Molecular Structure of BHC and its Related Compounds. Tosihiko ŌIWA, Ryoichi YAMADA, Masayuki YAMADA, Michiko INOUYE and Minoru OHNO (Takei Laboratory, Institute for Chemical Research, Kyoto University). Reseived Dec. 10. 1949. *Botyu-Kagaku* 14 : 42–43 (With English résumé p. 43)

7. BHC (1; 2, 3, 4, 5, 6 Hexachlorocylohexane) 及その近縁物質の分子構造に就て

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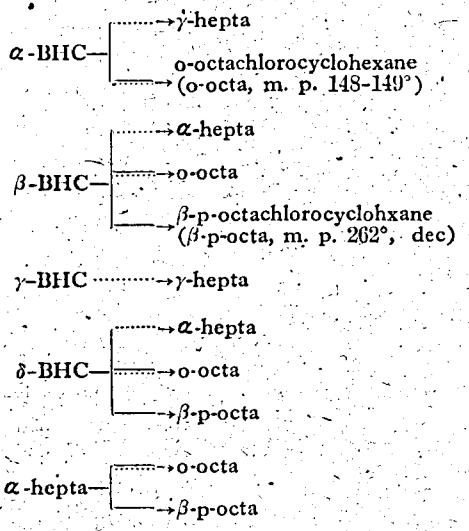
α-BHC, β-BHC, γ-BHC, δ-BHC, α-heptachlorocyclohexane (α-hepta, m. p. 153—154°)[3] 及び γ-heptachlorocyclohexane (γ-hepta, m. p. 85—86°)[3] を四塩化炭素溶液中で塩素化した処 Fig. 1 の様な反應が行はれることを知つた。図で実線は有機化学的に物質を單離した事を, 又点線は ポーラログラフ的観察[1-2-3] を示す。

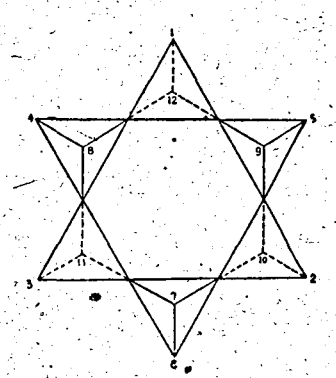
Fig. 1: Results of Chlorination of BHC and its Related Compounds



尚 γ-BHC からは o-octa よりアルカリに安定で半波電位約 -0.25 volt (N-甘汞電極規準) の物質も生成し, 又 γ-hepta からは半波電位約 -0.15 volt (N-甘汞電極規準) の物質は生成するが o-octa の生成は認められない。

α, β, γ 及び δ-BHC が何れも椅子型構造であり, β-BHC が II の構造 (Table 1) であることは既に決定されてゐる[4-5-6-7-8-9]。このことと吾々の実験結果から α-hepta, γ-hepta, o-octa 及び β-p-octa も椅子型構造であることが明かとなり, Table 1 及び Fig. 2 に示す様な α-BHC, δ-BHC, α-hepta, o-octa 及び β-p-octa の分子構造を決定し, γ-BHC 及び γ-heptaの分子構造を推定した。

Eig. 2: Cyclohexane Ring with Carbon Atom shown as Tetrahedra



以上の吾々の結論は X 線解析に依つて決定された γ-BHC の構造[13]や従來他の手段に依つて推定された

Table 1: Configurations of BHC and its Related Compounds

No.	Carbon Number	1		2		3		4		5		6	
	Position ot Substitution	12	1	5	9	10	2	6	7	11	3	4	8
I	α-$C_6H_6Cl_6$	Cl	H	Cl	H	H	Cl	Cl	H	H	Cl	H	Cl
II	β-$C_6H_6Cl_6$	H	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
III	γ-$C_6H_6Cl_6$	H	Cl	Cl	H	Cl	H	H	Cl	Cl	H	Cl	H
IV	δ-$C_6H_6Cl_6$	Cl	H	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
V	α-$C_6H_5Cl_7$	Cl	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
VI	γ-$C_6H_5Cl_7$	Cl	H	Cl	H	H	Cl	Cl	H	Cl	Cl	H	Cl
VII	o-$C_6H_4Cl_8$	Cl	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	Cl
VIII	β-p-$C_6H_4Cl_8$	Cl	Cl	Cl	H	H	Cl	Cl	Cl	H	Cl	Cl	H

構造[7 8 9 10 11 12]の多くのものと一致し，又種々の実験結果[4 5 6 7 8 9 10 11 12]をもよく説明することが出来る。然し乍ら δ-BHC の構造に関しては対称の中心を持つと云う Daasch[9] 及び Kulkarnijatkar 等[14] の推論した構造とは異るが倉谷等の有極性であると云う事実[15] 及び中島等が脱塩酸反應速度から推定[16] した構造とは一致する。

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Résumè

From the studies on photochlorination of α-BHC, β-BHC. γ-BHC. δ-BHC, α-heptachlorocyclohexane (α-hepta, m. p. 153—154°)[3] and γ-heptachlorocyclohexane (γ-hepta, m p. 85—86°)[3] in carbon tetrachloride solution, we found that the reactions shown in Fig. 1 took place. In this figure the solid lines are shown that materials were isolated substancially and the processes of the dotted lines were observed polarographically [1 2 3].

Moreover we did not obtain o-octa from either γ-BHC or γ-hepta, but observed polarographically from former a compound which half wave potential was about -0.25 volt (N calomel electrode standard) and from latter another compound being half wave potential about -0.15 volt (N calomel electrode standard).

It has been already determined that α-, β-, γ- and δ-BHC are chair form and the β-BHC is structure II (Table 1, Fig. 2).[4 5 6 7 8 9] From these facts and our experimental results, α-hepta, γ-hepta, o-octa and β-p-octa become necessarily to be chair form, and then we determined the molecular structures of α-BHC, δ-BHC, α-hepta, o-octa and β-p-octa and also assumed the structures of γ-BHC and γ-hepta as shown in Table 1.

Our above structures accord with the structure of γ-BHC determined by X-ray analysis[13] and with that of BHC assumed by various methods[7 8 9 10 11 12], and also can justify the many previous experimental results [4 5 6 7 8 9 10 11 12]. But the structure of δ-isomer we determined does not agree with the symmetrical form [9 14], but agrees with the fact that δ-form is polar[15] and with the structure which is assumed by the velocity of dehydorochlorination.[16]

防 虫 科 學 第 12 號 正 誤 表

頁	個 所	誤	正
14	右列 7 行目	200. 400. 800. 1600. 3200.	2000. 4000. 8000. 16000. 32000.
21	第 1 図	濃度にされた	濃度にさらされた