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Three-Dimensionally-Modified Tetracyanoquinodimethanes and Their Charge-Transfer Complexes with Tetrathiafulvalene Derivatives Having a Wide Range of Ionicity

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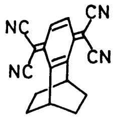
Eight different 1:1 charge-transfer(CT) complexes were prepared using tetrahydrobarreleno-tetracyanoquinodimethane(THBTCNQ), dihydrobarreleno-tetracyanoquinodimethane(DHBTCNQ), monobenzobarreleno-tetracyanoquinodimethane(MBBTCNQ), and dibenzobarreleno-tetracyanoquinodimethane(DBBTCNQ) as tetracyanoquinodimethane(TCNQ)-type acceptors, and tetrathiafulvalene(TTF), bis(tetramethyene)-tetrathiafulvalene(OMTTF), and tetramethyl-tetrathiafulvalene(TMTTF) as TTF-type donors. The complexes can be classified into three distinct groups, I—III, on the basis of the magnitude of both the degree of CT and the electrical resistivity of compacted powders. Group-I complexes are characterized by a small band gap semiconductivity and moderate CT, group-II complexes by low conductivity and small CT, and group-III complexes by low conductivity and complete CT. The stacking mode of the three groups of complexes are discussed, by comparing the electronic absorption spectra of the three groups of CT complexes with those of the complexes for which the crystal structures are known. A crystal structure analysis of OMTTF–DBBTCNQ revealed that it is the first example of a highly ionic CT complex of a TTF–TCNQ type with a regular mixed stacking mode. These three groups of complexes containing bulky acceptor groups will be of theoretical interest in studying the crystal properties of organic CT complexes.

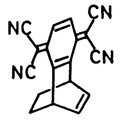
Highly-conducting organic charge-transfer (CT) complexes usually have the following structural and electronic properties in the solid state:[1] (a) a uniform segregated stacking of donors and acceptors and (b) an incomplete CT between the components. Several synthetic design criteria have been proposed for obtaining a high conductivity.[1,2] Generally, an effective overlap of the planar π-electron systems is required for an efficient charge transport. As a result, two-chain organic conductors composed of donor and acceptor components have been designed mainly with planar π-systems modified two-dimensionally. Therefore, three-dimensional modifications, which lead to a destruction of the molecular planarity, have not attracted much attention so far.[2b,3] In principle, however, such modifications will affect the following essential properties in the solid state: (i) The stacking mode of the component molecules, (ii) the ionicity, and (iii) intra- and interstack interactions. We started the first systematic study regarding these points by selecting tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) as basic skeletons. These are the most widely investigated donors and acceptors. In this paper we describe the preparations and properties of the three groups of CT complexes (having a wide range of ionicity) and stress that small band gap semiconductors (including a relatively highly conducting complex ($\rho=2.5\times10^{-2}\ \Omega\,\mathrm{cm}$)) can be prepared even from TCNQ having bulky groups. A rare example of highly ionic complexes with a mixed stacking mode was also prepared.[4]

Results and Discussion

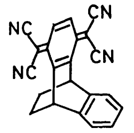
A) Classification of CT Complexes. In this study, we aimed at obtaining rigid, bulky modifications with small electronic perturbations on TCNQ (**1a**). To this end, four barreleno-TCNQ's, **1b**, **1c**, **1d**,[5] and **1e**,[6] were synthesized in which a TCNQ moiety was incorporated into the rigid barrelene skeleton.[7] The new acceptors, **1b** and **1c**, were



