

^{13}C AND ^1H NMR STUDIES ON THE 1, 4-ADDUCT FORMED BY THE REACTION OF TETRACYANOETHYLENE AND STYRENE

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A new species was accumulated in dichloromethane solution of tetracyanoethylene and styrene under high pressure. Its molecular structure, quenched to atmospheric pressure and at -50°C , has been determined by means of ^{13}C and ^1H NMR spectroscopy.

The present authors disclosed¹⁾ the formation of a new species in the system of tetracyanoethylene (TCNE) and styrene, and suggested that it might be a zwitterionic intermediate through which some kinds of the two-step cycloadditions were assumed to be taken place²⁻⁶⁾.

If that suggestion were correct, the ^{13}C NMR spectrum of this species would show some low-field chemical shifts, characteristic of the positively charged carbon atoms in the zwitterion. The facts that the species can be accumulated under high pressure and long-lived at low temperature, have made it possible to obtain ^{13}C NMR spectra of the new species which was produced in CD_2Cl_2 at room temperature under high pressure and then quenched to atmospheric pressure and at -50°C . An FX-100 NMR spectrometer (JEOL) was used for the measurement; magnetic field, 25.05 MHz; data points, 16K; frequency width, 10^4 Hz; pulse repetition, 4.0 sec; precision of chemical shifts, ± 0.05 ppm; internal reference, CD_2Cl_2 ($\delta = 53.60$ ppm to TMS); o. d. of a sample tube, 10mm. Over the range of 300 to -100 ppm, such a carbonium ion has not been detected. Then the species is not the zwitterion itself but its neutral isomer, 1, 4-adduct (1,1,2,2-tetracyano-1,2,3,8a-tetrahydronaphthalene) as depicted in Fig. 1. This could be produced possibly as a result of the delocalization of the positive charge which may initially induced on the carbon C-7 to the benzene ring accompanying with the loss of the ring aromaticity. This would be a reason why it is unstable at 1 bar.

Figs. 2 and 3 show, respectively, the ^{13}C and ^1H NMR spectra of the new species and parent

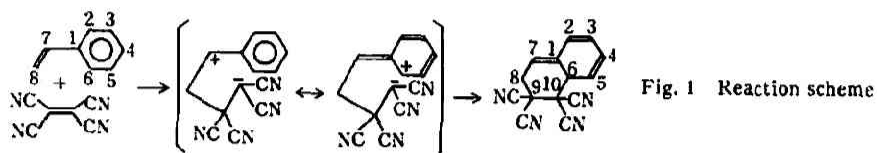


Fig. 1 Reaction scheme

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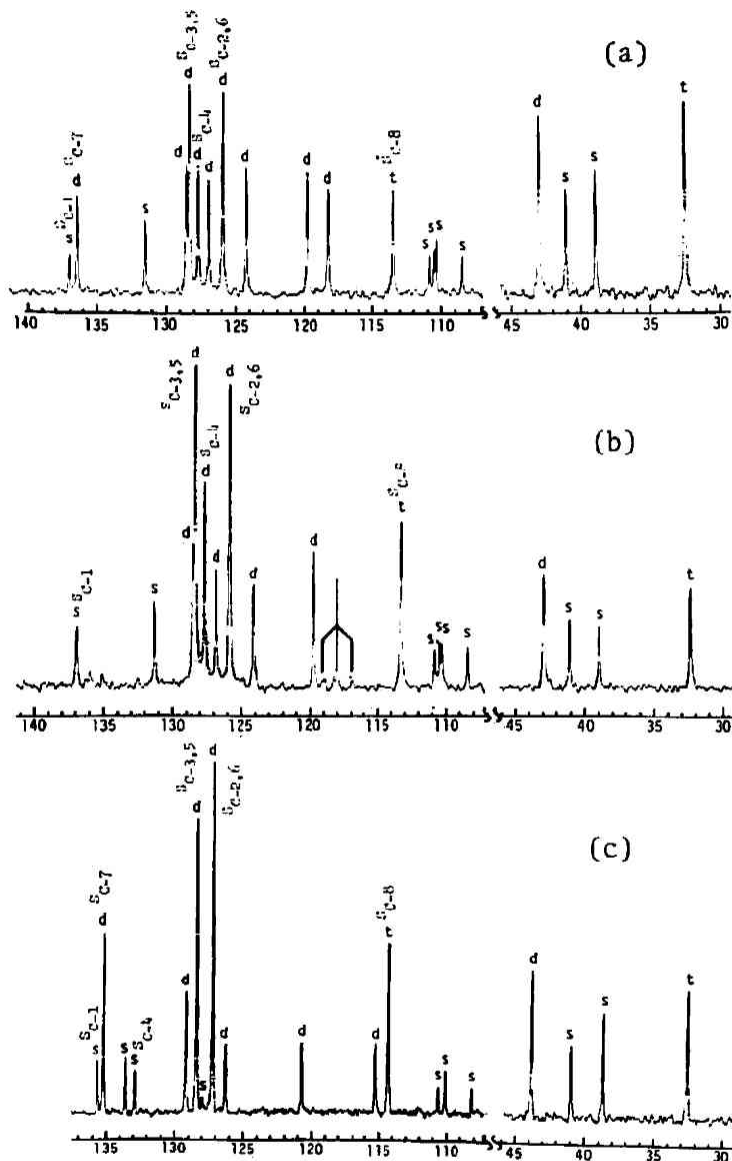


