Charge-transfer Complexes of 11,11,12,12-Tetracyanoanthraquinodimethans with Various Donors

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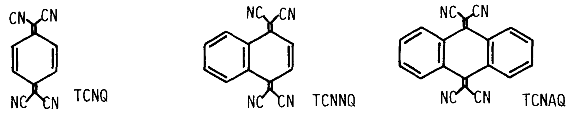
Synopsis. Titled compounds were found to form charge-transfer (CT) complexes with aromatic hydrocarbons or tetrathiafulvalene (TTF) and the molecular complexes could be isolated.

Since the high electrical conductivity was discovered in the charge-transfer (CT) complex of tetracyanoquinodimethan (TCNQ) and tetrathiafulvalene (TTF),[1] much attention has been paid to CT complexes of electron donors and acceptors such as tetracyano-1,4-naphthoquinodimethan (TCNNQ).[2,3] Recently four groups found facile synthetic methods of 11,11,12,12-tetracyanoanthraquinodimethan (TCNAQ) and its derivatives [4–7] which are dibenzo analogues of TCNQ and promising electron acceptors to form conductive complexes. However, it was reported that TCNAQ failed to form charge-transfer complexes because it is nonplanar due to a steric hindrance between the dicyanomethylene and the hydrogens at C_1, C_4, C_5, and C_8-positions.[5,8] As the first example we report here CT complexes of TCNAQs with various donors.



Scheme 1.

When naphthalene, phenanthrene, fluorene, and chrysene were used as donors, only shoulders or end absorptions due to the CT transition were observed. When pyrene, anthracene, perylene, and TTF were used as donors, however, the CT absorption maxima could be observed in the longer wavelength region since they have lower oxidation potentials.[9] These data are summarized in Table 1 together with reduction potentials. Linear correlation is observed between the CT transition energies and reduction potentials except for 1-chloro derivative **1d**, confirming that the absorptions are assigned to the CT transition. The deviation of **1d** from the line can be explained in terms of the larger steric hindrance of the substituent.[7]

In addition to the formation of the CT complexes in solution as described above, TCNAQs were found to form stable molecular complexes in solid state. They were obtained by dissolving TCNAQs and excess donors in dichloromethane. The melting points and colors of the complexes are shown in Table 2. According to elemental analyses, the mole ratio of acceptor to donor was determined to be 1:1 for benzene and diaminodurene, while that for naphthalene, anthracene, phenanthrene, pyrene, and TTF was 2:1. X-Ray analyses of **1e**–benzene complex and **1e**–pyrene complex also support that they are a 1:1 complex and a 2:1 complex, respectively.[10] This ratio is different from that of TCNNQ which is 1:2 for anthracene, phenanthrene, and pyrene.[2] This result may be attributed to the difference of the molecular sizes. Another interesting feature in the formation of the molecular complexes is that TCNAQs form complexes with benzene, while there is no report on the formation of the molecular complexes of TCNQ and TCNNQ with benzene. It should be noted that TCNAQs favorably form molecular complexes in spite of their nonplanar structures. Electical resistivities of complexes of TCNAQs **1b**, **e**, **f**, **g** with TTF show that they are insulators.[11] The high resistivities are mainly attributed to the nonplanar structures of TCNAQs.

Experimental

Materials. TCNAQ **1a** and substituted TCNAQs **1b—k** were prepared by our method[7] or Hünig's method.[4] Donors which were commercially available were purified by recrystallization or column chromatography.

Spectra. UV spectra were measured using a Hitachi 340 spectrophotometer. The charge-transfer maxima were measured at room temperature in spectrophotometric grade dichloromethane. The concentration of TCNAQs was ad-

Table 1. Charge transfer band maxima of TCNAQs with donors in CH_2Cl_2[a] and reduction potentials