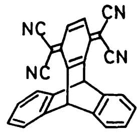
THBTCNQ
1b



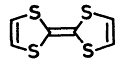
DHBTCNQ
1c



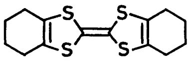
MBBTCNQ
1d



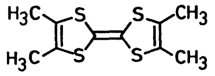
DBBTCNQ
1e



TTF
2a



OMTTF
2b



TMTTF
2c

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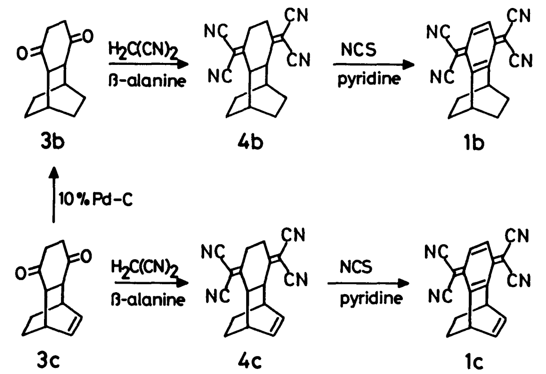
prepared by the Acker and Hertler procedure[8] for the synthesis of TCNQ (Scheme 1). The first half-wave reduction potentials ($E^{r}_{1/2}$) of **1b**—**e** show that the acceptor strength increases gently and gradually with an increasing unsaturation in the barrelene moieties[9] (Table 1). However, the difference of $E^{r}_{1/2}$ between TCNQ **1a** and both extremes **1b** or **1e** is only +0.07 V or −0.05 V, respectively. Thus, the electronic perturbation of TCNQ caused by an introduction of bridged segments is fairly small as judged from their $E^{r}_{1/2}$ values.



Scheme 1.

Table 1. Redox Potentials of Donors(**1a**—**e**) and Acceptors(**2a**—**c**) (V vs. SCE)[a)]

	1b	1c	1a	1d	1e	2a	2b	2c
$E^{r}_{1/2}$	0.11	0.14	0.18	0.18	0.23			
$E^{o}_{1/2}$						0.33	0.26	0.25

a) Measured by cyclic voltammetry in 0.1 mol dm^{-3} Et_4NClO_4/CH_3CN at a Pt electrode.

Eight different 1:1 CT complexes were prepared using **1b**—**e** as acceptors and molecules of the TTF family, namely TTF (**2a**), bis(tetramethylene)-TTF (OMTTF, **2b**), and tetramethyl-TTF (TMTTF, **2c**) as donors. Their selected physical properties are compiled in Table 2. The difference between the oxidation potential ($E^{o}_{1/2}$) of donor and the reduction potential ($E^{r}_{1/2}$) of acceptor, i.e., $\Delta E^{o,r}=E^{o}_{1/2}-E^{r}_{1/2}$, is a convenient experimental measure to predict the degree of CT for a complex.[1b,2b,2d] Such intermolecular HOMO-LUMO gap, $\Delta E^{o,r}$ values, for the eight complexes are in a narrow range (+0.02—+0.22 V) since the electronic perturbation resulting from a three-dimensional modification was nearly negligible. Therefore, we expected that the ground states of all these complexes were in incomplete CT states. The degree of CT, Z, for each complex was determined by both the infrared[10] and Raman[11] spectra. We obtained values for Z (Table 2) using the frequency shifts, $\Delta\omega$, between neutral molecules and ion-radical salts for these spectra (Tables 3 and 4). The two methods which reflect the electronic structure of both the acceptor and the donor components yield estimated Z values in good agreement each other. Interestingly, the values of Z for the complexes are in a wide range (0.1—1.0) despite the narrow range of the $\Delta E^{o,r}$ values.

These CT complexes can be classified into three distinct groups, I—III, on the basis of the magnitude of both the degree of CT, and the electrical resistivity, ρ, of compacted powders. The apparent activation energies E_a for semiconduction ($\rho=\rho_0\exp(-E_a/kT)$) are also given. Group I, II, and III complexes are characterized by a relatively high conductivity with a moderate CT (small band gap semiconducting complex), a low conductivity with a small CT

Table 2. Classification and Selected Physical Properties of Eight 1 : 1 CT Complexes

