 (4)	0.095 (4)	0.000 (3)	0.011 (3)	0.006 (3)
C 68	0.118 (4)	0.083 (4)	0.060 (3)	-0.000 (4)	0.021 (3)	-0.008 (3)
C 69	0.093 (4)	0.100 (4)	0.053 (3)	0.009 (3)	0.009 (2)	0.007 (3)
C 70	0.096 (5)	0.084 (5)	0.109 (5)	0.013 (4)	0.008 (4)	0.016 (4)
C 71	0.093 (4)	0.061 (4)	0.101 (4)	0.002 (3)	0.002 (3)	0.025 (3)
C 72	0.107 (5)	0.101 (4)	0.073 (4)	-0.015 (4)	-0.004 (3)	-0.004 (4)
C 73	0.107 (4)	0.048 (3)	0.108 (4)	-0.009 (3)	0.019 (3)	-0.011 (3)
C 74	0.086 (4)	0.118 (5)	0.082 (4)	-0.002 (3)	0.002 (3)	0.041 (4)
C 75	0.093 (4)	0.137 (6)	0.058 (3)	-0.013 (4)	0.001 (3)	0.014 (3)
C 76	0.073 (4)	0.156 (6)	0.123 (6)	-0.014 (4)	-0.007 (4)	0.073 (5)
C 77	0.144 (7)	0.089 (4)	0.098 (5)	0.024 (4)	-0.002 (4)	0.013 (4)
C 78	0.109 (6)	0.166 (9)	0.117 (6)	0.023 (6)	0.036 (4)	-0.030 (6)
C 79	0.123 (6)	0.117 (5)	0.116 (5)	-0.026 (5)	0.053 (4)	-0.024 (5)
C 80	0.132 (7)	0.130 (7)	0.181 (8)	0.032 (5)	-0.012 (6)	-0.097 (6)
C 81	0.146 (7)	0.087 (5)	0.147 (7)	-0.002 (5)	0.061 (6)	0.027 (4)
C 82	0.148 (8)	0.104 (6)	0.134 (6)	-0.006 (4)	0.036 (5)	-0.024 (5)
C 83	0.22 (1)	0.156 (7)	0.105 (6)	0.099 (7)	0.036 (5)	0.036 (6)
C 84	0.104 (5)	0.101 (5)	0.144 (6)	-0.030 (4)	0.001 (4)	-0.017 (5)
C 85	0.138 (7)	0.117 (6)	0.118 (6)	-0.045 (5)	0.025 (5)	0.034 (4)
C 86	0.176 (9)	0.128 (7)	0.103 (5)	0.020 (6)	0.070 (5)	0.020 (5)
C 87	0.164 (7)	0.110 (6)	0.125 (5)	0.006 (6)	0.079 (5)	0.010 (5)
C 88	0.178 (9)	0.18 (1)	0.121 (7)	0.009 (9)	-0.041 (6)	-0.044 (8)
C 89	0.156 (7)	0.087 (4)	0.135 (6)	0.013 (5)	0.020 (5)	0.008 (4)
C 90	0.092 (5)	0.161 (8)	0.167 (7)	0.023 (5)	-0.017 (5)	0.010 (7)
C 91	0.097 (5)	0.26 (1)	0.133 (6)	0.020 (6)	0.019 (5)	0.077 (7)
C 92	0.21 (1)	0.126 (8)	0.21 (1)	0.055 (9)	-0.08 (1)	0.002 (8)
C 93	0.178 (9)	0.124 (7)	0.091 (5)	0.022 (5)	-0.010 (5)	-0.000 (4)
C 94	0.143 (7)	0.110 (6)	0.22 (1)	0.006 (5)	-0.044 (7)	0.045 (6)
C 95	0.148 (8)	0.190 (9)	0.29 (1)	0.004 (7)	-0.130 (8)	-0.007 (8)
C 96	0.43 (2)	0.20 (1)	0.35 (2)	-0.17 (1)	-0.24 (2)	0.16 (1)
C 97	0.21 (1)	0.29 (2)	0.18 (1)	-0.03 (1)	-0.04 (1)	-0.08 (1)
C 98	0.44 (2)	0.124 (7)	0.090 (5)	-0.117 (8)	0.058 (8)	-0.032 (5)
C 99	0.29 (2)	0.77 (4)	0.23 (2)	-0.37 (2)	0.17 (2)	-0.26 (3)
C 100	0.107 (7)	0.23 (1)	0.41 (2)	0.049 (7)	-0.06 (1)	-0.17 (1)
C 101	0.19 (1)	0.43 (2)	0.32 (2)	-0.20 (1)	-0.02 (1)	0.10 (2)
C 102	0.40 (2)	0.68 (4)	0.34 (2)	0.41 (3)	0.25 (2)	0.31 (3)

Table 3. Bond length (Å) and angles (°) for **4** (n =5).

atom	atom	distance
Si1	--C 79	1.840 (7)
Si1	--C 90	1.866 (8)
Si1	--C 89	1.870 (7)
Si1	--C 62	1.877 (5)
Si2	--C 63	1.844 (6)
Si2	--C 78	1.855 (9)
Si2	--C 76	1.863 (8)
Si2	--C 59	1.903 (5)
Si3	--C 57	1.850 (5)
Si3	--C 87	1.855 (9)
Si3	--C 98	1.86 (1)
Si3	--C 91	1.875 (9)
Si4	--C 72	1.851 (7)
Si4	--C 77	1.857 (7)
Si4	--C 55	1.869 (5)
Si4	--C 85	1.872 (8)
Si5	--C 82	1.852 (8)
Si5	--C 83	1.86 (1)
Si5	--C 69	1.868 (6)
Si5	--C 86	1.876 (9)
Si6	--C 70	1.844 (7)
Si6	--C 93	1.849 (8)
Si6	--C 81	1.860 (8)
Si6	--C 60	1.875 (5)
Si7	--C 84	1.848 (7)
Si7	--C 92	1.86 (1)
Si7	--C 80	1.86 (1)
Si7	--C 53	1.871 (6)
Si8	--C 102	1.79 (2)
Si8	--C 74	1.850 (6)
Si8	--C 94	1.881 (9)
Si8	--C 95	1.93 (1)
Si9	--C 100	1.82 (1)
Si9	--C 101	1.83 (2)
Si9	--C 97	1.87 (1)
Si9	--C 73	1.880 (6)
Si10	--C 99	1.81 (2)
Si10	--C 88	1.83 (1)
Si10	--C 75	1.878 (7)
Si10	--C 96	1.88 (1)
N 11	--C 34	1.315 (5)
N 11	--C 25	1.377 (5)
N 12	--C 24	1.310 (5)
N 12	--C 21	1.360 (5)
N 13	--C 23	1.321 (5)
N 13	--C 41	1.370 (6)
N 14	--C 37	1.310 (5)
N 14	--C 28	1.363 (5)
N 15	--C 22	1.309 (5)
N 15	--C 31	1.363 (5)
N 16	--C 33	1.317 (5)
N 16	--C 32	1.352 (6)
N 17	--C 30	1.314 (5)
N 17	--C 36	1.358 (5)
N 18	--C 26	1.325 (5)
N 18	--C 44	1.363 (5)

atom	atom	distance
N 19	--C 29	1.316 (5)
N 19	--C 27	1.375 (5)
N 20	--C 40	1.308 (6)
N 20	--C 56	1.355 (6)
C 21	--C 31	1.429 (6)
C 21	--C 45	1.438 (6)
C 22	--C 24	1.424 (5)
C 22	--C 29	1.504 (5)
C 23	--C 34	1.422 (5)
C 23	--C 30	1.484 (5)
C 24	--C 34	1.501 (5)
C 25	--C 41	1.399 (6)
C 25	--C 48	1.420 (6)
C 26	--C 29	1.427 (5)
C 26	--C 37	1.480 (5)
C 27	--C 44	1.416 (6)
C 27	--C 51	1.422 (6)
C 28	--C 56	1.415 (7)
C 28	--C 35	1.421 (6)
C 30	--C 33	1.426 (6)
C 31	--C 38	1.421 (6)
C 32	--C 36	1.407 (6)
C 32	--C 61	1.425 (6)
C 33	--C 54	1.513 (7)
C 35	--C 50	1.370 (6)
C 35	--C 62	1.485 (7)
C 36	--C 43	1.427 (6)
C 37	--C 40	1.436 (6)
C 38	--C 65	1.370 (7)
C 38	--C 55	1.497 (7)
C 39	--C 66	1.368 (7)
C 39	--C 44	1.428 (6)
C 39	--C 53	1.492 (7)
C 40	--C 67	1.493 (7)
C 41	--C 42	1.438 (5)
C 42	--C 52	1.370 (8)
C 42	--C 73	1.479 (8)
C 43	--C 46	1.364 (7)
C 43	--C 59	1.484 (7)
C 45	--C 58	1.370 (6)
C 45	--C 57	1.498 (7)
C 46	--C 49	1.398 (8)
C 47	--C 64	1.364 (9)
C 47	--C 50	1.398 (9)
C 48	--C 71	1.384 (7)
C 48	--C 60	1.477 (7)
C 49	--C 61	1.372 (8)
C 51	--C 68	1.368 (7)
C 51	--C 69	1.487 (7)
C 52	--C 71	1.390 (8)
C 56	--C 64	1.433 (6)
C 58	--C 65	1.396 (8)
C 61	--C 75	1.488 (7)
C 64	--C 74	1.505 (9)
C 66	--C 68	1.398 (8)

atom	atom	atom	angle
C 79	--Si1	--C 90	110.1 (4)
C 79	--Si1	--C 89	109.0 (3)
C 79	--Si1	--C 62	110.6 (3)
C 90	--Si1	--C 89	108.4 (4)
C 90	--Si1	--C 62	111.0 (3)
C 89	--Si1	--C 62	107.6 (3)
C 63	--Si2	--C 78	110.4 (3)
C 63	--Si2	--C 76	108.0 (3)
C 63	--Si2	--C 59	109.3 (2)

atom	atom	atom	angle
C 44	--C 27	--C 51	120.8 (4)
N 14	--C 28	--C 56	119.5 (4)
N 14	--C 28	--C 35	119.4 (4)
C 56	--C 28	--C 35	121.1 (4)
N 19	--C 29	--C 26	122.2 (3)
N 19	--C 29	--C 22	115.9 (3)
C 26	--C 29	--C 22	121.8 (3)
N 17	--C 30	--C 33	122.1 (4)
N 17	--C 30	--C 23	114.0 (3)

