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The Synthesis of New Electron Acceptors, 9,10-Bis[cyano(ethoxycarbonyl)methylene]-9,10-dihydroanthracene and 10-[Cyano(ethoxycarbonyl)methylene]-9-anthrone

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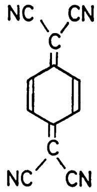
Synopsis. We synthesized two new electron acceptor molecules. Their electron affinities were estimated by measuring the charge-transfer absorption spectra with three donor molecules in a 2-methyltetrahydrofuran solution. The former molecule was estimated to have an electron affinity comparable to 1,3,5-trinitrobenzene, and the latter, to *m*-dinitrobenzene.

3,6-Bis(dicyanomethylene)-1,4-cyclohexadiene (**1**), often called TCNQ, is known to form highly conductive organic complexes with various donor molecules.1) The acceptor molecule, 9,10-bis(dicyanomethylene)-9,10-dihydroanthracene (**2**) is also expected to form highly conductive complexes, but it has not yet been synthesized. Although the attempt to prepare **2** was unsuccessful, we could obtain the precursor of **2**, 9,10-bis[cyano(ethoxycarbonyl)methylene]-9,10-dihydroanthracene (**3**), and a by-product, 10-[cyano(ethoxycarbonyl)methylene]-9-anthrone (**4**). Their electron affinities were estimated by measuring the charge-transfer (CT) absorption bands of the 2-methyltetrahydrofuran (MTHF) solution of these new acceptors and of three donor molecules.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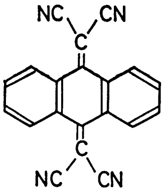
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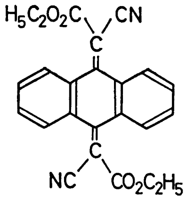
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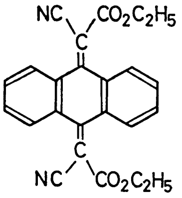
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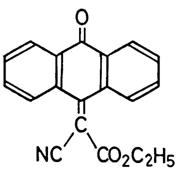
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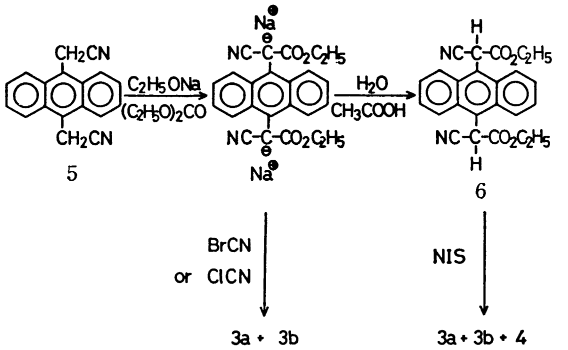
Results and Discussion

Synthesis of the New Acceptors. The synthetic route is illustrated below. 9,10-Bis(cyanomethyl)anthracene (**5**) was synthesized by the procedures described in the literature.2) The treatment of **5** with sodium ethoxide and diethyl carbonate, followed by hydrolysis, gave 9,10-bis[cyano(ethoxycarbonyl)methyl]anthracene (**6**). The dehydrogenation of **6** with *N*-iodosuccinimide (NIS) gave new electron acceptors, **3a**, **3b**, and **4**. The acceptors, **3a** and **3b**, were also obtained by the reaction of **5** with sodium ethoxide and diethyl carbonate, followed by the reaction with cyanogen chloride or cyanogen bromide.3)



Measurements of the Charge-transfer Absorption Spectra. The CT-absorption spectra of the new acceptors were measured in a 2-methyltetrahydrofuran (MTHF) solution of **3** and **4** with three donor molecules at room temperature or at 77 K. *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), *N,N*-dimethyl-*p*-phenylenediamine (DMPD), and *N,N*-dimethylaniline (DMA) were used as the donors. Figure 1 shows the electronic-absorption spectra of these donor molecules with **3**. All these solutions showed a purple color at 77 K, although the color was not seen at room temperature even with the concentrated solution. New absorption bands were observed at the region of wavelengths longer than 400 nm.4) The plot of the new

