*Studies on trans-Dicyanodiethoxycarbonyl Ethylene. I. The Determination of the Structure**

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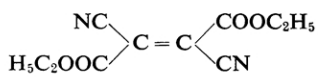
Cairns and coworkers[1] synthesized tetracyanoethylene containing four cyano groups and investigated its derivatives. However, there were only a few reports for the compounds of this class. Accordingly, studies on the properties and the behaviors of *trans*-dicyanodiethoxycarbonyl ethylene (I) containing two cyano and two ethoxycarbonyl groups were attempted in comparison with tetracyanoethylene in the present paper.



(I)

In 1955, Felton[2] reported that I was prepared in about 10% yield from ethyl cyanoacetate by the oxidation with selenium dioxide. Furthermore, it was also found that dicyanodiethoxycarbonyl ethane reported by Naik[3] in 1921 was identical to the ethylene compound I prepared by the Felton method. The precise structure of I, however, was not yet determined completely.

Consequently, the physical and the chemical properties of I were investigated to determine its structure. When I was dissolved in aromatic bases (e. g., benzene, toluene, xylenes, etc.), the solutions gave intense yellow colors. These colored solutions were attributed to the formation of π-comlexes between the aromatic bases and I. The π-complex spectra of I with the aromatic bases were shown in Fig. 1.

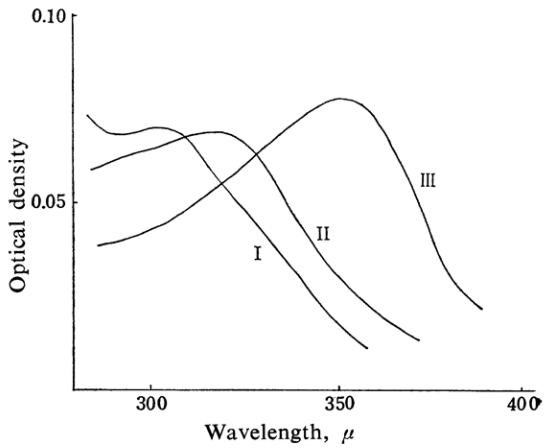


Fig. 1. The π-complex spectra of I with aromatic bases.
I (I) 0.514×10^{-4} mol./l., benzene
II (I) 0.522×10^{-4} mol./l., toluene
III (I) 0.522×10^{-4} mol./l., *o*-xylene

Furthermore, the concentration dependence of these spectra was analyzed by the mothod of Keefer and Andrews[4], and Merrifield and Phillips[5]. The relation, then, is given as

$$[\mathrm{I}]\,l/\log(I_0/I) = 1/K\varepsilon\,[\mathrm{B}] + 1/\varepsilon$$

where [I] and [B] are the molar concentration of I and the mole fractions of aromatic bases, respectively, K is the association constants, log I_0/I is the optical density, and l is the cell length.

If the complex is 1 : 1 as in the case of

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1) T. L. Cairns et al., *J. Am. Chem. Soc.*, **80**, 2775 (1958).
2) D. G. I. Felton, *J. Chem. Soc.*, **1955**, 515.
3) K. G. Naik, ibid., **119**, 1239 (1921).
4) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950); L. J. Andrews and R. M. Keefer, ibid., **73**, 462 (1951).
5) R. E. Merrifield and W. D. Phillips, ibid., **80**, 2778 (1958).