C 78	--Si2	--C 76	110.6 (4)
C 78	--Si2	--C 59	107.7 (3)
C 76	--Si2	--C 59	110.9 (3)
C 57	--Si3	--C 87	109.5 (3)
C 57	--Si3	--C 98	110.0 (3)
C 57	--Si3	--C 91	105.7 (3)
C 87	--Si3	--C 98	107.4 (5)
C 87	--Si3	--C 91	109.1 (4)
C 98	--Si3	--C 91	115.1 (6)
C 72	--Si4	--C 77	110.8 (3)
C 72	--Si4	--C 55	107.8 (2)
C 72	--Si4	--C 85	112.1 (3)
C 77	--Si4	--C 55	110.0 (3)
C 77	--Si4	--C 85	108.5 (4)
C 55	--Si4	--C 85	107.6 (3)
C 82	--Si5	--C 83	111.3 (4)
C 82	--Si5	--C 69	108.1 (3)
C 82	--Si5	--C 86	109.6 (4)
C 83	--Si5	--C 69	110.0 (4)
C 83	--Si5	--C 86	107.4 (4)
C 69	--Si5	--C 86	110.4 (3)
C 70	--Si6	--C 93	112.0 (3)
C 70	--Si6	--C 81	108.8 (3)
C 70	--Si6	--C 60	109.0 (3)
C 93	--Si6	--C 81	109.5 (4)
C 93	--Si6	--C 60	107.8 (3)
C 81	--Si6	--C 60	109.7 (3)
C 84	--Si7	--C 92	109.1 (5)
C 84	--Si7	--C 80	111.0 (4)
C 84	--Si7	--C 53	109.3 (3)
C 92	--Si7	--C 80	109.6 (5)
C 92	--Si7	--C 53	109.0 (4)
C 80	--Si7	--C 53	108.8 (3)
C 102	--Si8	--C 74	108.6 (7)
C 102	--Si8	--C 94	108.8 (9)
C 102	--Si8	--C 95	120.1 (8)
C 74	--Si8	--C 94	108.6 (4)
C 74	--Si8	--C 95	106.2 (4)
C 94	--Si8	--C 95	104.1 (5)
C 100	--Si9	--C 101	113.5 (8)
C 100	--Si9	--C 97	112.0 (8)
C 100	--Si9	--C 73	110.8 (4)
C 101	--Si9	--C 97	106.5 (8)
C 101	--Si9	--C 73	107.0 (5)
C 97	--Si9	--C 73	106.5 (5)
C 99	--Si10	--C 88	111.6 (7)
C 99	--Si10	--C 75	110.0 (8)
C 99	--Si10	--C 95	108.2 (9)
C 88	--Si10	--C 75	109.5 (4)
C 88	--Si10	--C 96	107.3 (5)
C 75	--Si10	--C 95	110.2 (5)
C 34	--N 11	--C 25	118.0 (3)
C 24	--N 12	--C 21	117.5 (3)
C 23	--N 13	--C 41	118.0 (3)
C 37	--N 14	--C 28	118.6 (4)
C 22	--N 15	--C 31	118.0 (3)
C 33	--N 16	--C 32	118.5 (4)
C 30	--N 17	--C 36	118.0 (3)
C 26	--N 18	--C 44	118.5 (3)
C 29	--N 19	--C 27	117.6 (3)
C 40	--N 20	--C 56	118.9 (4)
N 12	--C 21	--C 31	120.6 (3)
N 12	--C 21	--C 45	119.1 (4)
C 31	--C 21	--C 45	120.2 (4)
N 15	--C 22	--C 24	121.7 (3)
N 15	--C 22	--C 29	116.4 (3)
C 24	--C 22	--C 29	122.0 (3)
N 13	--C 23	--C 34	121.0 (4)
N 13	--C 23	--C 30	115.0 (3)
C 34	--C 23	--C 30	123.6 (3)
N 12	--C 24	--C 22	121.9 (3)
N 12	--C 24	--C 34	116.7 (3)
C 22	--C 24	--C 34	121.3 (3)
N 11	--C 25	--C 41	120.1 (4)
N 11	--C 25	--C 48	118.1 (4)
C 41	--C 25	--C 48	121.8 (4)
N 18	--C 26	--C 29	120.6 (3)
N 18	--C 26	--C 37	116.4 (3)
C 29	--C 26	--C 37	122.9 (3)
N 19	--C 27	--C 44	120.4 (4)
N 19	--C 27	--C 51	118.8 (4)
C 33	--C 30	--C 23	123.8 (4)
N 15	--C 31	--C 38	118.9 (4)
N 15	--C 31	--C 21	120.0 (3)
C 38	--C 31	--C 21	121.1 (4)
N 16	--C 32	--C 36	120.7 (4)
N 16	--C 32	--C 61	118.2 (4)
C 36	--C 32	--C 61	121.1 (4)
N 16	--C 33	--C 30	120.3 (4)
N 16	--C 33	--C 54	116.4 (4)
C 30	--C 33	--C 54	123.4 (4)
N 11	--C 34	--C 23	121.7 (4)
N 11	--C 34	--C 24	116.7 (3)
C 23	--C 34	--C 24	121.6 (3)
C 50	--C 35	--C 28	116.7 (5)
C 50	--C 35	--C 62	122.0 (5)
C 28	--C 35	--C 62	121.2 (4)
N 17	--C 36	--C 32	120.3 (4)
N 17	--C 36	--C 43	118.0 (4)
C 32	--C 36	--C 43	121.5 (4)
N 14	--C 37	--C 40	121.7 (4)
N 14	--C 37	--C 26	116.2 (4)
C 40	--C 37	--C 26	122.1 (4)
C 65	--C 38	--C 31	116.4 (4)
C 65	--C 38	--C 55	122.0 (4)
C 31	--C 38	--C 55	121.5 (4)
C 66	--C 39	--C 44	115.6 (4)
C 66	--C 39	--C 53	123.5 (5)
C 44	--C 39	--C 53	120.8 (4)
N 20	--C 40	--C 37	120.3 (4)
N 20	--C 40	--C 67	116.7 (4)
C 37	--C 40	--C 67	123.0 (4)
N 13	--C 41	--C 25	120.9 (4)
N 13	--C 41	--C 42	117.3 (4)
C 25	--C 41	--C 42	121.7 (4)
C 52	--C 42	--C 41	114.8 (5)
C 52	--C 42	--C 73	124.1 (5)
C 41	--C 42	--C 73	121.0 (4)
C 46	--C 43	--C 36	115.4 (4)
C 46	--C 43	--C 59	123.8 (4)
C 36	--C 43	--C 59	120.5 (4)
N 18	--C 44	--C 27	120.5 (4)
N 18	--C 44	--C 39	118.1 (4)
C 27	--C 44	--C 39	121.3 (4)
C 58	--C 45	--C 21	116.6 (4)
C 58	--C 45	--C 57	122.1 (4)
C 21	--C 45	--C 57	121.2 (4)
C 43	--C 46	--C 49	123.4 (5)
C 64	--C 47	--C 50	123.1 (5)
C 71	--C 48	--C 25	115.0 (4)
C 71	--C 48	--C 60	122.7 (5)
C 25	--C 48	--C 60	122.2 (4)
C 61	--C 49	--C 46	122.6 (5)
C 35	--C 50	--C 47	122.2 (5)
C 68	--C 51	--C 27	116.3 (4)
C 68	--C 51	--C 69	122.0 (4)
C 27	--C 51	--C 69	121.6 (4)
C 42	--C 52	--C 71	123.3 (5)
C 39	--C 53	--Si7	115.3 (3)
C 38	--C 55	--Si4	112.9 (3)
N 20	--C 56	--C 28	121.0 (4)
N 20	--C 56	--C 64	118.6 (5)
C 28	--C 56	--C 64	120.4 (4)
C 45	--C 57	--Si3	115.0 (3)
C 45	--C 58	--C 65	122.6 (4)
C 43	--C 59	--Si2	112.6 (3)
C 48	--C 60	--Si6	115.1 (3)
C 49	--C 61	--C 32	115.8 (4)
C 49	--C 61	--C 75	123.2 (5)
C 32	--C 61	--C 75	120.8 (5)
C 35	--C 62	--Si1	118.1 (3)
C 47	--C 64	--C 56	116.4 (5)
C 47	--C 64	--C 74	122.8 (5)
C 56	--C 64	--C 74	120.7 (5)
C 38	--C 65	--C 58	123.2 (4)
C 39	--C 66	--C 68	123.2 (5)
C 51	--C 68	--C 66	122.7 (5)
C 51	--C 69	--Si5	113.1 (4)
C 48	--C 71	--C 52	123.3 (5)
C 42	--C 73	--Si9	115.6 (4)
C 64	--C 74	--Si8	115.9 (4)
C 61	--C 75	--Si10	113.3 (4)