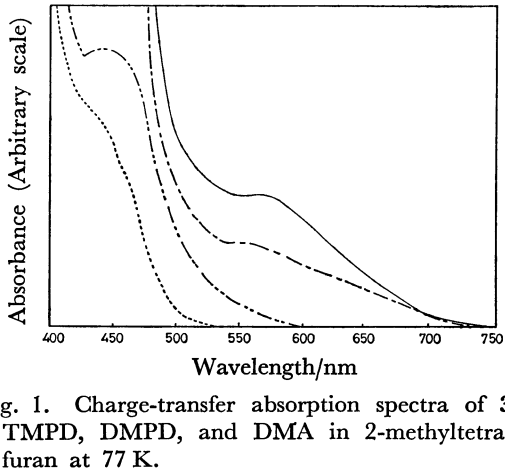


Fig. 1. Charge-transfer absorption spectra of **3** with TMPD, DMPD, and DMA in 2-methyltetrahydrofuran at 77 K.
[**3**] $= 1.37 \times 10^{-2}$ mol/l, [TMPD] $= 1.45 \times 10^{-2}$ mol/l, [DMPD] $= 1.38 \times 10^{-2}$ mol/l, [DMA] $= 2.0$ mol/l.
——: TMPD-**3**, — —: DMPD-**3**, ·······: DMA-**3**, — · —: **3** only.

absorption peak positions ($h\nu_{CT}$) against the ionization potentials (I_p) of the donor molecules[5] gave the linear relation approximated as $h\nu_{CT}=1.1\ I_p-5.3$ in eV units, which is almost identical with that obtained by the use of 1,3,5-trinitrobenzene with various donor molecules.[5] Similarly the electronic-absorption measurements of **4** with the same donor molecules at room temperature gave the linear relation of $h\nu_{CT}=0.9\ I_p-3.3$, almost identical with that obtained by the use of *m*-dinitrobenzene with various donors.[5] Thus, the new absorptions are ascribed to the CT-transition. The electron affinities of **3** and **4** are roughly equal to those of 1,3,5-trinitrobenzene and *m*-dinitrobenzene.[6]

Experimental

*Preparations of 9,10-Bis[cyano(ethoxycarbonyl)methylene]-9,10-dihydroanthracene (**3**) and 10-[Cyano(ethoxycarbonyl)methylene]-9-anthrone (**4**). 9,10-Bis[cyano(ethoxycarbonyl)methyl]anthracene (**6**)*: Sodium metal (0.5 g) was added to ethanol (20 ml), and the unreacted ethanol was distilled out. To the residual sodium ethoxide we then added a mixture of diethyl carbonate (10 g), toluene (3 ml), and **5** (1.5 g). The solution became yellow green. The resultant reaction mixture was stirred under reflux. Since the solvent was distilled out during the reaction, toluene was added from a dropping funnel in order to maintain a roughly constant volume of the reaction medium. After 1.5 h, the reaction mixture was cooled to room temperature and then hydrolysed by adding water (40 ml). Acetic acid (2 ml) was added, the mixtures was extracted three times with dichloromethane (50 ml), and the extract was shaken three times with 50 ml of water. The organic layer was separated and dried overnight over anhydrous magnesium sulfate. After the filtration of the magnesium sulfate, the dichloromethane was completely distilled out, hexane was added, we thus obtained 1.6 g of a brown solid (68%). After treatment with active charcoal, the raw material was recrystallized from diethyl ether to give a yellow powder of **6**: mp 198—205 °C; Found: C, 72.03; H, 5.01; N, 6.81%. Calcd for $C_{24}H_{20}N_2O_4$: C, 71.98; H, 5.03; N, 7.00%; MS: *m/e* 400 (M^+); IR (KBr): 2250 (C≡N), 1730 cm^{-1} (C=O); NMR ($CDCl_3$) $\delta=1.15$ (6H, m, CH_3), 4.20 (4H, m, CH_2), 6.20 (2H, s, tert H), 7.70 (4H, m, ring H), 8.30 (4H, m, ring H).