	Group I (SBGSC)[a)]		Group II (Nonionic)			Group III (Ionic)		
CT Complex	**2a-1b** TTF-THBTCNQ	**2a-1c** TTF-DHBTCNQ	**2b-1b** OMTTF-THBTCNQ	**2b-1c** OMTTF-DHBTCNQ	**2c-1c** TMTTF-DHBTCNQ	**2b-1d** OMTTF-MBBTCNQ	**2b-1e** OMTTF-DBBTCNQ	**2c-1e** TMTTF-DBBTCNQ
$\Delta E^{o,r}$, V	+0.22	+0.19	+0.15	+0.12	+0.11	+0.08	+0.03	+0.02
IR, cm^{-1}	2179	2177	2208	2209	2204	2180	2175	2176
(Z)[b)]	(0.76)	(0.84)	(0.11)	(0.13)	(0.24)	(0.92)	(1.00)	(0.97)
Raman, cm^{-1}	1444	1445	1510	1503	1500	1415	1422	1427
(Z)[b)]	(0.74)	(0.75)	(0.22)	(0.28)	(0.31)	(0.98)	(0.93)	(0.92)
ρ_{RT}, Ω cm[c)]	2.8 2.5×10^{-2} [d)]	13	6.8×10^{5}	5.5×10^{7}	4.2×10^{6}	2.1×10^{6}	2.2×10^{7}	2.8×10^{3}
E_a, eV	0.095 0.045[d)]	0.14	0.39	0.44	0.36	0.34	0.64	0.30
$h\nu_{CT}$ (obsd), cm^{-1}	4100	3700	5300	5100	4500	5600	6300	Shoulder
$h\nu_{CT}$ (calcd), cm^{-1} [b)]	4900	5200	5200	5000	4900	6000	6500	6500

a) Small band gap semiconductor. b) See text. c) Compacted powder measurements. d) Single crystal measurement.

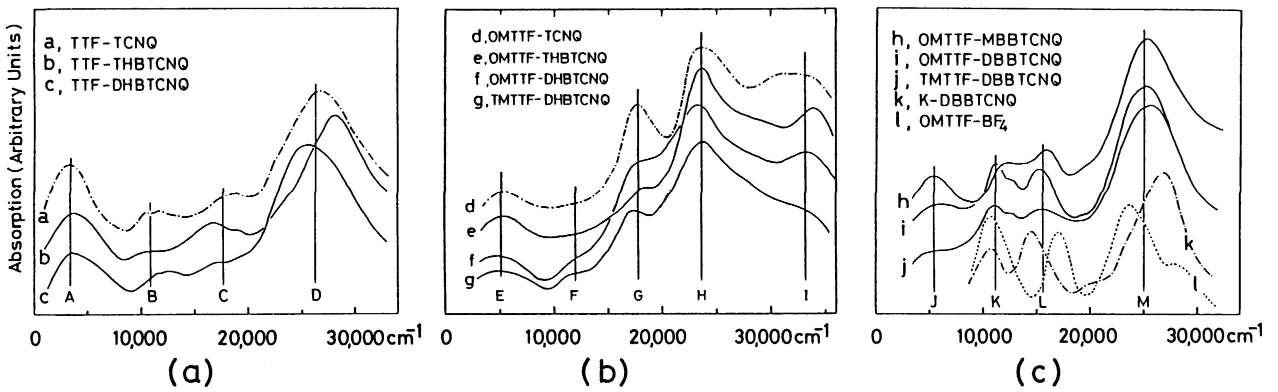


Fig. 1. Absorption spectra of three distinct groups of CT complexes as powders dispersed in KBr.

Table 3. Infrared Frequencies ($\omega_{C\equiv N}$, cm^{-1}) of Acceptors

	1a[b]	1b	1c	1d	1e
Neutral	2227	2213	2215	2216	2217
Anion radical[a]	2183	2168	2170	2177	2175
$\Delta\omega$	44	45	45	39	42

a) K salts. b) Ref. 10.

Table 4. Raman Frequencies ($\omega_{C=C}$, cm^{-1}) of Donors

	2a[b]	2b	2c[b]
Neutral	1518	1537	1537
Cation radical[a]	1420	1413	1418
$\Delta\omega$	98	124	119

a) BF$_4$ salts. b) Ref. 11.

(nonionic complex), and a low conductivity with a complete CT (ionic complex), respectively.