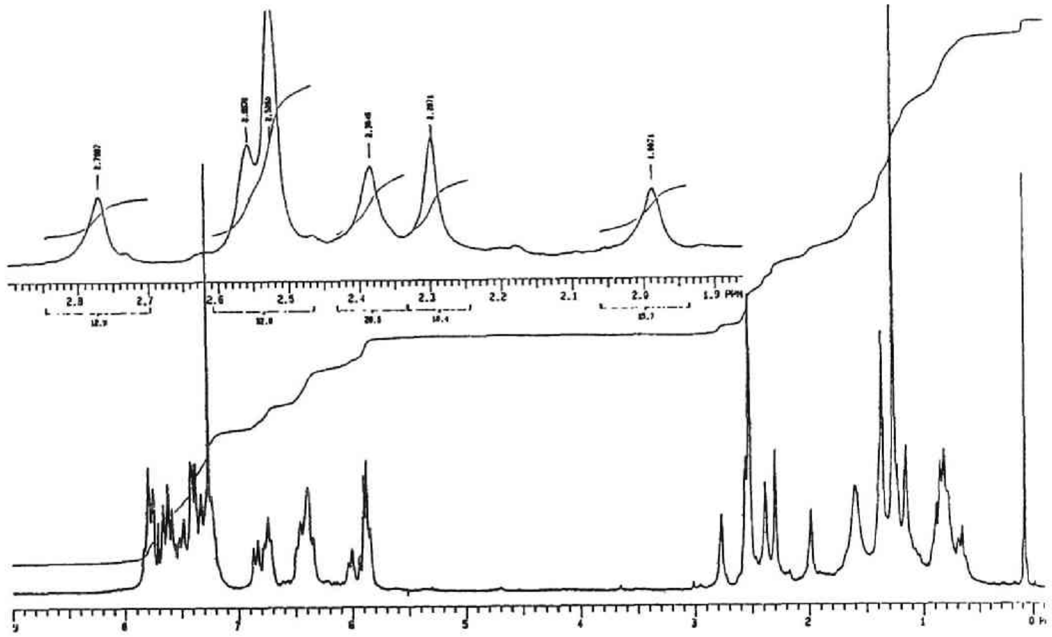


Figure 6. ^{1}H-NMR Spectrum of (-)-6

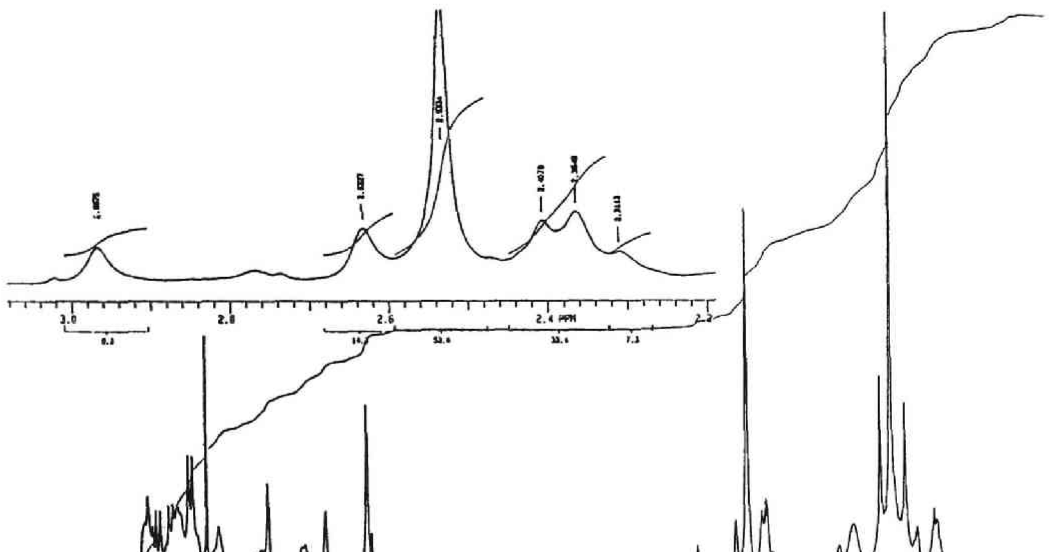


Figure 7. ^{1}H-NMR Spectrum of (+)-6

Chapter 5

Studies on Conformation of Helical Poly(2,3-quinoxaline)s. Empirical Energy Calculation and Theoretical Circular Dichroism.

Abstract

Empirical conformational energy calculations were performed on helical poly(2,3-quinoxaline)s to predict stable conformations. Two energy minimum conformations were found by varying dihedral angle (Ψ) between two adjacent quinoxaline units from 5° to 180°. Circular dichroism (CD) spectra were calculated for the two stable conformations (Ψ = 45° and 135°) on the basis of exciton theory. Experimental CD spectrum of (+)-poly(2,3-quinoxaline) was in accord with the theoretical spectrum for right-handed helical conformation with the dihedral angle of 135 .

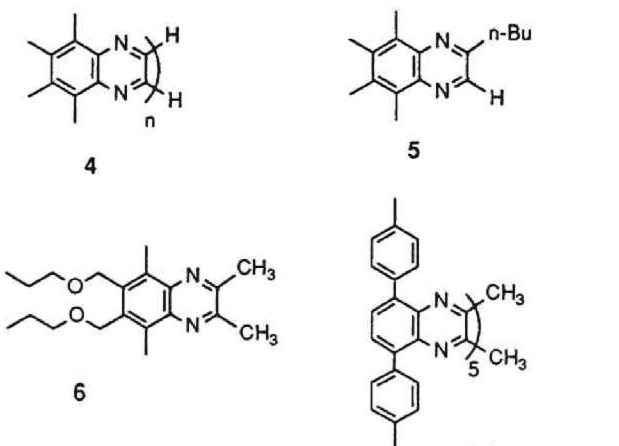
Introduction.

In the previous chapters, the author described aromatizing polymerization of 1,2-diisocyanoarenes catalyzed by organopalladium complexes giving poly(2,3-quinoxaline)s.[1,2] X-ray crystal structure of the oligo(2,3-quinoxaline) thus prepared suggested that the main chain structure of poly(2,3-quinoxaline) may be helical.[3] Actually, the author succeeded in the synthesis of enantiomeric isomers of poly(2,3-quinoxaline)s which showed the same optical rotations with opposite signs and CD spectra of complete mirror images.[2] They may be atropisomers in terms of helical sense and the exciton splitting in their CD spectra can be ascribed to the helical arrangement of quinoxaline chromophores. In this chapter, conformational energy calculations and theoretical CD calculations were carried out to predict the helical structure (e.g., the energetically stable conformation and the helical sense of each enantiomer) of chiral poly(2,3-quinoxaline)s.

Results and Discussion.

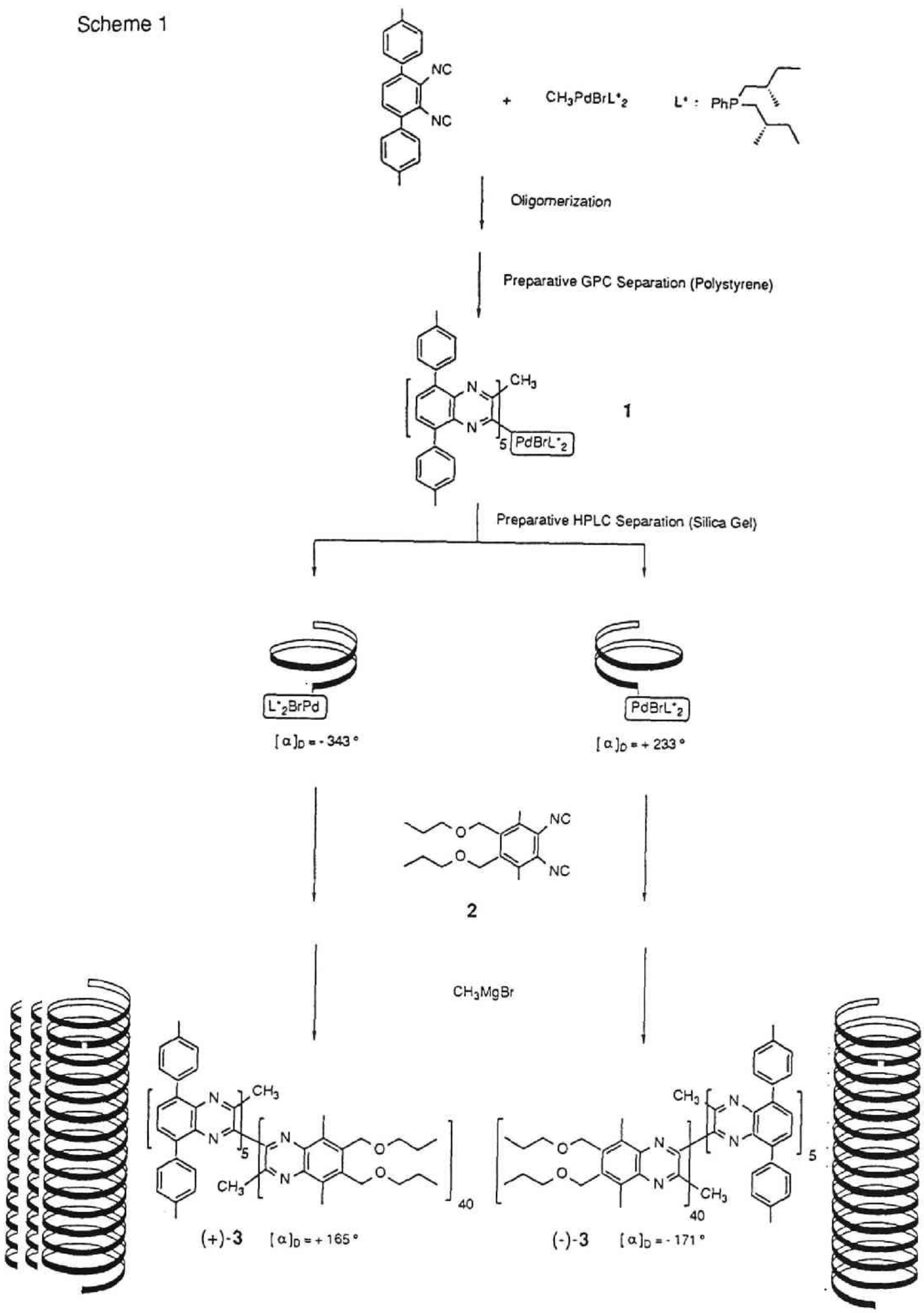
The chiral poly(2,3-quinoxaline)s **3** were prepared by block copolymerization of 1,2-diisocyano-3,6-dimethyl-4,5-bis(propyloxymethyl)benzene (**2**) with pentamer **1**.[3] The degree of polymerization of **2** was ca. 40. The empirical conformational energy calculations and theoretical CD calculations on the poly(2,3-quinoxaline) **3** may be adequately approximated by those on poly[2,3-(5,6,7,8-tetramethylquinoxaline)] **4**. The approximation may be justified for the following reasons. Both UV absorption spectra of monomeric quinoxalines **5** and **6** showed the same profiles. The energy profile of poly[2,3-(5,8-dimethyl-6,7-bis(propyloxymethyl)quinoxaline)] **3** would not be significantly changed from that of poly[2,3-(5,6,7,8-tetramethylquinoxaline)] **4**, even though the total energy may be increased by the propoxymethyl side chains, which spread out of the helical main chain of quinoxaline. Although the polymer **3** contains quinque(2,3-quinoxaline) part derived from the starting **1**, it was neglected in the CD calculation since the pentamer **7** did not show intense CD above 230 nm.

