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Structure Determination of the 1,4-Cycloadduct Quenched after the High-pressure Reaction of Tetracyanoethylene with Styrene and Its Derivatives

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The electronic, ^{13}C NMR, ^{1}H NMR, and IR spectra of the 1,4-cycloadducts of TCNE with styrene, styrene-α-d_1, *p*-chlorostyrene, *p*-methylstyrene, α-methylstyrene, and 1,1-diphenylethylene were taken at low temperatures at 1 bar after the high-pressure reaction; the ^{13}C NMR spectra were of decisive importance in determining the structure; the other kinds of spectra were consistent with the established structure. They have an electronic absorption band around 320 nm, which is assigned to the π-π^* transition of the triene system in the adducts. Neither *cis*- nor *trans*-stilbene, which have a lower ionization potential, provides the 1,4-cycloadduct even at high pressure.

Tetracyanoethylene (TCNE) is one of the strongest electron acceptors to give the EDA (electron-donor-acceptor) complexes with electron donors; it undergoes the 1,2-cycloaddition to electron-rich olefins and the 1,4-cycloaddition to dienes.[1-3] Styrene, which is composed of vinyl and phenyl groups conjugated together, has been considered to yield neither 1,2- nor 1,4-cycloadduct of TCNE under mild conditions,[4] while its derivatives with an electron-donating substituent at *para*-, α-, or β-position are known to afford the 1,2-cycloadducts.[4-7] Actually, a number of papers[8-11] have been published on the formation constant and molar absorption coefficient of the EDA complex between TCNE and styrene without noticing the coexistence of the 1,4-cycloadduct confirmed here.

The present authors found a strong piezochromism in the dichloromethane solution of TCNE and styrene, and showed that a new species having an absorption band around 320 nm was formed reversibly in the solution.[12] The concentration of the new species at atmospheric pressure is too low to provide its IR and NMR spectra, which are required for determining spectroscopically the molecular structure. But the concentration can be increased sufficiently by pressure and decomposition after pressure release can be prevented at a low temperature well below 0 °C. The striking influences of high pressure and low temperature on the unstable species fortunately allows the molecular structure to be clarified unambiguously from the ^{13}C NMR and other spectra.

Experimental

Materials. Styrene and α-methylstyrene were purified by the usual method and distilled immediately before use. Styrene-α-d_1 (98% D atom, Merck Sharp and Dohme Canada Ltd.) and commercial *p*-chlorostyrene (guranteed reagent grade, Nakarai Chemicals Co., Ltd.) were used without further purification. *p*-Methylstyrene and 1,1-diphenylethylene were synthesized according to the methods in the literature[13,14] and purified by repeated distillation at reduced pressure. *trans*-Stilbene was recrystallized twice from ethanol and *cis*-stilbene was distilled at reduced pressure before use. TCNE was sublimed three times or more *in vacuo* at 50—60 °C. Dichloromethane was purified by the usual method and distilled before use. Dichloromethane-d_2 (99.3% D atom) was supplied by CEA (France).

Apparatus and Procedure. Electronic absorption spectra were recorded on a Shimadzu UV-200S spectrophotometer at 1 bar (1 bar$=10^5$ Pa) and on a Union RA-405 spectrophotometer at high pressure. IR, ^{1}H NMR, and ^{13}C NMR spectra at 1 bar were measured with JASCO DS-402G, JEOL JNNM-PS-100, and JEOL FX-100 spectrometers, respectively. A high-pressure optical cell[15] with two sapphire windows of 1-cm thickness was used to measure electronic spectra at high pressure. Pressure was measured with a calibrated manganin-coil gage which was put in a flexible teflon capsule filled with silicone oil. The small teflon capsule was fixed on a plug inside the high-pressure optical cell. Thermostatted water was circulated around the cell to keep the temperature at 25±0.1 °C.