TCNAQ		$E_{1/2}^{red}/V$[b]	Pyrene	Anthracene λmax/nm	Perylene[c]	TTF
H[d]	**1a**	−0.37	470^{sh}	486	540	770
2-CH_3[d]	**1b**	−0.38	470^{sh}	480	529	690
2-C_2H_5	**1c**	−0.39	470^{sh}	478	534	685
1-Cl	**1d**	−0.41	470^{sh}	486	540^{sh}	700
2-Cl	**1e**	−0.32	490	508	578	740
2-CO_2CH_3	**1f**	−0.31	495	510	594	750
2-CN	**1g**	−0.27	518	532	607	800
2-NO_2	**1h**	−0.24	530	544	630	820
2-$NHCOCH_3$	**1i**	−0.38	495	495	—[e]	690
2-NH_2	**1j**	−0.43	—[e]	—[e]	—[e]	—[e]
2-$N(CH_3)_2$	**1k**	−0.44	—[e]	—[e]	—[e]	—[e]

a) TCNAQs; 6.67×10^{-3} mol dm^{-3}, Donors; 6.67×10^{-2} mol dm^{-3}. b) Ref.7. c) Saturated solution of perylene used; 1.66×10^{-2} mol dm^{-3}. d) Ref. 4. e) No absorption maxima is observed.

Table 2. Melting points and colors of the molecular complexes

TCNAQ		Mp θ_m/°C (Color)						
		Benzene	Naphthalene	Anthracene	Phenanthrene	Pyrene	TTF	Diaminodurene
H	**1a**	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$	165—300(decomp) (green)
2-CH_3	**1b**	90—95(decomp) (yellow)	—$^{a)}$	—$^{a)}$	250—255 (orange)	226—227 (red)	200—280 (decomp) (green)	185—188(decomp) (green)
1-Cl	**1d**	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$	160(decomp) (red)	—$^{a)}$	—$^{a)}$
2-Cl	**1e**	110—120(decomp) (yellow)	160—180 (decomp) (yellow)	224—225 (violet)	220—221 (orange)	239—240 (violet)	222—224 (decomp) (green)	198—200(decomp) (green)
2-CO_2Me	**1f**	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$	160—240 (decomp) (violet)	247—251 (decomp) (indigo)	138—191(decomp) (green)
2-CN	**1g**	140—150(decomp) (yellow)	160(decomp) (orange)	245—250 (violet)	240—241 (orange)	271—272 (violet)	239—242 (decomp) (green)	188—191(decomp) (green)
2-NO_2	**1h**	—$^{a)}$	130—140 (decomp) (orange)	—$^{a)}$	217—220 (red)	255—256 (brown)	—$^{a)}$	139—140(decomp) (green)
2-$N(CH_3)_2$	**1k**	unstable(violet)	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$	—$^{a)}$

a) These complexes could not be obtained.

justed to 6.67×10^{-3} mol dm^{-3}, and that of donors to 6.67×10^{-2} mol dm^{-3} except perylene in which case a saturated solution of perylene (1.67×10^{-2} mol dm^{-3}) was used because of its low solubility.

Complex Formation. The following is a general procedure to prepare complexes of TCNAQs with donors except benzene.[12] A TCNAQ derivative and an excess donor are dissolved in dichloromethane, and carbon tetrachloride or ethanol is added in order to precipitate a complex and prevent isolation of the excess donor. Concentration of the solvent is needed if crystals do not appear. For example, **1g**-pyrene complex was prepared by the following method. **1g** 100 mg and pyrene 61 mg were dissolved in hot dichloromethane 3 ml and the solution was concentrated to 1 ml. Ethanol 0.5 ml was added and the solution was allowed to stand. Separated red micro-crystals were filtered and washed with hot ethanol.