B) Electronic Spectra and Prediction of Stacking Mode. The stacking modes of the components are essential for understanding the solid-state properties of CT complexes. One of the group-III complexes, bis(tetramethylene)tetrathiafulvalene(OMTTF)-dibenzobarrelenotetracyanoquinodimethane(DBBTCNQ), crystallizes in a monoclinic lattice. However, group-I complex crystals are not suitable for X-ray structure analyses and group-II complexes gradually decomposed upon X-ray irradiation. Therefore, we estimated the stacking mode by comparing the electronic spectra of the three groups of CT complexes with those of the complexes for which the crystal structures are known. We will discuss the electronic spectra of powdered samples since they provide useful information, particularly for cases of CT complexes composed of TTF or TCNQ skeletons.[12]

For group-I complexes, we selected TTF-TCNQ as a reference complex. The two requisites, (a) and (b), for the highly conducting organic complexes, TTF-TCNQ for example, can be substantiated by the detection of a very low energy absorption band at about 3000 cm^{-1}. This was determined to be an intrastack CT transition in a segregated stack with an incomplete CT (intraband transition).[12a,13] Figure 1(a) shows the solid-state electronic spectra of TTF-THBTCNQ and TTF-DHBTCNQ as well as that of TTF-TCNQ. In addition to the similarity of the spectra between TTF-TCNQ and group-I complexes in bands B, C, and D, the presence of band A at about 4000 cm^{-1} suggests that the group-I complexes possess a segregated stacking mode. The electrical resistivity for a single crystal of TTF-THBTCNQ ($\rho=2.5\times10^{-2}\ \Omega$ cm) is fairly low and about two orders of magnitude smaller than that for a compacted powder sample. Such small resistivity and activation energy also support the prediction of a segregated stacking mode for the group-I complexes, although more data are needed to make this argument conclusive.

Group-II complexes are characterized by their nonionic nature. Such properties closely resemble those of OMTTF-TCNQ. We estimated the value of Z as 0.25 for OMTTF-TCNQ using the nitrile stretching frequency (2216 cm^{-1}). The crystal structure shows a mixed stack of alternating donor and acceptor components.[14] As shown in Fig. 1(b)[15] we found a weak CT transition for OMTTF-TCNQ (curve d) at 5100 cm^{-1} (band E). The strong absorption bands H and I are nearly identical with the molecular absorption of neutral TCNQ and OMTTF, respectively: this is consistent with the small degree of CT of the complex. These spectral features are recognized exactly in group-II complexes (Fig. 1(b)). Hence, we expect that group-II complexes possess a mixed stacking mode.

Group-III complexes are characterized by an almost completely ionic nature. In agreement with the complete CT, the absorption bands K, L, and M of group-III complexes were also found in the ionic salts of corresponding components, K-MBBTCNQ, K-DBBTCNQ and OMTTF-BF_4 (Fig. 1(c)). Furthermore, an additional band at 6000 cm^{-1} (band J) was observed for each of the group-III complexes, which can be assigned to a back CT transition between the anion and the cation radicals.[16] These results strongly suggest a mixed stacking mode of this group. The crystal structure of OMTTF-DBBTCNQ actually contains a mixed stacking donor and an acceptor (vide infra).

The single-crystal polarized reflection-spectra revealed that the CT band E of OMTTF-TCNQ and J of OMTTF-DBBTCNQ proved to be a transition polarized along the c-axis. This is very close to the stacking direction of the donor and the acceptor.[17] Furthermore, OMTTF-TCNQ is shown to be mostly nonionic with two CT configurations in which the lowest energy one contributes to the ground state only to a small extent, and OMTTF-DBBTCNQ to be ionic with only one CT configuration in the ground state by means of the analysis of the crystal and electronic structure.

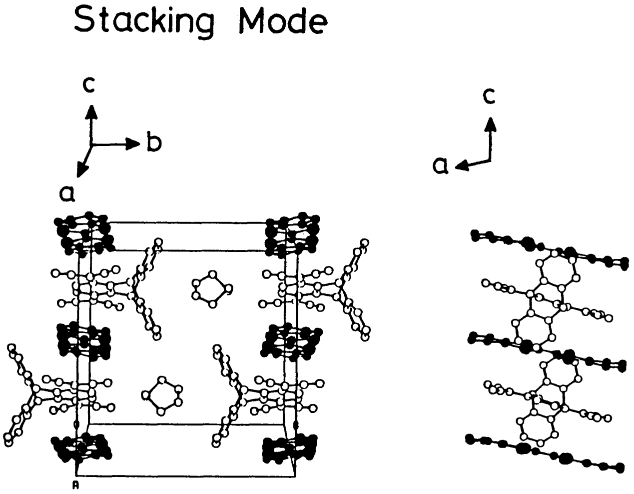


Fig. 2. Two views of the molecular packing in the crystal structure of OMTTF–DBBTCNQ–C_6H_6; (left) a view along a* axis, and (right) a view along b axis.