TABLE I. π-COMPLEXES FORMED BETWEEN I AND AROMATIC BASES
(Solvent, CH_2Cl_2; Temperature, 20°C)

π-Base	K	λ_{max} mμ	ε l·cm^{-1} mol^{-1}	K	λ_{max} mμ	ε l·cm^{-1} mol^{-1}
Benzene	4.1	308	1300	—	—	—
Toluene	3.3	320	1250	—	—	—
o-Xylene	1.3	355	2632	—	—	—
m-Xylene	1.1	354	2900	—	—	—
p-Xylene	2.6	340	2000	—	—	—
Naphthalene	14.5	324	454	1.6	405	1333
Chlorobenzene	9.8	315	633	—	—	—
Anisole	10.7	310	649	1.9	390	909
Pyridine	1.2	315	826	—	—	—

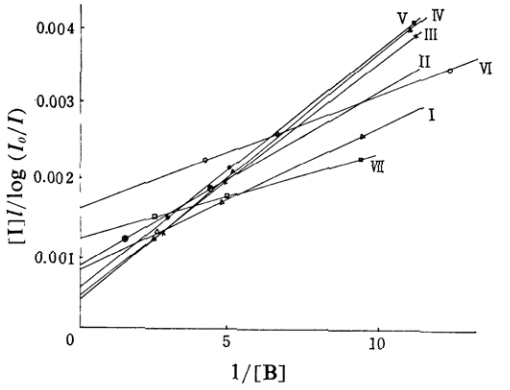


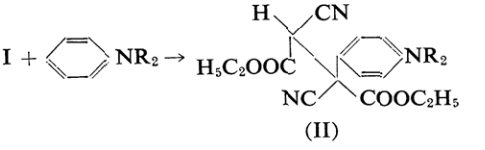
Fig. 2. Determination of K and ε for some I-aromatic complexes in CH_2Cl_2.
I Benzene II Toluene
III *o*-Xylene IV *m*-Xylene
V *p*-Xylene VI Chlorobenzene
VIII Pyridine

tetracyanoethylene, a plot of $[I]l/\log(I_0/I)$ vs. $1/[B]$ should be linear and yield ε as the reciprocal of the intercept, and the product $K\varepsilon$ as the reciprocal of the slope. These plots of I-aromatic complexes were shown in Fig. 2. Association constants, K, wavelength of maximum absorption, λ_{max}, and extinction coefficients for maximum absorption, ε, for nine I-aromatic complexes were listed in Table I.

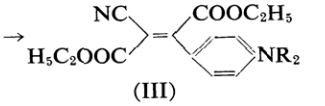
From these data it appears that I is a π-acid like tetracyanoethylene[5]. However, I does not appear to be nearly as strong a π-acid; the complexes of I have an absorption maxima at shorter wavelengths than do the corresponding complexes of tetracyanoethylene. Furthermore, whereas the π-complexes of tetracyanoethylene show a progressive increase of K and λ_{max} with increasing methylation of benzene, the complexes of I do not show a similar increase.

The ultraviolet absorption spectrum of I showed a band at λ_{max} 242 mμ (log ε ; 4.0313). The infrared absorption spectrum showed two bands at 1740 cm^{-1} and 1260 cm^{-1} which were attributed to the stretching vibration of C=O and C–O of ester groups, respectively, but the conjugated alkyl C≡N band at 2225±10 cm^{-1} could not be detected (Fig. 3). These results, however, are not unexpected from the fact[6] that the introduction of an oxygenated group into the molecule results in a "quenching" of the C≡N absorption intensity to a remarkable extent. The Raman spectrum showed an intense band at 1650 cm^{-1} which was attributed to the symmetrical ethylenic double bond. As a chemical evidence, the ethanolysis of I gave ethyl ethylenetetracarboxylate.

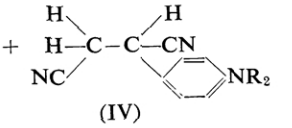
Finally, the geometrical structure of I was determined by the following manner. The reaction of I with tertiary aromatic amines



(II)



(III)



(IV)

resulted in addition of a benzene nucleus to the ethylenic double bond with the formation of 4-α, β-dicyano-α, β-diethoxycarbonyl-*N*, *N*-dialkylanilines (II). When the products II were heated with 10% aqueous sodium carbonate solution, 4-*trans*-α,β-diethoxycarbonyl-β-cyanovinyl-*N*, *N*-dialkylaniline (III) and 4-α, β-dicyanoethyl-*N*, *N*-dialkylanilines (IV) were obtained.