Chart 1



4 5 6 (+)-7 and (-)-7

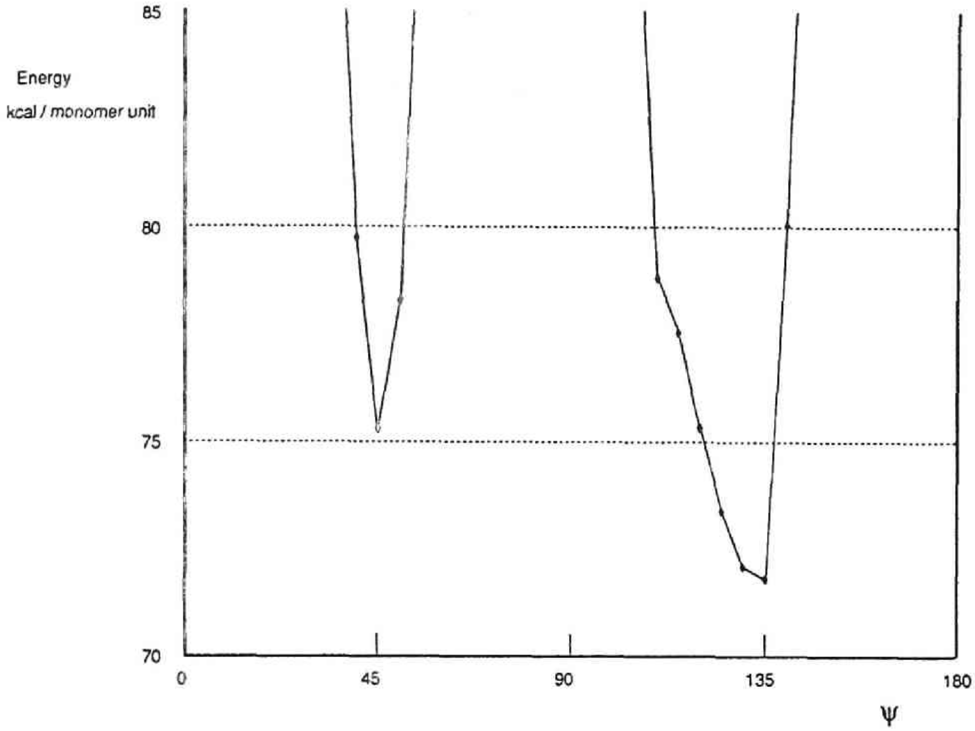
Scheme 1

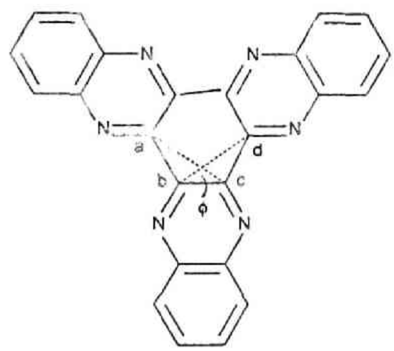

NC
NC
+
$CH_3PdBrL^*_2$
L* : PhP
Oligomerization
Preparative GPC Separation (Polystyrene)
CH_3
N
N
5
$PdBrL^*_2$
1
Preparative HPLC Separation (Silica Gel)
L^*_2BrPd
$[\alpha]_D = -343°$
$PdBrL^*_2$
$[\alpha]_D = +233°$
NC
NC
2
CH_3MgBr
(+)-3 $[\alpha]_D = +165°$
(-)-3 $[\alpha]_D = -171°$
40
5

Conformational Calculations. The conformational energy calculations were carried out by using POLYGRAF.[4] The structural parameters (bond lengths and angles) for quinoxaline group were taken from crystallographic data of ter(2,3-quinoxalinyl)palladium complex.[5] Total energy of quinoxaline 20mers was calculated varying the dihedral angle (Ψ) between two adjacent quinoxaline units from 5° to 180° with interval of 5°. The dihedral angle ϕ shown in Figure 1 was assumed to be 0°. In some cases, however, the latter dihedral angle was also varied. In those cases, the dihedral angle between the plane a-b-c and the plane of quinoxaline ring was set to $\phi/2$. All bond angles and bond lengths were fixed in this calculation.

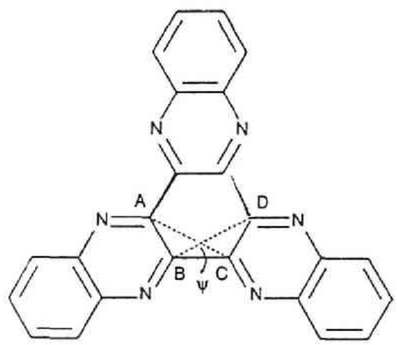
As shown in the energy profile in Figure 1, two energy minima appeared at Ψ = 45° and 135°. The minima are separated by a high energy barrier, indicating the existence of two stable conformers which are not interconvertible. The slight deviation of Ψ from 0° resulted in the rise of total energy. The NAMOD ball-and-stick models[6] of the two conformers are shown in Figure 2. Of the two possible conformations, that with Ψ = 135° is more likely, because of its lower energy (3.5 kcal/residue mol) and wider allowed region. X-ray structural analysis of the propagating quater(2,3-quinoxalinyl)palladium(II) complex (Figure 3) revealed that the four sequential quinoxaline units take a helical structure with Ψ = 123°-148°. The finding also suggests that the conformer with Ψ = 135° is more likely for the poly(2,3-quinoxaline) **3**. The conclusion is supported by the results of CD calculation to be described below.

Theoretical Circular Dichroism. Theoretical CD was computed on the basis of exciton theory developed by Woody.[7] The CNDO/S-CI MO calculation and experimental peak assignment for quinoxaline has been reported.[8] The absorption peak at 316 nm (ε $6.32x10^3$, CH_2Cl_2) is polarized along long axis. However, the MO calculation predicted two transitions in this region, one being long-axis polarized and the other being short-axis polarized. The peak must have some contribution from n-π^* transition. Therefore, the assignment of the peak at 316 nm is not clear. The intense peak at 233.5 nm (ε $2.92x10^4$, CH_2Cl_2) is shown to be long-axis polarized, in accordance with the MO data. The other peak at shorter wavelengths are not assigned. In the CD





ϕ = dihedral angle between a-b-c and b-c-d

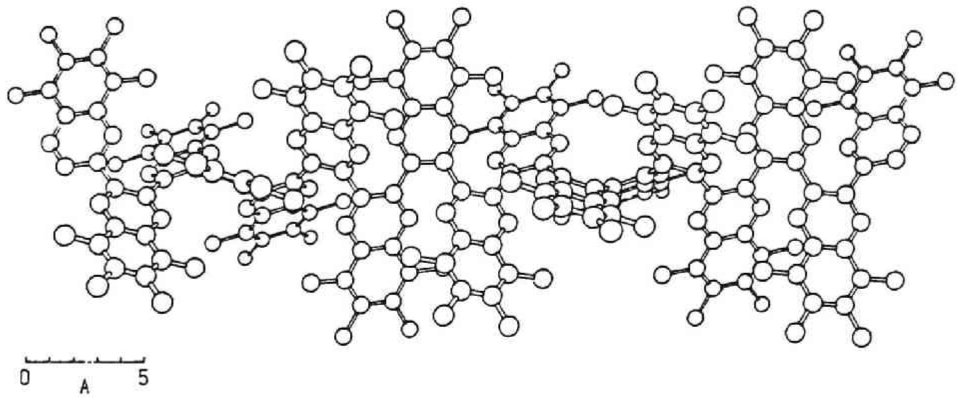


ψ = dihedral angle between A-B-C and B-C-D

Figure 1. Energy profile of polyquinoxaline (4). ϕ is fixed to 0°

Figure 2. Ball and stick molecular models for
two energy minimum conformations of polyquinoxaline **4.**

Poly(quinoxaline) minimum-energy conformation. ($\phi = 0°$, $\psi = 135°$)



Poly(quinoxaline) 2nd minimum-energy conformation. ($\phi = 0°$, $\psi = 45°$)

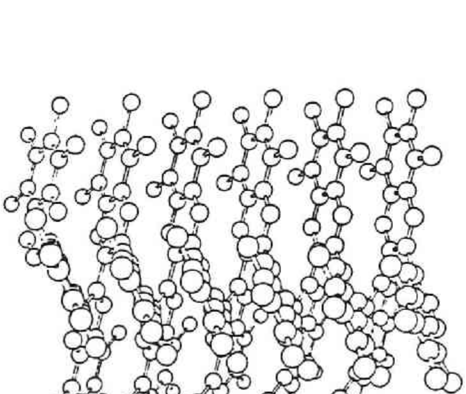
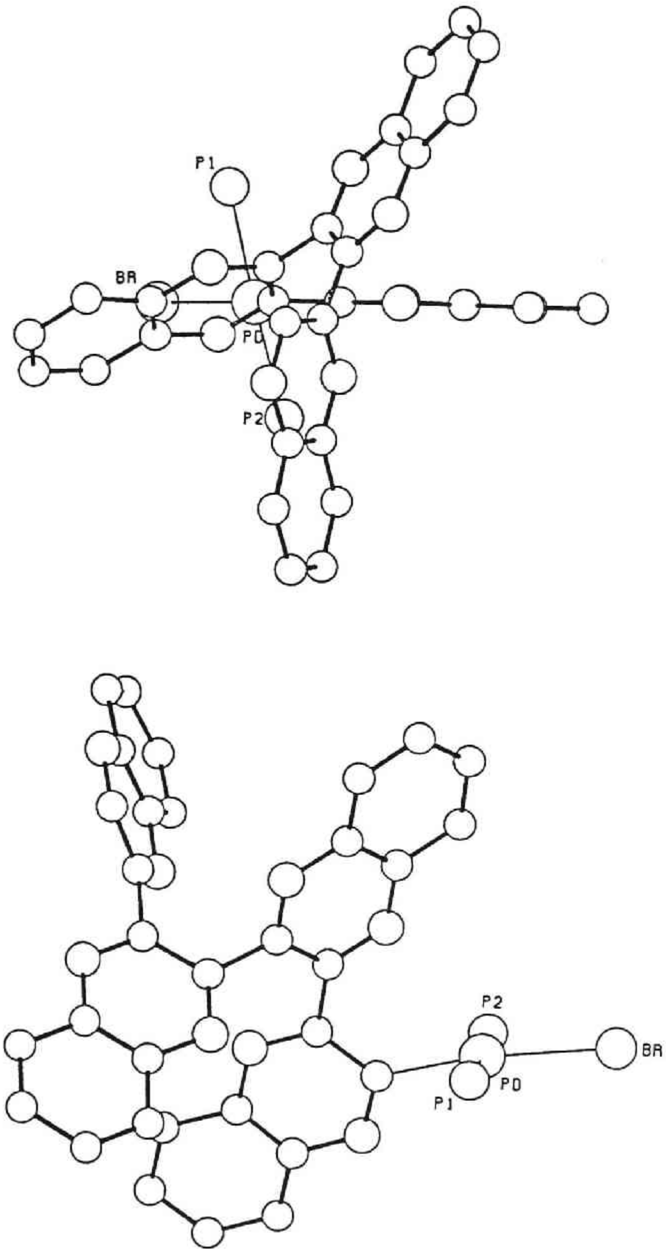


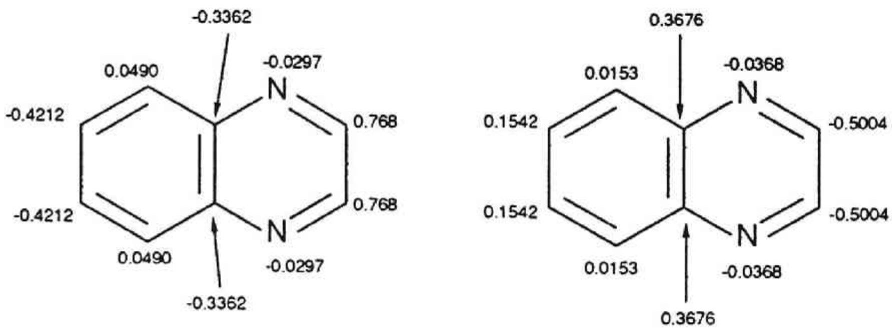
Figure 3. X-ray crystal structure of quaterquinoxalinyl-Pd complex.



calculation, the allowed π-π^* band at 233.5 nm and small band at 316 nm both being long-axis polarized were taken into consideration. Since the assignment of 316 nm-band is not clear, the comparison between theoretical and experimental spectra may be made only at the allowed band.