Recently, Torrance et al. showed the simple linear relationship[16] between the energies of the CT transition ($h\nu_{\mathrm{CT}}$) and the intermolecular HOMO–LUMO gap ($\Delta E^{\mathrm{o,r}}$): $h\nu_{\mathrm{CT,neutral}}=\Delta E^{\mathrm{o,r}}+0.5$; $h\nu_{\mathrm{CT,ionic}}=0.83-\Delta E^{\mathrm{o,r}}$ (eV). Using this equation, we calculated the $h\nu_{\mathrm{CT}}$ values for each complex of the three groups. These are summarized in the last two rows of Table 2 together with the observed values. The agreement is good for both the nonionic group II and the ionic group III complexes, considering the simplicity of the approximation. In addition, the calculated value for OMTTF-TCNQ (5000 cm^{-1}) is also in good agreement with the observed one (5100 cm^{-1}) (vide supra). However, for the ionic group I complexes, the agreement is relatively poor. This also supports our estimation for the stacking mode as a segregated but not a mixed type.

C) Crystal Structure of OMTTF-DBBTCNQ.

OMTTF-DBBTCNQ contains a solvent molecule, benzene (see experimental section). As shown in Fig. 2, the donor and the acceptor form mixed stacking columns along the c-axis with alternating the two components. The acceptors arrange themselves in a columnar array so as to release any unfavorable steric repulsion between the bulky dibenzo-barreleno moiety on TCNQ. The mean separation distance between the π-electron frameworks of the donor and acceptor is 3.46 Å. The dihedral angle between the two planes is about 1.26°. The overlapping mode and a view of the interstack interaction are depicted in Fig. 3. The two components are shifted from the direct overlap mode as found in OMTTF-TCNQ,[14] in which the symmetry plane perpendicular to the long axis coincides nearly with each other. Interestingly, there exist no short interstack interactions of the S···S and S···N types. The shortest S···N contact distance is 4.69 Å, and is much longer than the sum of the appropriate van der Waals radii. Thus, the mixed columns in OMTTF-DBBTCNQ are completely

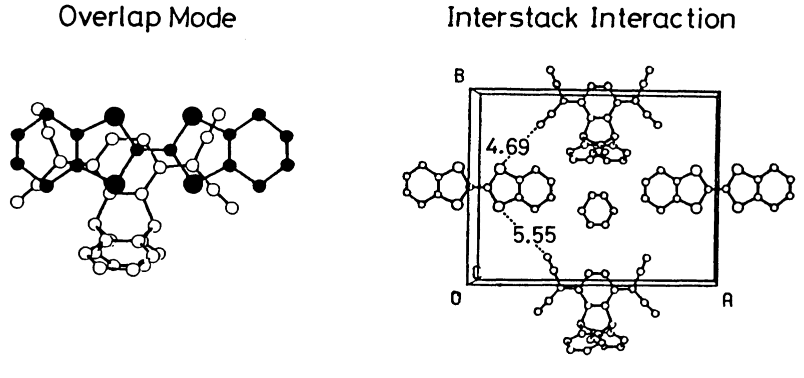


Fig. 3. Overlap mode; (left) viewed along the normal to the TCNQ plane. Interstack interaction; (right) viewed along c axis.

Table 5. Typical Examples of Mixed Stacking Mode Complexes of TTF-TCNQ Type

	Z[a]	Interplanar spacing (Å)	Overlap mode	Interstack S···N distance (Å)
OMTTF-TCNQ[b]	0.25[c]	3.53	Direct	3.36
TMTSF-TCNQ[d]	0.21[e]	3.5	Direct	3.56
DBTTF-TCNQ[f,g]	0.25[f]	3.30	Shifted	
	0.47[g]	3.4		3.48
DBTTF-TCNQF$_2$[g]	0.65[g]	3.4	Shifted	3.47
OMTTF-DBBTCNQ[c]	1.0[c]	3.46	Shifted	4.69

a) Values determined by IR procedure. b) Ref. 14. c) This work. d) Ref, 18. e) Ref. 10. f) H. Kobayashi and J. Nakayama, *Bull. Chem Soc. Jpn.*, **54**, 2408 (1981). g) Ref 20.