These addition reactions were accompanied by the production of a transient color, which would be attributed to formation of the π-complexes between I and *N*,*N*-dialkylaniline,

6) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

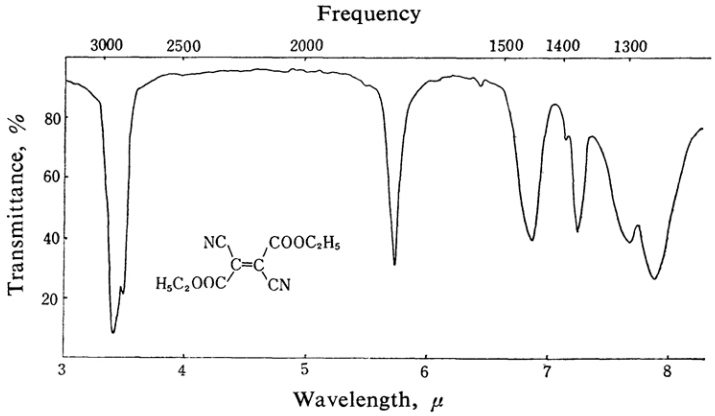
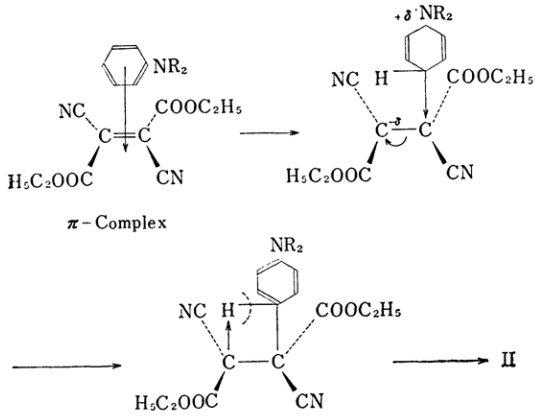


Fig. 3. Infrared absorption spectrum of I in Nujol mull.

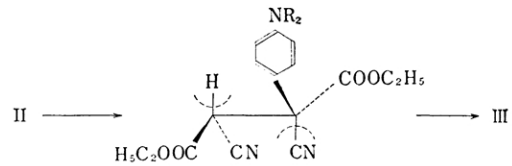
since the intense electronic absorption bands of the reaction mixture at λ_{max} 323 mμ and λ_{max} 560 mμ are attributable to neither I nor *N,N*-dimethylaniline, but to the π-complex itself as a new molecular species.

Furthermore, the course of the addition reactions was sterically specific.

From these data it appears that the addition reactions of I with *N,N*-dialkylanilines are initiated by an ionic reaction involving electron transfer from the benzene nucleus to I. This step is probably rapid and results in th π-complex formation. The second, probably rate controlling, step in the addition reactions is a rearrangement of the π-complex to yield the adducts II. Accordingly, the course of the addition reactions would be a purely cis addition as follows:



It is generally recognized that most of the base-catalized elimination reactions, e.g., elimination of hydrogen halide or cyanide, to form a new carbon-carbon double bond proceed in a trans steric course. Accordingly, the elimination of hydrogen cyanide of II should occur in a H and a CN trans orientation (staggered form) driven by a rotation about the central carbon-carbon bond.



Thus, the evidence that the elimination product III had only a ethoxycarbonyl-ethoxycarbonyl trans geometry would drive to the conclusion that I had a trans geometry for the cyano and cyano groups.