*9,10-Bis[cyano(ethoxycarbonyl)methylene]9,10-dihydroanthracene (**3a**, **3b**) and 10-[Cyano(ethoxycarbonyl)methylene]-9-anthrone (**4**) Method A*: After **5** has been reacted with sodium ethoxide and diethyl carbonate by the procedures described above, BrCN (3.75 g) was stirred in, the mixture was heated gradually up to 55—60 °C for 2 h, and kept overnight at room temperature, and the toluene was distilled out. The addition of cold water, followed by the filtration of the precipitate, gave a raw product (**3**). An additional precipitate was obtained after keeping the filtrate for several days. Purification by means of a liquid chromatograph (Japan Analytical Industry, LC 07), using chloroform as the eluent, gave 1.58 g of **3** (66%) as a pale yellow powder. In the above procedure, ClCN can also be used instead of BrCN. Compound **3**: mp 145—152, 176—182 °C, arising from *cis*- and *trans*-isomers. Found: C, 72.70; H, 4.52; N, 6.96%. Calcd for $C_{24}H_{18}N_2O_4$: C, 72.35; H, 4.55; N, 7.03%. MS: *m/e* 398 (M^+); IR (KBr) 2210 (C≡N), 1720 (C=O), 1580 cm^{-1} (C=C); NMR ($CDCl_3$) $\delta=1.25$ (6H, m, CH_3), 4.30 (4H, m, CH_2), 7.50 (4H, m, ring H), 8.15 (4H, m, ring H).

Method B: The reaction vessel was covered with aluminum foil. Into the acetonitrile (12 ml) solution of *N*-iodosuccinimide (0.6 g) we stirred, drop by drop, an acetonitrile (60 ml) solution of **6** (0.5 g) under a nitrogen atmosphere. The solution was stirred for 3 h at room temperature under the nitrogen atmosphere, 400 ml of chloroform was added, and the solution was shaken four times with 200 ml of an aqueous solution of sodium thiosulfate and potassium hydroxide (both 5%) in the separatory funnel. The organic layer was washed with water until the aqueous layer became neutral. The solution was then dried overnight over calcium chloride, and the solvent was distilled out, we thus obtained a reddish-brown oil. The addition of hexane gave a yellow powder (0.32 g). The raw material was purified by liquid chromatograph, using chloroform as the eluent, to give **3** (0.2 g, 40%) and **4** (0.1 g, 43%). The recrystallization of **4** from a benzene–hexane mixed solvent gave yellow, needle-like crystals. Compound **4**: mp 146—147 °C. Found: C, 75.00; H, 4.06; N, 4.47%. Calcd for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62%. MS: *m/e* 303 (M^+). IR (KBr) 2210 (C≡N), 1720, 1690 (C=O), 1580 cm^{-1} (C=C). NMR ($CDCl_3$) $\delta=1.20$ (3H, m, CH_3), 4.20 (2H, m, CH_2), 7.65 (4H, m, ring H), 8.24 (4H, m, ring H).

Electronic-absorption Measurements. The electronic-absorption spectra were measured by means of a Hitachi 340 recording spectrophotometer.

References

1) For example, "Molecular Metals," ed by W. E. Hatfield, Nato Conference Series, VI, Plenum Press, New York and London (1979).

2) M. W. Miller, R. W. Amidon, and P. O. Tawney, *J. Am. Chem. Soc.*, **77**, 2845 (1954); J. H. Golden, *J. Chem. Soc.*, **1961**, 3741; D. D. Reynolds and K. R. Dunham, U. S. Patent 2798971 (1957).

3) Attempts of the separation of **3a** from **3b** by repeated liquid chromatography, using chloroform as the eluent, were unsuccessful. The attempt to convert **3** or **4** to the corresponding acid amide by the reaction of **3** or **4** with aqueous ammonia or liquid ammonia was also unsuccessful.

4) The CT-absorption peak positions of **3** and **4** with three donor molecules (nm): **3**–TMPD 570; **3**–DMPD 550; **3**–DMA 475; **4**–TMPD 490; **4**–DMPD 465; **4**–DMA 430.

5) R. Foster, "Organic Charge-transfer Complexes," Academic Press, London and New York (1969), pp 40—69.

6) The electron affinities of 1,3,5-trinitrobenzene and *m*-dinitrobenzene are 0.7 eV and 0.3 eV respectively (see Ref. 5, p. 387). An irreversible chemical reaction occurred during the measurements of the cyclic voltammetry of **3** and **4**. Thus, we could not obtain their half-wave reduction potentials.