Table 6. Degree of CT Determined from TCNQ Geometries[a]

	Ratio[b] $c/(b+d)$	Calculated CT (Z)
TCNQ^0 [a]	0.476	0.00
TCNQ$^-$ [a]	0.500	1.00
OMTTF-TCNQ	0.474	−0.08[c]
OMTTF-DBBTCNQ	0.502	1.08

a) Ref. 18. b) Bond lengths were averaged over assumed mmm symmetry. c) Bond lengths used in this calculations were taken from Ref. 14.

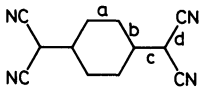
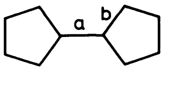


Table 7. Comparison of Bond Lengths (Å) in TTF Skeleton of Neutral and Ionic States

	a[d]	Δa	b[d]	Δb
TTF[a]	1.349		1.757	
TTF$^+$ClO$_4^-$ [b]	1.404	0.055	1.713	−0.044
OMTTF[c]	1.326		1.759	
OMTTF-TCNQ[c]	1.330	0.004	1.758	−0.001
OMTTF-DBBTCNQ	1.388	0.062	1.716	−0.043

a) W. F. Cooper, N. C. Kenny, J. N. Edmonds, A. Nagel, F. Wudl, and P. J. Coppens, *J. Chem. Soc., Chem. Commun.*, **1971**, 889, b) K. Yakushi, S. Nishimura, T. Sugano, and H. Kuroda, *Acta Crystallogr.*, **B36**, 358 (1980). c) Ref. 14. d) Bond lengths were averaged over assumed mmm symmetry.



isolated from each other (Table 5).

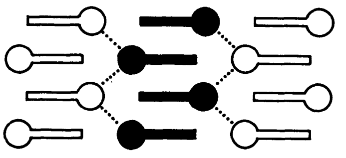
Applying the bond-length-ratio procedure of Kistenmacher et al.,[18] we calculated the degree of CT as shown in Table 6. For OMTTF-DBBTCNQ, the calculated Z is 1.08, which indicates a complete charge transfer. This value is consistent with the Z determined by IR and Raman procedures. Furthermore, the donor geometry also suggests a strong ionic nature (Table 7). Thus, the difference in the central double-bond length between OMTTF and OMTTF in the complex, 0.062 Å, is comparable to that between TTF and TTF-ClO$_4$, 0.055 Å. The same procedure for OMTTF–TCNQ leads to the result that there is no charge on the donor or the acceptor. This is in good agreement with an estimation by the IR procedure.

Conclusion

Usually, the ionicity of CT complexes can be controlled by selecting the donor–acceptor combination so as to change the $\Delta E^{o,r}$ values to a large extent. It should be noted that we prepared the three groups of CT complexes with a wide range of ionicity using the three dimensionally modified TCNQ's, despite the small electronic perturbation on the acceptor and the narrow range of $\Delta E^{o,r}$ values. However, another important feature in this study is that the $\Delta E^{o,r}$ values are kept small at a positive region near zero, the so-called neutral-ionic boundary.[16] Therefore, our results indicate that, in these conditions, the solid-state properties are influenced to a large extent by small steric and/or electronic perturbations in the three-dimensional modifications which influence the intra- and interstack interactions in the complexes.

Recently, Soos et al. presented experimental and theoretical aspects regarding ionicity and paramagnetism of strong organic CT complexes. One of their important results was that TMPD-TCNQF$_4$ is the first highly ionic ($Z \geq 0.9$) and paramagnetic organic CT complex to be found with a regular mixed stacking mode.[19] Although OMTTF-DBBTCNQ is found to be another example of such a highly ionic CT complex, the complex is, to best of our knowledge, the first example for the TTF-TCNQ type complexes. The Z value of 0.65 of DBTTF-TCNQF$_2$[20] is the most strong ionicity known so far in mixed-stacking mode complexes of the TTF–TCNQ type (Table 5). Interestingly, although the acceptor strengths of MBBTCNQ and DBBTCNQ are close to that of TCNQ and much weaker than that of TCNQF$_4$,[21] the group III complexes are complete CT.