The structures of II and IV were estimated on the basis of the infrared absorption spectra (Fig. 4). The structure of III was established definitely by the following manner. The infrared absorption spectrum of III (R ; CH_3), showed C=O bands at 1720 cm^{-1} and 1736 cm^{-1} and a C≡N band at 2220 cm^{-1} (Fig. 4). As a chemical evidence, the hydrolysis of III (R ; CH_3) with sulfuric acid gave an intramolecular acid anhydride. In addition, the structure was confirmed by the use of mixture melting points of the material with 4-*trans*-α,β-diethoxycarbonyl-β-cyanovinyl-*N,N*-dialkylaniline synthesized by an another method. Finally, the geometrical structure of III was determined on the basis of the infrared absorption spectrum. As described above, the ester C=O bands at 1736 cm^{-1} and 1720 cm^{-1} were attributed to the ester groups of α- and β-position for the benzene nucleus, respectively. Since the ester group of α-position is sterically more hindered than the other ester group, the frequency of the ester group on the α-position should shift toward a shorter wavelength from the normal position. In addition, the infrared absorption spectrum of 4-α-ethoxycarbonyl-β,β-dicyanovinyl-*N,N*-dimethylaniline[7] (V) showed an ester band at 1736 cm^{-1} (Fig. 4). The fact that the infrared absorption band of the ester on the α-position

7) B. C. McKusick et al., *J. Am. Chem. Soc.*, **80**, 2806 (1958).

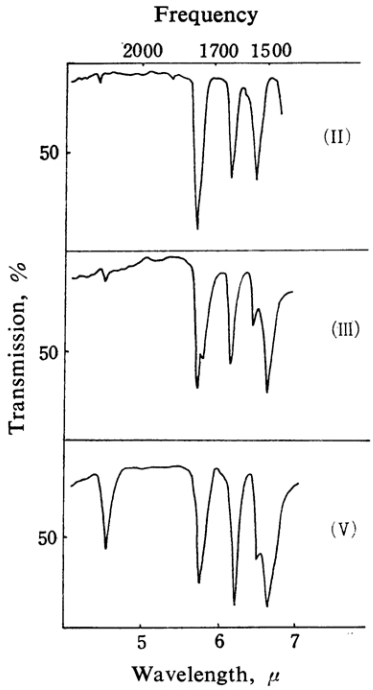
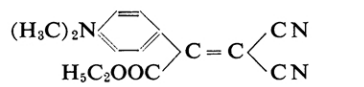


Fig. 4. Infrared absorption spectra of II, III and V.

of V coincided completely with that of the ester on the α-position of III (R ; CH_3) suggests that the α-ester group of III (R ; CH_3) is also hindered by a benzene and a cyano group, but not by an another ester group. Incidentally, Felton[8] reported that the ester C=O frequency



(V)

shifts of compounds, in which more than one ester or cyano group is attached to an ethylenic double bond, depended upon mainly the steric repulsion between these substituents. Consequently, it seems to be plausible that the configuration of III is concluded to be a trans type.

Experimental

Hydrolysis of I to Ethyl Ethylenetetracarboxylate. — A mixture of 4.4 g. of (I), 8 g. of 95% ethanol, and 8 g. of 98% sulfuric acid was heated under reflux for 7 hr. After cooling, the mixture was extracted with ether. The extract was washed with 5% sodium carbonate solution, dried with sodium sulfate, and distilled to expel ether and the residue crystallized to a colorless crystal, m. p. 54.5～55.5°C.

II(R ; CH_3).—A mixture of 22 g. (0.1 mol.) of I and 17 g. (0.14 mol.) of *N*, *N*-dimethylaniline in 50 ml. of dimethylformamide was heated at 50～60°C with stirring for 20 min. After cooling, the solvent was evaporated under reduced pressure, the residue was triturated with 50% methanol, and stood in an ice-box for several days. The solidified product was collected by filtration, washed with 50% methanol, and recrystallized from methanol-water to give 33 g. (97%) of II (R ; CH_3), m. p. 81～88°C, as colorless crystals.