The transition moments and the monopole charges of two π-π^* bands were calculated from PPP-CI molecular orbitals. The magnitude of the monopole charges were corrected to reproduce the experimental spectrum of the model monomer **5**. As the energy of the π-π^* transitions, the peak wavelength of the experimental spectrum of 5 (252 and 329 nm) were used instead of the calculated ones (225 and 309 nm) for quinoxaline. The monopole charges for the two π-π^* transitions are listed in Figure 4.

Figure 4. Monopole charges for two $\pi\pi$* transitions of quinoxaline chromophore



Trantion at 252 nm   Transition at 329 nm

CD spectra were calculated on the possible conformations of **4** predicted from the above energy calculations. The number of quinoxaline units n, was 20 in the calculation. The calculated $\Delta\varepsilon$ divided by n becomes flat when n>10.

Figure 5 shows theoretical CD spectrum of right-handed poly(2,3-quinoxaline) 20mer with ψ = 135°. The spectrum exhibits a negative exciton couplet at 260 nm and this pattern is same as the observed spectrum of (+)-poly(2,3-quinoxaline) **3** in Figure 6.

Figure 5. Theoretical CD curve for
right-handed polyquinoxaline of $\psi = 135°$.

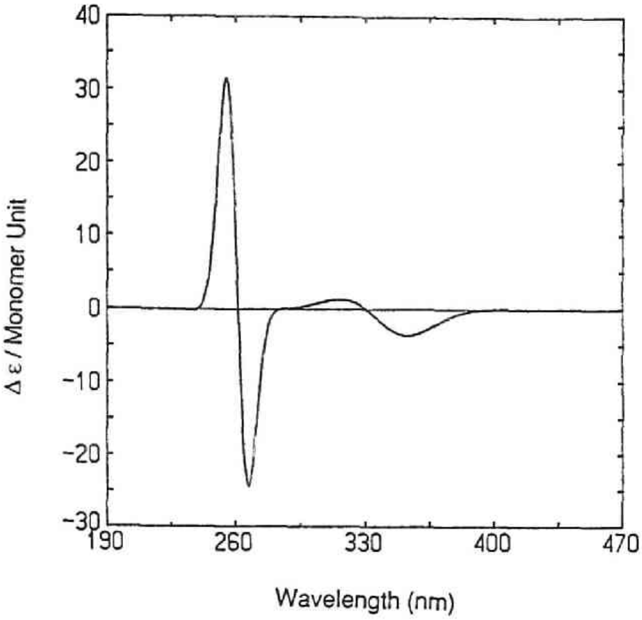
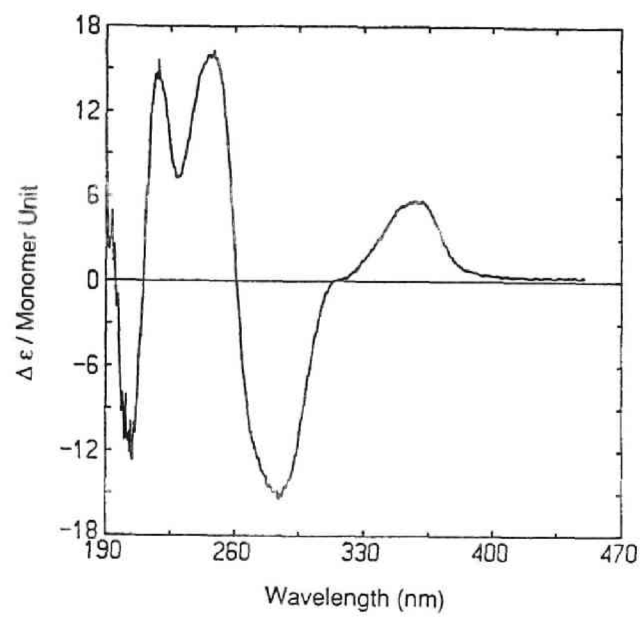
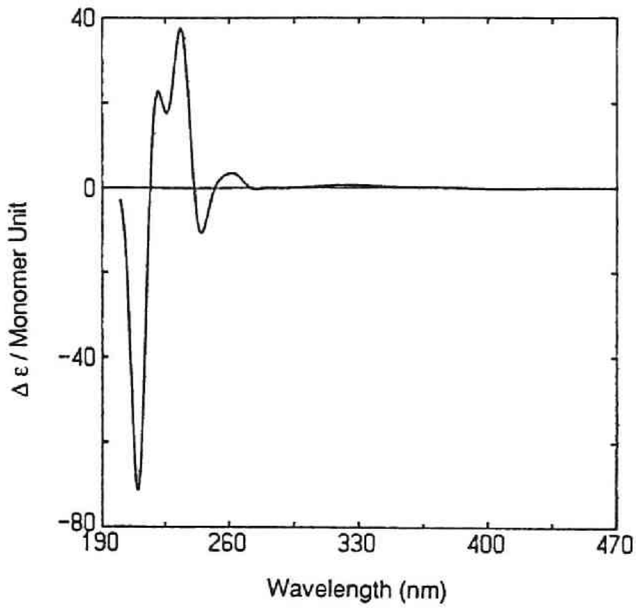


Figure 6. CD spectrum of (+)-polyquinoxaline (**3**).



The observed spectrum also exhibits a positive couplet at 215 nm and a positive cotton effect at 360 nm. They may be originate from higher energy transitions and n-π* transitions of quinoxaline chromophore respectively, and both are not considered in this calculation. CD spectrum was also calculated on the helical structure with ψ = 45°.(Figure 7)

Figure 7. Theoretical CD curve for right-handed polyquinoxaline of ψ = 45°.



The calculated spectrum is quite different from the experimental one either for (+)-poly(2,3-quinoxaline) derivative or for (-)-derivative. This result supports our assumption that the conformation with ψ = 135° is more likely than that with ψ = 45° for the poly(2,3-quinoxaline) derivative and that the (+)-poly(2,3-quinoxaline) exists in right-handed helical conformation. Inversely, the (-)-poly(2,3-quinoxaline) derivative exists in left-handed helix with ψ = -135°.

To study the origin of the exciton splitting, the chirality parameter was calculated for 1-2, 1-3 and 1-4 pairs of quinoxaline units.(Figure 8)[9]
The chirality parameter is defined as, $\zeta = \mathbf{r}_{12}(\mathbf{m}_1 \mathrm{x} \mathbf{m}_2)$ where $\mathbf{r}_{12}$ is a unit vector along the center-to-center interchromophore

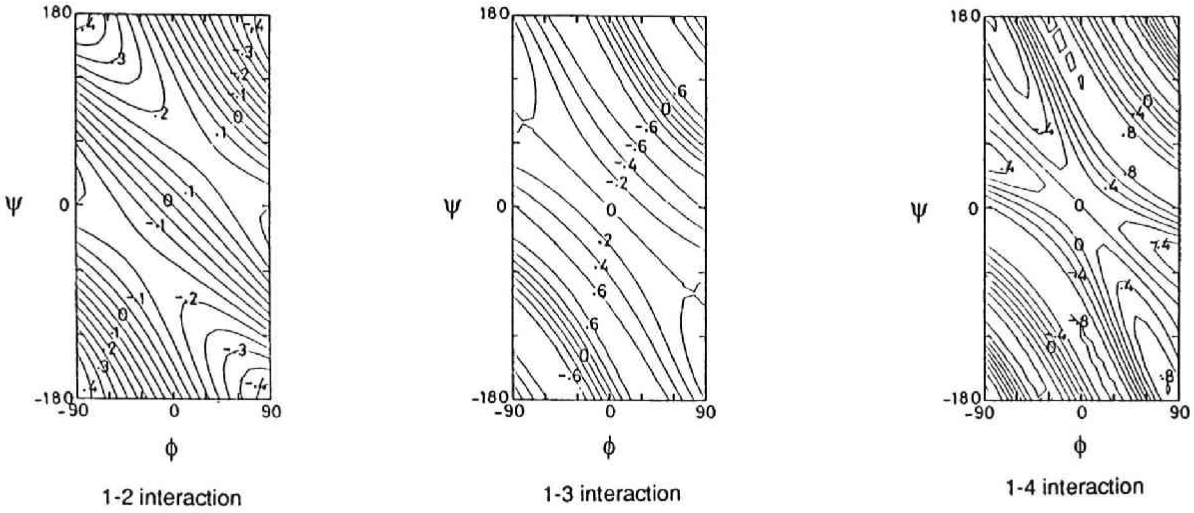
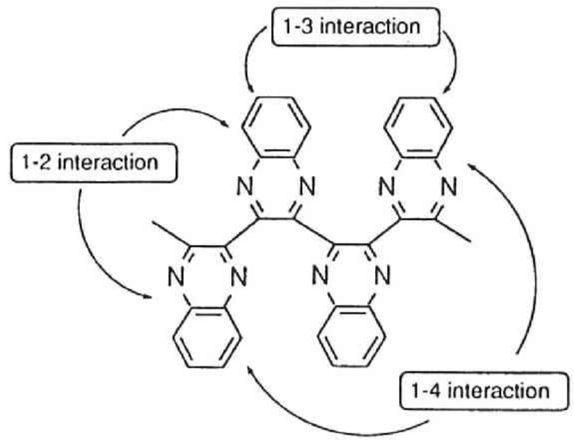


Figure 8. Contour maps of chirality parameters for three types of interactions.



vector and $\mathbf{m}_1$ and $\mathbf{m}_2$ are the unit vectors along the long axis of quinoxaline ring. Negative ζ-values indicate positive (lower wavelength) - negative (higher wavelength) exciton couplet as shown in Figure 5. Contrary to the theoretical CD spectrum calculated taking all contributions (Figure 5), the 1-2 and 1-4 interaction showed positive chirality parameters. This indicates that the contributions of 1-2 and 1-4 interactions are small compared with that of the 1-3 interaction where strong ζ-value is obtained around the region of $\Phi = 0°$, $\Psi = 135°$. Therefore, the negative exciton couplet at 260 nm is mainly ascribed to the right-handed helical arrangement of quinoxaline chromophore in 1-3 interactions.

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4) The author acknowledges Simulation Technology Inc. for the energy calculation by POLYGRAF.