In addition, relatively highly-conducting complexes were also prepared, although our modification leads to the TCNQ's carrying the bulky groups. All these results will be of theoretical interest in studying the crystal properties of organic CT complexes.[22] Finally, this study may open an unexplored area for chemical modifications to design molecular conductors, since many variations of the barrelene skeleton are possible.[23] Furthermore, if such molecules with bulky groups pack in a crystal as shown schematically in **5**, a segregated stacking mode of CT complexes will be formed. This is our model for future studies concerning new effects of three-dimensional modifications on intra- and interstack interactions, that is, the enhancement of low dimensionality and introduction of a new types of interstack interactions.



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Experimental

General. All the melting points are uncorrected. Infrared spectra and electronic spectra were recorded on JASCO DS-402G and Hitachi 340 spectrometers, respectively. Each IR spectrum was calibrated with indene as the standard. Laser Raman spectra were recorded with Ar$^+$ (514.8 nm) excitation by using a JASCO R-800 spectrometer for samples of KBr disks or powders. Proton NMR spectra were measured by using Varian XL-100-15 and JEOL JNM-PMX-60 spectrometers. All chemical shifts are reported in parts per million (δ) relative to internal tetramethylsilane. The cyclic voltammetry was carried out at room temperature under nitrogen using Yanagimoto P-1100. The electrical resistances for the compacted pellet and the single crystal were measured with two probe and four probe methods, respectively.

Preparation of the Acceptors. **5,8-Bis(dicyanomethylene)-1,4,4a,6,7,8a-hexahydro-1,4-ethanonaphthalene (4c).** A mixture of 1,4,4a,6,7,8a-hexahydro-1,4-ethanonaphthalene-5,8-dione (**3c**)[24] (2.99 g, 15.7 mmol), malononitrile (3.12 g, 47.2 mmol) and β-alanine (18 mg, 0.20 mmol) in 3.5 mL of water was stirred for 9 h at 70 °C. The crude product was recrystallized from acetonitrile to give 3.06 g (68%) of **4c** as yellow prisms: Mp 244—245 °C; ^{1}H NMR (CD_2Cl_2) δ=1.67 (4H, m, H-5,6), 2.88 (6H, br s, H-1,4,9,10), 3.49 (2H, br s, H-7,12), 6.33 (2H, q-like, H-2,3); IR (KBr) 2230 cm^{-1}. Found: C, 75.46; H, 4.97; N, 19.72%. Calcd for $C_{18}H_{12}N_4$: C, 75.51; H, 4.93; N, 19.57%.

1,2,3,4,4a,6,7,8a-Octahydro-1,4-ethanonaphthalene-5,8-dione (3b). The hydrogenation of **3c** with 10% Pd-C in methanol gave **3b** (93%) which continued to produce **4b**.

5,8-Bis(dicyanomethylene)-1,2,3,4,4a,6,7,8a-octahydro-1,4-ethanonaphthalene (4b). A mixture of **3b** (20 g, 0.104 mol), malononitrile (16.5 g, 0.25 mol) and β-alanine (250 mg) in 5 mL of water was stirred for 3 d at 65—75 °C. The crude product was recrystallized from acetonitrile-benzene to give **4b** (37%) as colorless needles: Mp 167—168 °C, IR (KBr) 2230 cm^{-1}; Found: C, 74.65; H, 5.53; N, 19.38%. Calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43%.