Sample solutions of the reaction mixtures of TCNE with styrene and its derivatives were prepared for the spectroscopic investigation in a special way as follows. Styrene or its derivatives were put together with TCNE in a flexible teflon capsule containing (deuterated) dichloromethane ($\approx$1.6 cm^3). The amount of TCNE which was mixed was 2 or 3 times as much as the solubility ($<$0.1 mol dm^{-3}) in the solvent at room temperature at 1 bar, because pressure markedly enhanced its conversion into the adduct. The capsule was sealed with a teflon plug and a rubber O-ring, and placed in a usual piston-cylinder device having a jacket for thermal control. A pressure of $\approx$8 kbar was applied to the capsule for several hours at room temperature using silicone oil as a pressure-transmitting fluid, and ice-cold water was circulated through the jacket for an hour. As soon as pressure was released at 0 °C, the cold capsule was taken out from the piston-cylinder device and immersed in liquid N_2 to stock the quenched sample for a long time. Just before a spectroscopic study, the solid solution was melted again at about -95 °C and transferred by a previously chilled syringe to a cell. Cells for electronic and IR spectra were cooled at around 0 °C during the course of the measurements, while NMR glass tubes 10 mm in diameter were kept at -50 °C by circulating cold N_2 vapor around the tubes.

Results and Discussion

Electronic Spectra. On mixing the dichloromethane solutions of styrene and TCNE, a red color appears instantaneously because the EDA-complex formation is a diffusion-controlled reaction. Figure 1 shows the time dependence of the absorption spectrum of the reaction mixture at 1 bar. The absorption peaks at 396 and 480 nm are due to the EDA complex between styrene and TCNE; styrene and TCNE have no absorp-

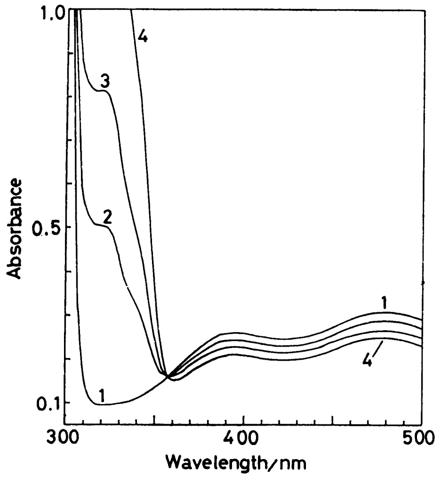


Fig. 1. Time dependence of the electronic spectra of TCNE–styrene mixture in CH_2Cl_2 at room temperature at 1 bar. Concentration (mol dm^{-3}): TCNE, 1.5×10^{-3}; styrene, 0.5. 1, 30 s after mixing; 2, 18.5 min; 3, 47.5 min; 4, 14 h.

tions in the visible region. The absorption of the EDA complex decreases slowly with time, while a new band develops around 320 nm. The absorption spectrum reaches a stationary state after a long time, leaving an isosbestic point at 357 nm. These facts suggest that a new species assigned to the 320-nm band (confirmed later as the 1,4-cycloadduct) is in equilibrium with the EDA complex as

$$D + A \overset{K_1}{\rightleftharpoons} C \overset{K_2}{\rightleftharpoons} P, \tag{1}$$

where D, A, C, and P are the donor (styrene), acceptor (TCNE), EDA complex, and new species, respectively, and K_1 and K_2 are equilibrium constants.

Although we could not measure at 1 bar the electronic, IR, and NMR spectra dominated by the new species P, a large pressure effect on the formation equilibrium (K_2) of P was found. The spectra A, B, C, D, and E (except B′) in Fig. 2 were taken at each pressure after they changed no more with time. The decrease with pressure in the absorption of the EDA complex is tremendous, especially at 8 kbar. If only a single equilibrium K_1 were involved in the solution as assumed elsewhere,[8–11] the absorbance would increase with pressure owing to the increase with pressure in the molar absorption coefficient and in the concentration of the EDA complex.[16,17] As a matter of fact, the trend exists transiently in Fig. 2; at 2 kbar, the initial absorbance B′ is larger than the equilibrium one B. The difference indicates that the EDA complex is slowly converted into the new species. The backward reaction from the new species to the complex is also slow, above all at 1 bar, so that the new species can be quenched in the solution.