5) The structural parameters were taken from X-ray crystal data of the central quinoxaline units of ter(2,3-quinoxalinyl)palladium(II) complexes.[1]

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Chapter 6

Synthesis of Novel Thermotropic Liquid Crystalline Poly(2,3-quinoxaline)s.

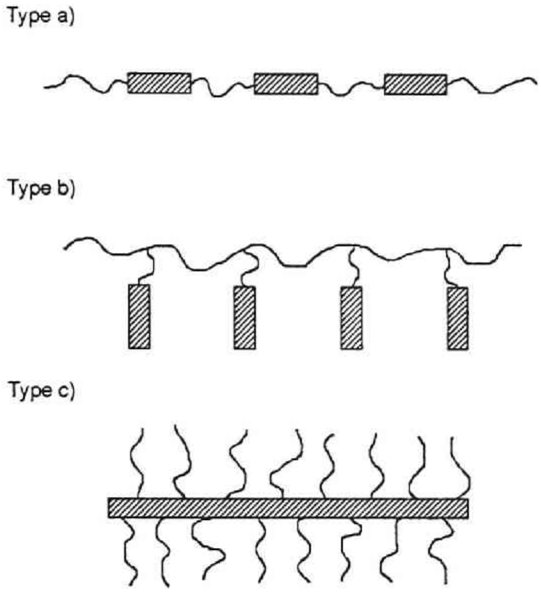
Abstract

The living polymerization of 4,5-bis(alkoxymethyl)-3,6-dimethyl-1,2-diisocyanobenzene (alkoxy = propyloxy. pentyloxy and heptyloxy) was catalyzed by methylpalladium(II) complex to give poly(2,3-quinoxaline)s. Poly(2,3-quinoxaline)s with various degree of polymerization (DP) and narrow molecular weight distribution were prepared and their thermal phase behavior was analyzed by optical polarized microscope. The phase behavior depended on the DP as well as the side chain length of the starting monomer. Of note was that the poly(2,3-quinoxaline)s having a longer side chain revealed thermotropic liquid crystallinity at higher degree of polymerization. The relationship may indicate that the rigid segment of poly(2,3-quinoxaline)s propagates with the progress of the living polymerization.

Introduction

Much attention has been paid for the synthesis of liquid crystalline polymers. In general, thermotropic liquid crystalline polymers are classified into three types; a) main-chain LC polymer, b) side-chain LC polymer and c) rigid-rod LC polymer.(Figure 1)[1] LC polymers of type a) and b) possess liquid crystallinity due to the mesogenic properties of their monomer units. In LC polymers of type c), on the other hand, the mesogenic rigidity is derived from rod-like structure of the main chain which is formed with the progress of polymerization, and is balanced with surrounding flexible side chains of the polymer. Thus, the liquid crystallinity of LC polymers of type c) does not originate in the structure of the monomer but in the polymer structure constructed.

Figure 1.



Dependency of thermal behavior of LC polymers on the molecular weight is a subject of interest and has been studied using side-chain LC polymer.[2] In the synthesis of the rigid-rod LC polymer, the rigid rod-like structure grows with the progress of polymerization. The polymers of low DP would not have enough backbone rigidity to reveal liquid crystallinity. At a certain critical DP, the rigid-rod polymer would begin to have enough rigidity to exhibit thermotropic liquid crystalline nature. However, such dependency of phase behavior of rigid-rod LC polymer on DP has not so far reported, because the known rigid-rod polymers such as polypeptide,[1] poly(isocyanate),[3] cellulose[4] and polyester[5] were not easily accessible with control of DP.

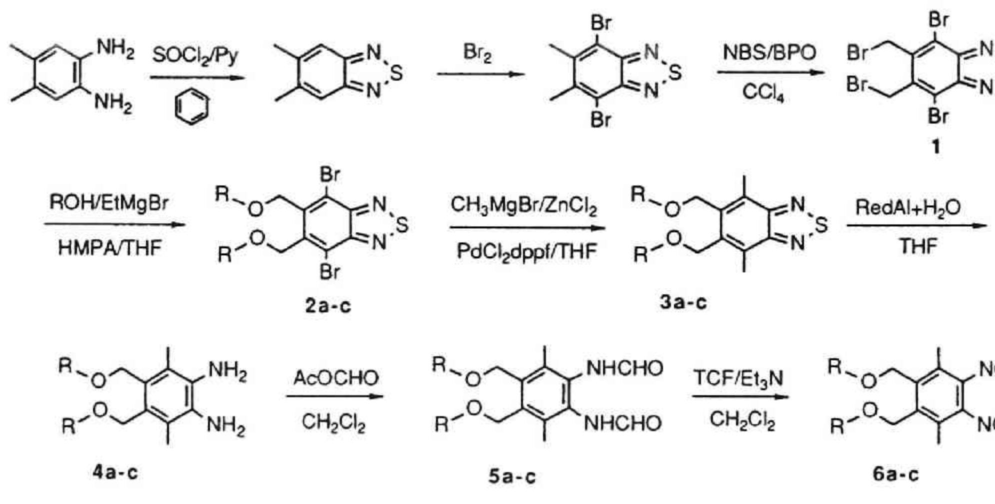
The author described new living polymerization of 1,2-diisocyanoarenes catalyzed by methylpalladium(II) complexes giving poly(2,3-quinoxaline)s, which have helical structures.[6,7] Furthermore, a screw-sense selective polymerization of 1,2-diisocyanoarenes was successfully achieved by chiral palladium catalysts having helical conformations.[7]

Empirical energy and theoretical CD calculations supported that the main chain structure of the poly(2,3-quinoxaline) is composed of rigid helix.[8] In this chapter, the author describes that the polymerization of 1,2-diisocyanoarenes with varying alkoxymethyl side chains provides novel thermotropic rigid-rod LC polymers. It is remarked that the liquid crystallinity was revealed on balancing of the rigidity of the poly(2,3-quinoxaline) backbone with the flexibility due to the side chains.

Results and Discussion

Monomer Synthesis. 4,5-Bis(alkoxymethyl)-3,6-dimethyl-1,2-diisocyanoarenes (**6a-c**) were prepared according to Scheme 1. Tetrabromobenzo-2,1,3-thiadiazole **1**, prepared by stepwise bromination of 5,6-dimethylbenzo-2,1,3-thiadiazole, was treated with the corresponding alkoxymagnesium(II) and then with methylzinc chloride in the presence of [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) chloride to afford **3a-c**. Reduction into o-phenylenediamine derivatives **4a-c**, formylation with acetic formic anhydride, and dehydration with trichloromethyl chloroformate furnished the corresponding 4,5-bis(alkoxymethyl)-3,6-dimethyl-1,2-diisocyanoarenes **6a-c** in satisfactory overall yield from **1** (45-55%).

Scheme 1



a R = n-C_3H_7, **b** R = n-C_5H_{11}, **c** R = n-C_7H_{15}

Aromatizing Polymerization. Polymerization of 4,5-bis(alkoxymethyl)-3,6-dimethyl-1,2-diisocyanoarenes **6** thus prepared was catalyzed by methylpalladium(II) complex in THF. After the monomer **6** was completely consumed, the propagating quinoxalinylpalladium(II) moiety was quenched by a coupling reaction with methylmagnesium bromide to give poly(2,3-quinoxaline)s **8** having various alkoxymethyl side chains on 6- and 7- positions in high yield.(Scheme 2, Table 1) In accord with the living polymerization, the molecular weights were controlled by the feeding ratio of the monomer to the palladium catalyst (6/7) and the molecular weight distribution were very narrow.

Scheme 2

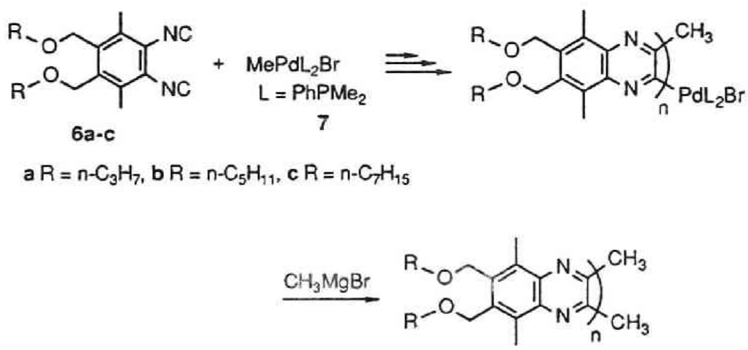


Table 1.

Entry	6/7	Condition[a]	Yield(%)	GPC Mn	GPC Mw/Mn	Liquid Crystallinity[b]
C3 (Propyloxymethyl Side Chain)						
1	10	A	98	2670	1.12	×
2	20	A	98	3540	1.12	×
3	30	A	87	7650	1.17	○
4	50	A	84	13410	1.23	○
5	70	A	84	20550	1.18	○
6	100	A	93	33100	1.22	○
C5 (Pentyloxymethyl Side Chain)						
7	30	A	72	7500	1.09	×
8	50	A	67	13670	1.14	○
9	70	B	73	19780	1.09	○
10	100	B	99	31370	1.08	○
C7 (Heptyloxymethyl Side Chain)						
11	30	B	99	8140	1.11	×
12	40	B	86	9750	1.19	×
13	50	B	96	12410	1.14	×
14	70	B	100	17120	1.12	○
15	100	B	90	31360	1.16	○

a) A: at r.t. B: at reflux.

b) A sample marked ○ exhibited liquid crystallinity while a sample marked × did not pass mesophase.

Thermal Phase Behavior. Phase behavior of poly(2,3-quinoxaline)s were examined by optical polarized microscope and analyzed in terms of the degree of polymerization.(Table 1) Mesophases were observed in the temperature range of higher than 120°C, although the exact phases were not assigned. Noteworthy was that only the poly(2,3-quinoxaline)s of sufficiently high DP exhibited the mesophase, whereas poly(2,3-quinoxaline)s of low molecular weight did not pass any mesophase at all. In the case of poly(2,3-quinoxaline) **8a** having propyloxymethyl side chains, the critical point of DP for the appearance of mesophase exists between 20 and 30. The DP range for the appearance of liquid crystalline nature depends upon the length of alkoxymethyl side chains. A higher DP was required for the poly(2,3-quinoxaline) having a longer side chain to display liquid crystallinity. These findings may suggest that the helical backbone, which is built from 2,3-quinoxaline units, provides the rigid mesogenic segment of the LC polymer. In order to reveal liquid crystallinity, the rigidity due to the helical backbone of poly(2,3-quinoxaline)s is to be balanced by the flexibility of the polymer which depends on the length of the side chains. The poly(2,3-quinoxaline) of lower DP than the critical point could not exhibit mesophase because of the insufficient rigidity. Figure 2 shows the optical textures of the poly(2,3-quinoxaline)s observed by microscope.