Found : C, 63.07 ; H, 6.24 ; N, 12.31 ; mol. wt., 337(Rast). Calcd. for $C_{18}H_{21}O_4N_3$: C, 62.96 ; H, 6.16 ; N, 12.24% ; mol. wt., 343

Its infrared absorption spectrum had a C≡N band at 2250 cm^{-1} and a C=O band at 1760 cm^{-1}.

II(R ; C_2H_5).—In a similar procedure, II(R ; C_2H_5), m. p. 86～87.5°C, was obtained in 80% yield.

Found : C, 64.36 ; H, 6.54 ; N, 11.49 ; mol. wt., 366(Rast). Calcd. for $C_{20}H_{25}O_4N_3$: C, 64.67 ; H, 6.78 ; N, 11.31% ; mol. wt., 371.

Its infrared absorption spectrum had a C≡N band at 2250 cm^{-1} and a C=O band at 1740 cm^{-1}.

Decarbethoxylation or Elimination of Hydrogen Cyanide of II(R ; CH_3).—A mixture of 5 g. II (R ; CH_3) and 5 g. of sodium carbonate in 45 ml. of water was heated under reflux for about 20 min. to give a red oily layer. The oily layer was separated from the aqueous layer, recrystallized from benzene-petroleum benzine, and gave III (R ; CH_3), m. p. 121～122°C, as the red crystals.

Found : C, 64.45 ; H, 6.51 ; N, 8.77. Calcd. for $C_{17}H_{20}O_4N_2$: C, 64.54 ; H, 6.37 ; N, 8.86%

The crystals from the aqueous layer were collected by filtration, washed with water, and recrystallized from ethanol-water. There was obtained IV (R ; CH_3), m. p. 98～100.5°C. as yellow crystals.

Found : C, 72.25 ; H, 6.64 ; N, 21.28 ; mol. wt., 196(Rast). Calcd. for $C_{12}H_{13}N_3$: C, 72.33 ; H, 6.57 ; N, 21.09% ; mol. wt., 199.

The ultraviolet absorption spectrum of III (R ; CH_3) showed a band at λ_{max} 252 mμ (log ε ; 3.978). The infrared absorption spectrum of IV (R ; CH_3) had a C≡N band at 2250 cm^{-1} and benzene bands at 1620 cm^{-1} and 1530 cm^{-1}.

Synthesis of III (R ; CH_3) from Ethyl 4-Dimethylaminophenyl Glyoxylate.—A solution of 4 g. (0.02 mol.) of ethyl 4-dimethylaminophenyl glyoxylate, 9 g. (0.08 mol.) of ethyl cyanoacetate, and 0.5 ml. of piperidine in 7 ml. of absolute ethanol was refluxed for 30 hr. The mixture was concentrated under reduced pressure to dryness. The residue was recrystallized from benzene-petroleum benzine to give 2.8 g. (48%) of III (R ; CH_3) as red crystals, m. p. 121～122°C.

Cyclization of III (R ; CH_3) to 4-Dimethylaminophenylmaleic Anhydride.—A solution of 5 g. of III (R ; CH_3) in 40 ml. of 75% sulfuric acid was heated on boiling water for 6 hr. After cooling, the solution was poured into 100 ml. of ice-water under stirring and the aqueous mixture was neutrallized with sodium carbonate. The precipitated crystals were collected by filtration and recrystallized from acetone. There was obtained 0.8 g. (21%) of intramolecular acid anhydride in the form of dark red crystals, m. p. 179～179.5°C.

Found : C, 66.58 ; H, 5.18 ; N, 6.28 ; mol. wt., 219(Rast). Calcd. for $C_{12}H_{11}O_3N$: C, 66.35 ; H, 5.10 ; N, 6.45% ; mol. wt., 217.

8) D. G. I. Felton et al., *J. Chem. Soc.*, 1955, 2170.

Its infrared absorption spectrum showed C=O bands at 1820 cm^{-1} and 1775 cm^{-1}.

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