Fig. 2 ^{13}C NMR (complete decoupling) spectra of the 1,4-adduct in CD_2Cl_2 at -50°C . (a), TCNE+styrene; (b), TCNE+styrene- α - d_1 ; (c), TCNE+*p*-chlorostyrene. Symbols, s, d, t indicate, respectively, singlet, doublet and triplet in off-resonance decoupling measurement. Superscript s denotes the free styrene.

styrenes. The free TCNE does not appear at -50°C within integration of a few thousand pulses because of its low solubility in CD_2Cl_2 at such a low temperature. Fig. 2 (a) reveals that 4 carbon atoms of the new species ($-\text{CH}$, $-\dot{\text{C}}-$, $-\text{C}-$ and CH_2) are saturated; this situation can be seen partially in the ^1H NMR spectra of Fig. 3. The peak at the highest field can be assigned to C-8 carbon

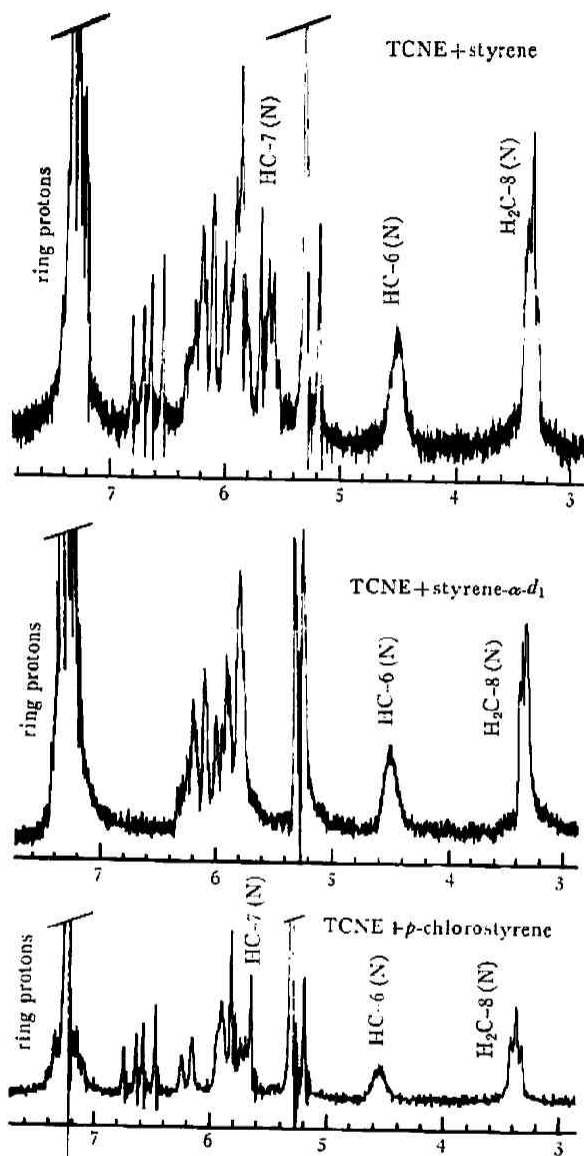


Fig. 3 ^1H NMR spectra in CD_2Cl_2 at -50°C . Chemical shifts are expressed in δ/ppm relative to TMS (internal standard).

of the new species, because only to this carbon attach two protons. Two singlet peaks at the next highest field (39.03 and 41.12 ppm) are ascribable to two nonprotonated carbons C-9 and C-10 in the TCNE moiety, because the cyano carbons appear between 108 and 111 ppm⁷⁾. The remaining singlet

7) In the case of the *p*-chlorostyrene adduct, the central 2 peaks overlap, the same trend being observed for the styrene adduct at *ca.* -20°C . The 1, 2-adduct of TCNE to *p*-methoxystyrene also shows only 3 peaks for the cyano groups in acetone- d_6 at *ca.* 20°C . Different conformations of the cyano groups seem to be thermally averaged except for at very low temperature.