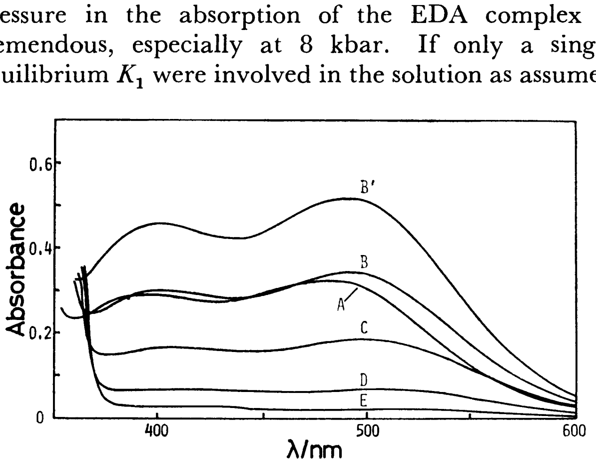


Fig. 2. Effect of pressure on the charge-transfer band of TCNE–styrene mixture in CH_2Cl_2 at 25 °C. Concentration (mol dm^{-3}): TCNE, 6.5×10^{-3}; styrene, 0.26. Path length, 5 mm. A, 1 bar; B and B′ (see the text), 2 kbar; C, 4 kbar; D, 6 kbar; E, 8 kbar.

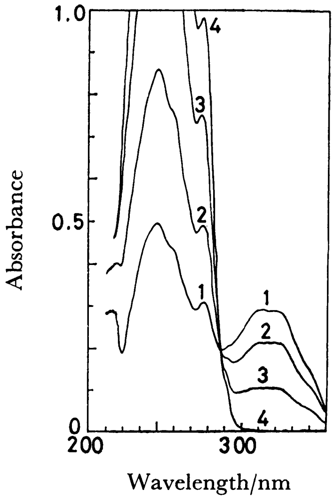


Fig. 3. UV spectra of the decomposing TCNE–styrene adduct in CH_2Cl_2 at room temperature at 1 bar. 1, 10 s after the quenched solution was diluted; 2, 10 min; 3, 30 min; 4, 16 h.

The UV spectra in Fig. 3 are taken at 1 bar after diluting the quenched reaction mixture. The well resolved spectrum of the new species is seen above the isosbestic point at 288 nm; it has a broad maximum between 310 and 325 nm with a shoulder at the longer wavelength. The spectrum below the isosbestic point corresponds to the parent molecules; when we denote the molar absorption coefficient of X at the wavelength λ by $\varepsilon_\lambda(X)$, ε_{250}(styrene) and ε_{250}(TCNE) are, respectively, 1.48×10^4 and 1.10×10^4 cm^{-1} mol^{-1} dm^3 and ε_{278}(TCNE) and ε_{278}(styrene) are, respectively, 1.26×10^4 and 1.2×10^2 cm^{-1} mol^{-1} dm^3. Thus, the variation with time of the absorbances in Fig. 3 discloses that the new species is an adduct between styrene and TCNE. The adduct is composed of an equal number of the parent molecules, because the quantity

$$\frac{A^2_{250}-A^1_{250}}{\varepsilon_{250}(\text{styrene})+\varepsilon_{250}(\text{TCNE})} = 1.36\times10^{-5} \tag{2}$$

agrees well with

$$\frac{A^2_{278}-A^1_{278}}{\varepsilon_{278}(\text{styrene})+\varepsilon_{278}(\text{TCNE})} = 1.40\times10^{-5}, \tag{3}$$

where A^1 and A^2 are the absorbances of spectra 1 and 2, respectively. In the dilute solution, the EDA complex is negligible. Hence, if the adduct has the stoichiometry expressed by reaction 1, ε of the adduct at 320 nm is given by the equation:

$$\frac{A^1_{320}-A^i_{320}}{A^i_\lambda - A^1_\lambda}\{\varepsilon_\lambda(\text{styrene})+\varepsilon_\lambda(\text{TCNE})\} = (5.5\pm0.1)\times 10^3, \quad (4)$$

where λ=250 and 278 nm and i=2, 3, and 4. Adducts of the same type are found for the substituted styrenes except for the stilbenes, as shown in Table 1. It is unknown at present why neither *cis*- nor *trans*-stilbene provides the adduct under the same condition despite the fact that the ionization potentials are lower than those of the other electron donors.[18)]

TABLE 1. ELECTRONIC ABSORPTIONS OF EDA COMPLEXES AND ADDUCTS FORMED BY THE REACTION OF TCNE WITH STYRENE AND ITS DERIVATIVES IN CH_2Cl_2 AT 25 °C

Donor	EDA complex λ_{max}/nm	Adduct[a)] λ_{max}/nm
Styrene	480±1, 396±1	320±3
p-Chlorostyrene	483±1, 362±1	318±3
p-Methylstyrene	525±1, 401±1	317±3
α-Methylstyrene	495±1, 399±1	325±3
1,1-Diphenylethylene	507±1, ≈400	329±3
trans-Stilbene	597±1, ≈390	—[b)]
cis-Stilbene	528±1, 389±1	—[b)]

a) Obtained by diluting reaction mixtures quenched after pressurization. b) Adducts are not formed.

^{13}C and ^{1}H NMR spectra. The ^{13}C NMR spectra of the quenched reaction mixtures of TCNE with styrene, styrene-α-d_1, and *p*-chlorostyrene are of great use in proving that the adduct is really composed of one molecule of styrene and one molecule of TCNE, as in reaction 1, and in deciding how the donor molecule is combined with the acceptor. The ^{13}C NMR spectrum of the 1,4-cycloadduct is anticipated to give fourteen separate signals for the nonequivalent carbons. As a matter of fact, fourteen separate signals are found for the adduct, besides those for the parent molecules (Fig. 4), and the peaks in Fig. 4 are assigned to the carbon atoms numbered in the structural formula for the 1,4-cycloadduct, as summarized in Table 2.[19)] The deuteration experiment elegantly reveals that the α-carbon in styrene remains in the sp^2 state in the adduct. This is compatible with the conjugated triene system in the 1,4-cycloadduct. Although it is reported that two acceptor (maleic anhydride) molecules combine with one styrene molecule after the reaction in benzene at 80 °C,[20)] such a kind of cycloadduct has not been recognized in the present system. Actually, there is no other possibility than the present one that is consistent with the number, multiplicity, and position of the peaks found in the ^{13}C NMR spectra.

TABLE 2. ASSIGNMENT OF THE ^{13}C NMR PEAKS OF THE 1,4-CYCLOADDUCTS[a)]

Carbon No. (C-X)	Styrene adduct	Styrene-α-d_1 adduct	*p*-Chloro-styrene adduct
X=1	131.47	131.27	133.52
2[b)]	128.54	128.50	129.17
3[b)]	126.94	126.84	126.25
4[b)]	124.21	124.11	127.96
5	119.82	119.77	120.75
7	118.31	118.2	115.24
6	43.02	42.93	43.85
10	41.12	41.07	41.03
9	39.03	38.98	38.69
8	32.60	32.40	32.64

a) The 4 peaks between 111 and 108 ppm are due to the cyano carbons. b) The distinction among these is less reliable.