Figure 4.

a) **8a-30** at 140 °C (x 200)

b) **8b-50** at 130 °C (x 200)

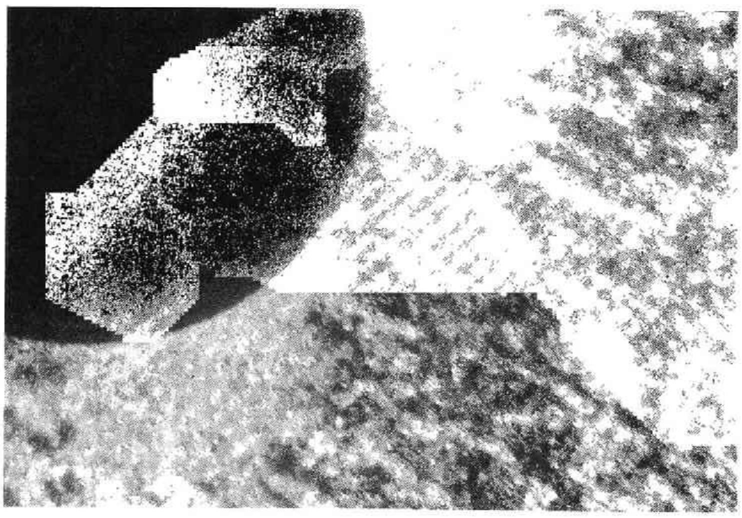
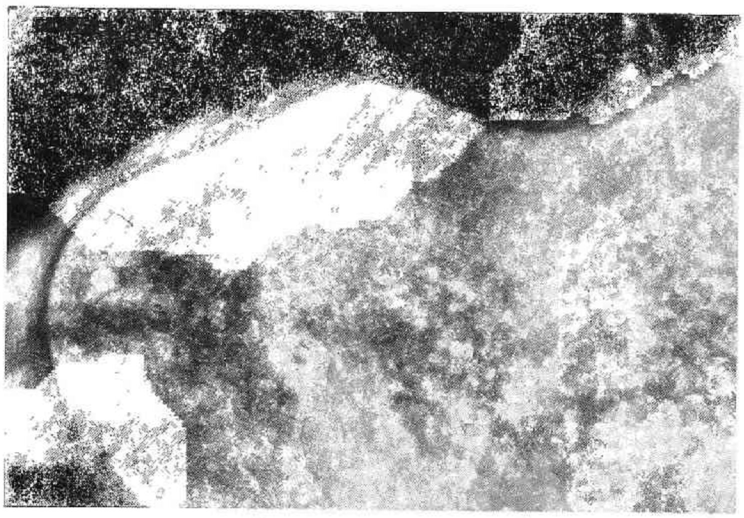


Figure 4. (continued)

c) **8c-100** at 120 °C (x 200)



Experimental Section

General. ^{1}H-NMR spectra were measured with Varian VXR-200 and Gemini-200 spectrometer in $CDCl_3$. Chemical shifts are reported in δ ppm. Infrared spectra were measured with a Hitachi 270-30 spectrometer. Data are given in cm^{-1}. Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. Gel permeation chromatographic analysis (GPC) were carried out on a JASCO TRIROTOR (SHODEX AC 803) by using $CHCl_3$ as a eluent and polystyrene as a standard. Recycling HPLC purification was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns ($CHCl_3$). A OPTIPHOT-POL optical polarized microscope (Magnification 200x) equipped with a Mettler 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.

Materials. All solvents were dried over appropriate desiccants and distilled under nitrogen. 4,7-Dibromo-5,6-dimethyl-2,1,3-benzothiadiazol was prepared according to the literature method.[9]

Preparation of 1.

A CCl_4 solution (300 mL) of 4,7-Dibromo-5,6-dimethyl-2,1,3-benzothiadiazol (13.4 g, 41.5 mmol), N-bromosuccinimide (29.5 g, 166 mmol) and benzoylperoxide (0.45 g, 1.66 mmol) was heated at reflux for 2 days. The cooled reaction mixture was filtrated and the solvent was removed from the filtrate by rotary evaporator. Drying in vacuo of the residual solid afforded 1 in 84% yield.

1 ; ^{1}H-NMR ($CDCl_3$) 5.04 (s, 4H). IR (KBr) 2988, 1272, 1208, 1112, 868, 826, 584, 474 cm^{-1}. MS m/s 479 (M+). Anal. Calcd for $C_8H_4N_2SBr_4$: C, 20.03; H, 0.84; N, 5.84. Found: C, 20.16; H, 1.00; N, 5.88.

Preparation of 4,7-dibromo-5,6-bis(propyloxymethyl)-2,1,3-benzothiadiazol (2a).

To a THF solution (100 mL) of n-PrOH (4.7 mL, 65.2 mmol), was added a ether solution of EtMgBr (32.6 mmol) and the mixture was stirred at r.t. for 1 hr. Then, HMPA (10.9 ml, 65.2 mmol) and 1 (3.0 g, 6.5 mmol) was added and the mixture was heated at reflux for 24 hrs. Extractive workup with ether and water followed by column chromatography on silica gel (n-hexane : ether = 5:1) gave **2a** in 88% yield.

^{1}H-NMR ($CDCl_3$) 0.90 (t, 6H, J=7.3 Hz), 1.61 (sex, 4H, J=7.0 Hz), 3.53 (t, 4H, J=6.4 Hz), 4.99 (s, 4H). IR (KBr) 2972, 2940, 2884, 1118, 1098, 956 cm^{-1}.

4,7-dibromo-5,6-bis(pentyloxymethyl)-2,1,3-benzothiadiazol (**2b**, 89%) and 4,7-dibromo-5,6-bis(heptyloxymethyl)-2,1,3-benzothiadiazol (**2c**, 94%) were prepared in a similar manner.

2b ; ^{1}H-NMR ($CDCl_3$) 0.89 (t, 6H, J=6.7 Hz), 1.18-1.46 (m, 8H), 1.63 (qui, 4H, J=6.6 Hz), 3.60 (t, 6.5 Hz), 5.01 (s, 4H). IR (KBr) 2964, 2940, 2872, 1104, 1016 cm^{-1}.

2c ; ^{1}H-NMR ($CDCl_3$) 0.87 (t, 6H, J=6.6 Hz), 1.12-1.51 (br-s, 16H), 1.62 (qui, 4H, J=6.5 Hz), 3.60 (t, 4H, J=6.5 Hz), 5.01 (s, 4H). IR (KBr) 2964, 2940, 2856, 1012, 994, 984 cm^{-1}.

Preparation of 4,7-dimethyl-5,6-bis(propyloxymethyl)-2,1,3-benzothiadiazol (3a).

To a THF solution (70 mL) of $ZnCl_2$ (10.5 g, 76.7 mmol), ether solution of CH_3MgBr (38.3 mmol) was added dropwise and the mixture was stirred for 30 min at r.t. Then, a mixture of **2a** (4.1 g, 9.6 mmol) and $PdCl_2$dppf (0.7 g, 0.96 mmol) in THF (30 mL) was added. The mixture was heated at reflux for 40 hrs. Extractive workup with ether and water followed by column chromatography on silica gel (n-hexane : ether = 5:1) afforded **3a** in 90% yield.

3a ; ^{1}H-NMR ($CDCl_3$) 0.96 (t, 6H, J=7.4 Hz), 1.67 (sex, 4H, J=6.7 Hz), 2.79 (s, 6H), 3.56 (t, 4H, J=6.6 Hz), 4.74 (s, 4H). IR (neat) 2972, 2940, 2880, 1096, 1042 cm^{-1}.

4,7-dimethyl-5,6-bis(pentyloxymethyl)-2,1,3-benzothiadiazol (**3b**, 90%) and 4,7-dimethyl-5,6-bis(heptyloxymethyl)-2,1,3-benzothiadiazol (**3c**, 97%) were prepared in a similar procedure.

3b ; ^{1}H-NMR ($CDCl_3$) 0.89 (t, 6H, J=6.8 Hz), 1.23-1.45 (m, 8H), 1.64 (qui, 4H, J=6.6 Hz), 2.78 (s, 6H), 3.58 (t, 4H, J=6.4 Hz), 4.72 (s, 4H). IR (neat) 2940, 2868, 1100 cm^{-1}.

3c ; ^{1}H-NMR ($CDCl_3$) 0.87 (t, 6H, J=6.5 Hz), 1.13-1.55 (br-s, 16H), 1.64 (qui, 4H, J=6.2 Hz), 2.79 (s, 6H), 3.58 (t, 4H, J=6.5 Hz), 4.73 (s, 4H). IR (KBr) 2940, 2864, 1100 cm^{-1}.

Preparation of 1,2-diamino-3,6-dimethyl-4,5-bis(propyloxymethyl)benzene (4a).

To a THF (50 mL) solution of **3a** (1.0 g, 3.3 mmol), a Toluene solution (9.5 mL) of Red-Al (1 eq. of hydride was quenched with H_2O, 32.3 mmol) was added dropwise at r.t. and the mixture was stirred at r.t. for 1.5 hrs. To the cooled reaction mixture, H_2O was added carefully at 0°C. Extractive workup with CH_2Cl_2 and water followed by column chromatography on silica gel (AcOEt) afforded **4a** in 87% yield.

4a ; ^{1}H-NMR ($CDCl_3$) 0.94 (t, 6H, J=7.4 Hz), 1.63 (sex, 4H, J=7.4 Hz), 2.21 (s, 6H), 3.04-3.35 (br-s, 4H), 3.48 (t, 4H, J=6.6 Hz), 4.51 (s, 4H). IR (KBr) 3436, 3372, 324, 2976, 2936, 2884, 1466, 1356, 1112, 1084, 1024 cm^{-1}.

1,2-diamino-3,6-dimethyl-4,5-bis(pentyloxymethyl)benzene (4b, 92%) and 1,2-diamino-3,6-dimethyl-4,5-bis(heptyloxymethyl)benzene (4c, 86%) were prepared in a similar procedure.

4b ; ^{1}H-NMR ($CDCl_3$) 0.89 (t, 6H, J=6.8 Hz), 1.22-1.50 (m, 8H), 1.61 (qui, 4H, J=6.6 Hz), 2.20 (s, 6H), 2.70-3.33 (br-s, 4H), 3.51 (t, 4H, J=6.5 Hz), 4.50 (s, 4H). IR (neat) 3368, 2938, 2868, 2800, 1620, 1470, 1462, 1360, 1094 cm^{-1}.