peak at 131.47 ppm which is ascribable to C-1 is still in the sp^2 state. Although a 1,2-adduct could be conceivable as an alternative, it was completely denied by the deuterium incorporation approach: as can be seen in Fig. 2 (b), the triplet peak due to C-7 centered at 118 ppm is unsaturated in contrast to that of C-8; correspondingly, in the 1H NMR spectrum of the styrene- α - d_1 adduct there is no peak at 5.6 ppm. The double bond between C-7 and C-1 can be produced when the initially induced positive charge is delocalized to the benzene ring, which results in the loss of the large resonance energy inherent in the aromatic ring. Such a drastic change in the ring character has been detected by IR, UV and 1H NMR, and now by ^{13}C NMR. The possibility of the delocalization of the positive charge on the ortho and para positions requires certain reliable reasons why the peak at 43.0 ppm is attributed to the ortho carbon, C-6. The first reason is that the five ring carbons which have each one proton show nonequivalent doublet peaks as shown in Fig. 2. This fact is difficult to be explained in terms of the para bonding. The second and most decisive one is that the corresponding peak around 43.0 ppm of the adduct derived from *p*-chlorostyrene is observed as doublet on the off-resonance decoupling measurement. The third one is that the methine proton peak can be observed also in the *p*-chlorostyrene adduct at about 4.6 ppm, as shown in Fig. 3. Thus, the bonding between C-10 and C-6 is confirmed, yielding 1,1,2,2-tetracyano-1,2,3,8a-tetrahydronaphthalene.

The ^{13}C NMR peaks are assignable to each carbon as shown in Table 1. The reasons why C-9 and C-10 are distinguished are: 1) the peak intensity of C-9 is always stronger than that of C-10, which is considered to be caused by the fact that two and one protons are attached to C-9 and C-10 through C-8 and C-6, respectively, 2) the ratio of the peak intensity of C-9 to that of C-10 reverses in the TCNE-styrene- α - d_1 adduct, in which a deuterium atom sites nearer to C-9 than C-10, relatively making the C-9 resonance peak weak, 3) the ^{13}C NMR spectrum of the 1, 2-adduct between TCNE and *p*-methoxystyrene shows that C-9 (connected with C-8) and C-10 (connected with C-7) appear at 34.40 and 45.61 ppm, respectively, the former also having a stronger intensity than

Table 1. Assignment of the ^{13}C NMR peaks of the 1,4-adduct

carbon No. (C-X)	styrene adduct	styrene- α - d_1 adduct	<i>p</i> -chlorostyrene adduct
1	X-1	131.47 ppm	131.27 ppm
2	3*	128.54	128.50
3	4*	126.94	126.84
4	2*	124.21	124.11
5	5	119.82	119.77
6	7	118.31	~118.2
7	6	43.02	42.93
8	10	41.12	41.07
9	9	39.03	38.98
10	8	32.60	32.40

* The distinction among C-2, C-3, and C-4 is less reliable.

the latter⁸⁾. It is difficult to distinguish the ring carbons, C-2, 3, 4 and 5. However, since the doublet peak at the highest field in the sp^2 region is undoubtedly ascribable to C-7 as referred to the above, the other terminal carbon C-5 in the conjugated triene system (C-7, 1, 2, 3, 4 and 5) may appear at the next highest field, 119.82 ppm. We may see a similar trend that the terminal carbons lie at the higher field than the inner ones in such a conjugated triene system as cycloheptatriene^{9,10)}. In the *p*-chlorostyrene adduct, C-4 appears at 127.96 ppm as a weak singlet peak (Fig. 2 (c)), which occurs between the meta (C-3, 5) and ortho (C-2, 6) carbons of the parent molecule. If the sequence $^5\text{C}-3, 5 > \text{C}-4 > ^5\text{C}-2, 6$, where superscript ⁵ denotes the free styrene, can be assumed to be the same in both styrene and *p*-chlorostyrene adducts, the peaks around 127 ppm in Figs. 2 (a) and (b) are assigned to C-4. The carbons, C-2 and 3 are assigned tentatively as described in Table 1 so that the extent of the influence of the chlorination at C-4 and the deuteration at C-7 result in the sequence $\text{C}-2 > \text{C}-4 > \text{C}-3$ and $\text{C}-2 \sim \text{C}-4 > \text{C}-3$, respectively.

The idea that this 1, 4-cycloaddition proceeds not by the concerted mechanism but by a step-wise one is based on the following kinetic evidences: 1) the present reaction is markedly accelerated by solvent polarity and high pressure¹⁾, and 2) the rate of the cycloreversion (unimolecular decomposition) of the 1,4-adduct between TCNE and α -methylstyrene in 1,2-dichloroethane is also accelerated by high pressure despite the bond-breakage reaction¹¹⁾. These facts indicate that the transition state is strongly solvated as a result of some charge separation.

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- 8) The complete, off-resonance and gated decoupling spectra have been measured for the assignment. The carbons C-9 and C-8 have been distinguished by their relative intensities and patterns of the long-range coupling between ^{13}C and ^1H .
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