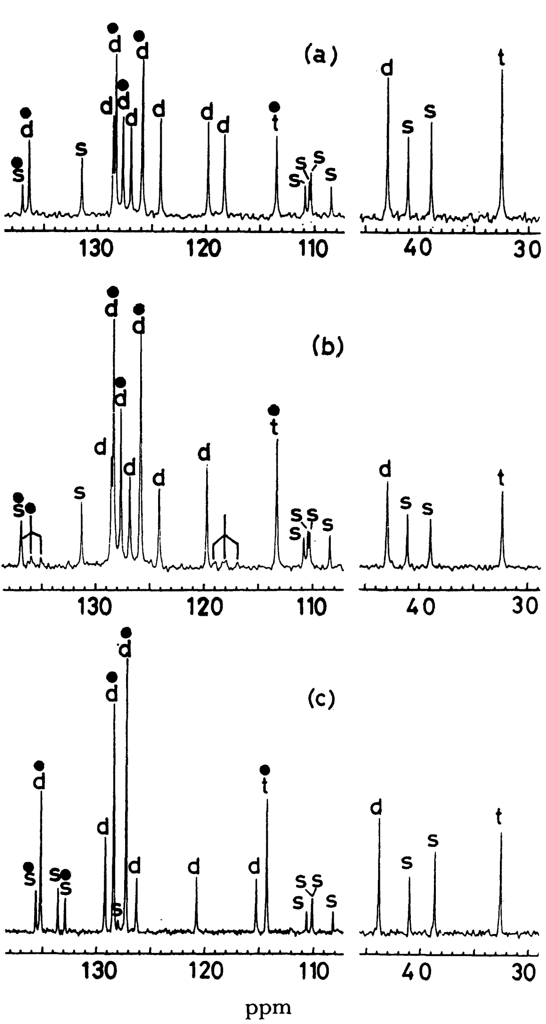
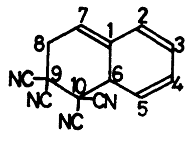


Fig. 4. ^{13}C NMR (complete decoupling) spectrum of the 1,4-cycloadduct in CD_2Cl_2 at −50 °C at 1 bar. (a), TCNE+styrene; (b), TCNE+styrene-α-d_1; (c), TCNE+*p*-chlorostyrene. Symbols s, d, and t denote singlet, doublet, and triplet in off-resonance decoupling, respectively. ●, Due to free styrene or its derivatives. The solubility of TCNE at the low temperature is too low to give signals. Chemical shifts are relative to the TMS reference.



All the information from the ^{1}H NMR spectra[19)] of

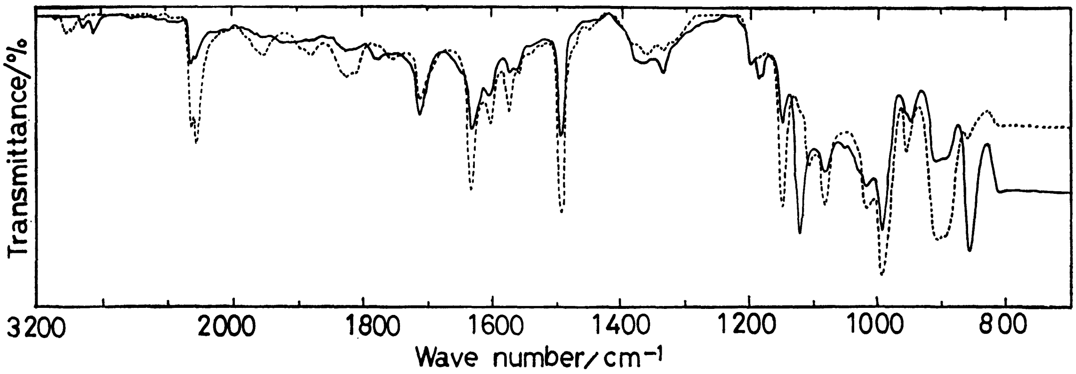


Fig. 5. IR spectra of TCNE–styrene mixture in CH_2Cl_2 around 0 °C at 1 bar. ——, Dominated by the adduct; ----, after the adduct being decomposed.