Analytical data are as follows.[13] Bz: benzene, Nap: naphthalene, Ant: anthracene, Phen: phenanthrene, Pyr: pyrene, DAD: diaminodurene. Found, % (Calcd,† %). **1a**-DAD, C, 76.86; H, 5.07; N, 18.13 (C, 76.90; H, 5.16; N, 17.94). **1b**-Bz, C, 81.98; H, 4.35; N, 14.29 (C, 81.80; H, 4.07; N, 14.13). **1b**-Phen, C, 82.71; H, 3.95; N, 14.02 (C, 82.54; H, 3.71; N, 13.75). **1b**-Pyr, C, 83.19; H, 3.85; N, 13.49 (C, 83.40; H, 3.60; N, 13.36). **1b**-TTF, C, 68.24; H, 3.05; N, 13.22; S, 15.17 (C, 68.55; H, 2.88; N, 13.32; S, 15.25). **1b**-DAD, C, 76.53; H, 5.46; N, 17.23 (C, 77.15; H, 5.43; N, 17.41). **1b**-Pyr, C, 76.59; H, 2.98; N, 11.82; Cl, 8.47 (C, 76.45; H, 2.75; N, 12.74; Cl, 8.06). **1e**-Bz, C, 74.81; H, 3.14; N, 13.44; Cl, 8.50 (C, 74.91; H, 3.17; N, 13.78; Cl, 8.64). **1e**-Nap, C, 74.54; H, 2.97; N, 13.75; Cl, 9.08 (C, 74.54; H, 2.75; N, 13.91; Cl, 8.80). **1e**-Ant, C, 75.59; H, 3.01; N, 13.11, Cl, 8.60 (C, 75.79; H, 2.83; N, 13.09; Cl, 8.28). **1e**-Phen, C, 75.51; H, 2.93; N, 13.12; Cl, 8.47 (C, 75.79; H, 2.83; N, 13.09; Cl, 8.28). **1e**-Pyr, C, 76.29; H, 2.91; N, 12.70; Cl, 8.36 (C, 76.45; H, 2.75, N, 12.74; Cl, 8.06). **1e**-TTF, C, 63.01; H, 2.30; N, 12.71; Cl, 8.36; S, 14.59 (C, 62.65; H, 2.06; N, 12.71; Cl, 8.04; S, 14.54). **1e**-DAD, C, 71.48; H, 4.41; N, 16.69; Cl, 7.45 (C, 71.63; H, 4.61; N, 16.70; Cl, 7.05). **1f**-Pyr, C, 77.30; H, 3.28; N, 12.07 (C, 77.75; H, 3.26; N, 12.09). **1f**-TTF, C, 64.54; H, 2.73; N, 12.05; S, 13.85 (C, 64.64; H, 2.60; N, 12.06; S, 13.81). **1g**-Bz, C, 79.59; H, 3.19; N, 17.21 (C, 79.59; H, 3.22; N, 17.19). **1g**-Phen, C, 80.64; H, 2.92; N, 16.82 (C, 80.37; H, 2.89; N, 16.74). **1g**-Pyr, C, 81.18; H, 2.98; N, 16.26 (C, 80.92; H, 2.81; N, 16.27). **1g**-TTF, C, 66.24; H, 2.14; N. 16.30; S, 13.58 (C, 66.81; H, 2.10; N, 16.23; S, 14.86). **1h**-Phen, C, 74.17; H, 2.50; N, 15.45 (C, 73.97; H, 2.76; N, 15.79), **1h**-Pyr, C, 74.49; H, 2.53; N, 14.69 (C, 74.66; H, 2.69; N, 15.55).

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†These values are calculated assuming that the mole ratio of the TCNAQ to donor is 1:1 for Bz, DAD complexes, and is 2:1 for other complexes.

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10) "The details will be soon reported elsewhere" by C. Kabuto, Y. Fukazawa, T. Suzuki, Y. Yamashita, T. Miyashi, and T. Mukai.

11) Electrical resistivities were measured as compacted samples at room temperature. **1b**-TTF; $<10^{13}$ Ωcm, **1e**-TTF; 8.2×10^{10} Ωcm, **1f**-TTF; 2.7×10^{13} Ωcm, **1g**-TTF; 5.7×10^{10} Ωcm. We thank Dr. Gunzi Saito at The University of Tokyo for providing the measurement of the resistivities.

12) The benzene complexes were obtained just by recrystallization of TCNAQs from benzene.

13) All of the complexes could not be recrystallized since they easily dissociate into indivisual components by dissolution in solvent. Therefore, some complexes showed unsatisfactory elemental analyses which still establish the mole ratio of the TCNAQs to donors.