4c ; 1H-NMR ($CDCl_3$) 0.88 (t, 6H, J=6.6 Hz), 1.13-1.51 (m, 16H), 1.60 (qui, 4H, J=6.6 Hz), 2.20 (s, 6H), 2.80-3.36 (br-s, 4H), 3.51 (t, 4H, J= 6.5 Hz), 4.50 (s, 4H). IR (neat) 3360, 2944, 2864, 2800, 1622, 1470, 1360, 1096 cm^{-1}.

Preparation of 1,2-diformamido-3,6-dimethyl-4,5-bis(propyloxymethyl)benzene (5a).

To a CH_2Cl_2 solution (10 mL) of **4a** (1.0 g, 3.6 mmol) was added acetylformate (0.94 mL, 14.3 mmol) dropwise at 0 C. The mixture was stirred for 16 hrs gradually warming up to r.t. Residual solid after filtration was washed with MeOH and dried in vacuo. 5a was obtained in 74% yield.

5a ; ^{1}H-NMR ($CDCl_3$) 0.94 (t, 6H, J=7.4 Hz), 1.64 (sex, 4H, J=7.4 Hz), 2.27 (s, 6H), 3.50 (t, 4H, J=6.6 Hz), 4.55 (s, 4H), 7.62 (br-s, 2H), 8.30 (br-s, 2H). IR (KBr) 3244, 2972, 2944, 2884, 1664, 1096 cm^{-1}.

1,2-diformamido-3,6-dimethyl-4,5-bis(propyloxymethyl)benzene (5b) and 1,2-diformamino-3,6-dimethyl-4,5-bis(propyloxymethyl)benzene (5c) were prepared in a similar manner.

5b ; ^{1}H-NMR ($CDCl_3$) 0.91 (t, 6H, J=6.9 Hz), 1.20-1.46 (m, 8H), 1.59 (qui, 4H, J=6.6 Hz), 2.28 (s, 6H), 3.53 (t, 4H, J=6.5 Hz), 4.55 (s, 4H), 7.62 (br-s, 2H), 8.32 (br-s, 2H). IR (KBr) 3244, 2968, 2940, 2868, 1670, 1670, 1534, 1402, 1094 cm^{-1}.

5c ; ^{1}H-NMR ($CDCl_3$) 0.88 (t, 6H, J=6.6 Hz), 1.10-1.42 (m, 16H), 1.60 (qui, 4H, J=6.6 Hz), 2.29 (s, 6H), 3.52 (t, 4H, J=6.5 Hz), 4.54 (s, 4H), 7.55 (br-s, 2H), 8.33 (br-s, 2H). IR (KBr) 3244, 2968, 2936, 2864, 1668, 1098 cm^{-1}.

Preparation of 1,2-diisocyano-3,6-dimethyl-4,5-bis(propyloxymethyl)benzene (6a).

A CH_2Cl_2 suspension (10 mL) of 5a (0.8 g, 2.4 mmol) and Et_3N (5 mL, 35.9 mmol) was cooled to -78°C. A CH_2Cl_2 solution (12 mL) of trichloromethylchloroformate (1.5 mL, 12.4 mmol) was added dropwise at -78°C. The mixture was stirred for 8 hrs at -78°C, then gradually warmed up to -30°C. At -30°C, 10% Na_2CO_3 aq. (50 mL) was added dropwise. Extractive workup with CH_2Cl_2 and 10% Na_2CO_3 aq. followed by column chromatography on silica gel (n-hexane : ether = 4:1) gave **6a** in 88% yield.

6a ; ^{1}H-NMR ($CDCl_3$) 0.94 (t, 6H, J=7.5 Hz), 1.63 (sex, 4H, J=7.0 Hz), 2.50 (s, 6H), 3.50 (t, 4H, J=6.6 Hz), 4.52 (s, 4H). IR (neat) 2972, 2944, 2880, 2120, 1100, 1044 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 71.67; H, 8.08; N, 9.11.

1,2-diisocyano-3,6-dimethyl-4,5-bis(pentyloxymethyl)benzene (6b) and 1,2-diisocyano-3,6-dimethyl-4,5-bis(heptyloxymethyl)benzene (**6c**) were prepared in similar manner.

6b ; ^{1}H-NMR ($CDCl_3$) 0.90 (t, 6H, J=6.9 Hz), 1.20-1.48 (m, 8H), 1.61 (qui, 4H, J=6.6 Hz), 2.49 (s, 6H), 3.53 (t, 4H, J=6.5 Hz), 4.51 (s, 4H). IR (neat) 2944, 2872, 2120, 1466, 1362, 1102 cm^{-1}. Anal. Calcd for $C_{22}H_{32}N_2O_2$: C, 74.12; H, 9.05; N, 7.86. Found: C, 74.16; H, 9.15; N, 7.67.

6c ; ^{1}H-NMR ($CDCl_3$) 0.88 (t, 6H, J=6.5 Hz), 1.16-1.44 (m, 16H), 1.58 (qui, 4H, J=6.6 Hz), 2.49 (s, 6H), 3.53 (t, 4H, J=6.5 Hz), 4.51 (s, 4H). IR (neat) 2936, 2864, 2120, 1102 cm^{-1}. Anal. Calcd for $C_{26}H_{40}N_2O_2$: C, 75.67; H, 9.78; N, 6.79. Found: C, 75.60; H, 10.05; N, 6.75.

Typical procedure of polymerization of **6a** catalyzed by **7**.

A THF solution (5 mL) of **6a** (14.6 mg, 0.049 mmol) and **7** (2.32 mg, 0.0049 mmol) was stirred at r.t. for 24 hrs. A large excess of CH_3MgBr (ether solution) was added and the mixture was stirred at r.t. for 1 hr. Extractive workup with CH_2Cl_2 and water followed by preparative GPC purification afforded **8a-10** in 98% yield.

Spectral Data for Poly(2,3-quinoxaline)s.

8a-10. ^{1}H-NMR ($CDCl_3$) 0.62-1.05 (br-s), 1.36-1.77 (br-s), 1.95-2.53 (br-s), 3.25-3.82 (br-s), 4.26-4.96 (br-s). IR (neat) 2972, 1260, 1096, 1036 cm^{-1}.

8a-20. ^{1}H-NMR ($CDCl_3$) 0.74-1.08 (br-s), 1.43-1.80 (br-s), 2.07-2.45 (br-s), 3.33-3.68 (br-s), 4.35-4.93 (br-s). IR (neat) 2972, 1096, 1040 cm^{-1}.

8a-30. ^{1}H-NMR ($CDCl_3$) 0.63-1.13 (br-s), 1.38-1.80 (br-s), 2.04-2.70 (br-s), 3.15-3.68 (br-s), 4.10-5.12 (br-s). IR (neat) 2972, 2932, 2872, 1462, 1360, 1096 cm^{-1}.

8a-50. ^{1}H-NMR ($CDCl_3$) 0.90 (t, J=7.3 Hz), 1.36-1.82 (br-s), 1.92-2.68 (br-s), 3.18-3.72 (br-s), 4.10-5.20 (br-s). IR (neat) 2968, 2944, 2880, 1094, 1042 cm^{-1}.

8a-70. ^{1}H-NMR ($CDCl_3$) 0.90 (t, J=7.0 Hz), 1.35-1.80 (br-s), 1.97-2.76 (br-s), 3.05-3.83 (br-s), 4.02-5.15 (br-s). IR (neat) 2972, 2936, 2880, 1136, 1096, 1042 cm^{-1}.

8a-100. ^{1}H-NMR ($CDCl_3$) 0.90 (t, J=6.9 Hz), 1.40-1.83 (br-s), 2.00-2.83 (br-s), 3.07-3.92 (br-s), 4.05-5.25 (br-s). IR (neat) 2940, 2872, 1380, 1360, 1138, 1096, 1040 cm^{-1}.

8b-30. ^{1}H-NMR ($CDCl_3$) 0.68-1.05 (br-s), 1.10-1.45 (br-s), 1.45-1.78 (br-s), 2.07-2.62 (br-s), 3.32-3.68 (br-s), 4.35-4.95 8br-s). IR (neat) 2944, 2872, 1470, 1098 cm^{-1}.

8b-50. ^{1}H-NMR ($CDCl_3$) 0.65-1.00 (br-s), 1.06-1.42 (br-s), 1.43-1.75 (br-s), 2.08-2.55 (br-s), 3.28-3.70 (br-s), 4.28-4.88 (br-s). IR (neat) 2936, 2870, 1358, 1098 cm^{-1}.

8b-70. ^{1}H-NMR ($CDCl_3$) 0.72-0.97 (br-s), 1.13-1.43 (br-s), 1.46-1.73 (br-s), 2.12-2.48 (br-s), 3.30-3.70 (br-s), 4.31-4.91 (br-s). IR (neat) 2936, 2846, 1380, 1358, 1264, 1100 cm^{-1}.

8b-100. ^{1}H-NMR ($CDCl_3$) 0.72-1.02 (br-s), 1.08-1.43 (br-s), 1.45-1.75 (br-s), 2.05-2.57 (br-s), 3.23-3.73 (br-s), 4.23-4.98 (br-s). IR (neat) 2968, 2940, 2864, 1460, 1264, 1090 cm^{-1}.

8c-30. ^{1}H-NMR ($CDCl_3$) 0.73-0.95 (br-s), 1.07-1.43 (br-s), 1.45-1.75 (br-s), 2.16-2.43 (br-s), 3.33-3.70 (br-s), 4.35-4.88 (br-s). IR (neat) 2968, 2860, 1264, 1100 cm^{-1}.

8c-40. ^{1}H-NMR ($CDCl_3$) 0.68-0.97 (br-s), 1.02-1.42 (br-s), 1.45-1.73 (br-s), 2.12-2.47 (br-s), 3.33-3.65 (br-s), 4.32-4.90 (br-s). IR (neat) 2968, 2864, 1264, 1102 cm^{-1}.

8c-50. ^{1}H-NMR ($CDCl_3$) 0.68-0.97 (br-s), 1.04-1.44 (br-s), 1.45-1.77 (br-s), 2.04-2.50 (br-s), 3.32-3.72 (br-s), 4.28-4.95 (br-s). IR (neat) 2972, 1262, 1096 cm^{-1}.

8c-70. ^{1}H-NMR ($CDCl_3$) 0.73-0.96 (br-s), 1.05-1.43 (br-s), 1.46-1.77 (br-s), 2.10-2.58 (br-s), 3.32-3.72 (br-s), 4.32-4.97 (br-s). IR (neat) 2936, 2864, 1264, 1100 cm^{-1}.

8c-100. ^{1}H-NMR ($CDCl_3$) 0.70-0.96 (br-s), 1.06-1.44 (br-s), 1.45-1.77 (br-s), 2.07-2.54 (br-s), 3.28-3.76 (br-s), 4.25-5.03 (br-s). IR (neat) 2936, 2860, 1360, 1264, 1100 cm^{-1}.

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