the quenched reaction mixtures of TCNE with styrene, styrene-α-d_1, and *p*-chlorostyrene is consistent with the conclusion reached above. There are three peaks, at 3.2—3.4, 4.4—4.6, and 5.5—5.7 ppm (internal TMS reference), whose peak ratio is 2 : 1 : 1; they are assigned to H_2C-8, HC-6, and HC-7, respectively. The facts that the styrene-α-d_1 adduct loses the peak at 5.5—5.7 ppm and that the *p*-chlorostyrene adduct does not lose the peaks at 3.2—3.4 and 4.4—4.6 ppm support the 1,4-cycloadduct. The complicated peaks in the range of 5.8 to 6.3 ppm are due to the protons involved in the conjugated triene system. Although a spin-decoupling experiment was attempted to reaffirm the above assignment, the low S/N ratio in the spectra due to the low concentration of the adduct made it difficult to see changes in the signal multiplicity.

IR Spectra. IR spectra tell us more about the molecular structure of the found adduct than do the electronic spectra. Vibrational spectra of the symmetric molecule TCNE have been well studied,[21–24] and the group frequencies related to the complicated molecule of styrene are available.[25,26] Figure 5 shows the IR spectra of the reaction mixture of styrene and TCNE, which is taken by using the quenching technique described in the experimental section. In the adduct, the bands at 2245 and 2220 cm^{-1} characteristic of the C≡N stretches in TCNE decrease in intensity, accompanied by a shift ($\approx$15 cm^{-1}) to the higher frequencies. These changes indicate the loss of the conjugation of the double and triple bonds in TCNE; as a result, the C≡N bonds become stronger in the adduct than in TCNE. The C–C stretching vibrations at 1150 and 955 cm^{-1} in TCNE also decrease in intensity, and the corresponding bands in the adduct appear at the lower frequencies 1123 and 945 cm^{-1}, respectively. Thus, the loss of the conjugation makes also the C–C bonds weaker. The following bands of styrene decrease in intensity as reaction 1 proceeds; the vinylic C–H deformation bands at 990 and 890—910 cm^{-1}, the vinylic C–C stretching band at 1632 cm^{-1}, the aromatic C=C stretching bands at 1600, 1580, and 1500 cm^{-1}, and the combinations and overtones characteristic of the benzene ring[27] at 2000—1700 cm^{-1}. These spectral features of styrene show that both vinyl and phenyl groups are modified by the addition of TCNE; that is to say, the new species found is not the 1,2-cycloadduct. Thus, the IR spectral information supports the structure determination based on the ^{13}C NMR spectra.

Chromophore of the Band around 320 nm. It has been proved that the new species having the band around 320 nm is the 1,4-cycloadduct formed by the reaction of TCNE with styrene and its derivatives. The absorption band is attributed to the conjugated triene system rather than the C≡N group, because the 1,4-cycloadduct is predicted to have a band at 303 nm according to the additivity rule for the conjugated trienes.[28]

There is a short communication[29] which states that styrene derivatives benzylidenecyclopropane and (diphenylmethylene)cyclopropane having the exocyclic or strained double bond, 1,4-cycloadduct thermally to TCNE. In the latter case, the UV absorption at 333 nm with log $\varepsilon=3.91$ is comparable with the present results; moreover, the ^1H NMR signals agree well with those of the 1,4-cycloadduct confirmed here. In the former case, however, two strong peaks at 269 (log $\varepsilon=4.23$) and at 278 nm (log $\varepsilon=4.21$) are reported, although a bathochromic shift is anticipated because of the presence of the electron-donating three-membered ring.[28]

Recent studies on the thermal polymerization of styrene in bulk showed the existence of an absorption band with a maximum at 325 nm. This band is attributed to a Diels-Alder adduct of two styrene molecules, which is considered to be responsible for the initiation of the spontaneous polymerization.[30–32] The present thorough studies on the 1,4-cycloadduct between styrene and TCNE are in favor of the suggestion of the styrene adduct based on the UV spectrum.

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