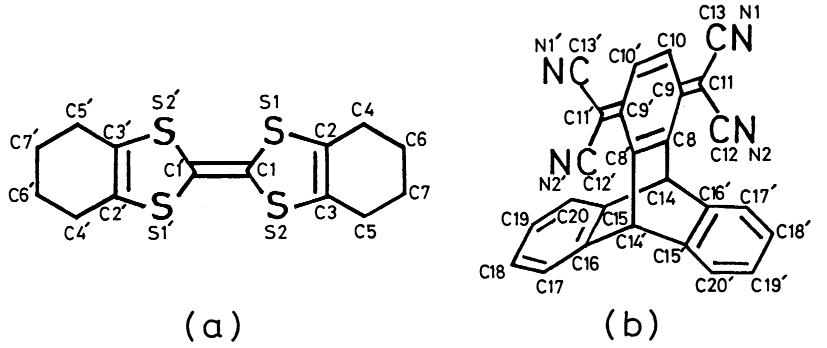
5,8-Bis(dicyanomethylene)-1,4-dihydro-1,4-ethanonaphthalene (dihydrobarreleno-TCNQ, DHBTCNQ) (1c). A mixture of **4c** (1.01 g, 3.51 mmol), *N*-chlorosuccinimide (1.61 g, 12.0 mmol), pyridine (1.15 mL, 14.2 mmol) and dichloromethane (60 mL) was refluxed for 4 h. After the usual workup, the crude product was purified by column chromatography on silica gel. Elution with dichloromethane yielded 0.72 g (73%) of **1c** as red solids which was recrystallized from methanol: Red needles, mp 171.5—173.5 °C; ^{1}H NMR ($CDCl_3$) δ=1.63 (4H, AA′BB′, H-5,6), 5.31 (2H, br s, H-1,4), 6.52 (2H, q-like, H-2,3), 7.41 (2H, s, H-9,10); IR (KBr) 2215 cm^{-1}; UV λ_{max} (CH_3CN) 248 (log ε 3.71), 380 (sh, 4.46), 401 (4.59), 460 nm (sh, 3.98).

5,8-Bis(dicyanomethylene)-1,2,3,4-tetrahydro1,4-ethanonaphthalene (tetrahydrobarreleno-TCNQ, THBTCNQ) (1b). The title compound was prepared as described above (67%): Golden yellow needles (recrystallized from C_6H_6-C_6H_{12}), mp 195—197 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=1.65 (8H, m, H-2,3,5,6), 4.24 (2H, br s, H-1,4), 7.43 (2H, s, H-9,10); IR (KBr) 2213 cm^{-1}; UV λ_{max} (CH_3CN) 244 (log ε 3.68), 402 nm (4.61). Found: C, 76.10; H, 4.24; N, 19.61%. Calcd for $C_{18}H_{12}N_4$: C, 76.04; H, 4.25; N, 19.71%.

Preparation of Charge-Transfer Complexes. All CT complexes described in this paper were prepared by

Table 8. Solvents Used for the Preparation of Eight CT Complexes and Their Properties

	2a-1b	2a-1c	2b-1b	2b-1c	2c-1c	2b-1d	2b-1e	2c-1e
Solvent	CH_3CN	CH_3CN	C_6H_6	C_6H_6	CH_3CN/ C_6H_6	Cl-C_6H_5	C_6H_6	C_6H_6
Yield/%	78	32	69	81	25	84	80	80
Appearance	Black needles	Deep-violet needles	Reddish-purple needles	Purple needles	Deep-violet needles	Dark-green needles	Dark-purple needles	Deep-purple needles
Mp (θ_m/°C) (decomp)	148	138	180	178	161	179	170	193



(a) (b)

Fig. 4. Atomic numbering scheme of OMTTF-DBBTCNQ. OMTTF (a) and DBBTCNQ (b) lie on the center of symmetry and the two-fold axis, respectively.

Table 9. Crystallographic Data for OMTTF-DBBTCNQ-C_6H_6

Formula	$C_{40}H_{28}N_4S_4$ C_6H_6
Formula wt	771.0
Crystal system	Monoclinic
Space group	*C2/c*
a, Å	18.535(2)
b, Å	14.417(2)
c, Å	14.906(3)
β, deg	98.89(1)
V, Å^3	3935.3(9)
Z	4
Scan type	θ—2θ
Max 2θ, deg	120
No. of reflections	2380 with $F_{\text{obsd}} \geq 2\sigma(F)$
R	0.091

Table 10. Selected Interatomic Distances (l/Å) and Angles (deg) in OMTTF-TCNQ

Bond Legths(l/Å)		Bond Angles(ϕ/°)	
C(1)-C(1′)	1.390(8)	C(1′)-C(1)-S(1)	123.3(4)
C(1)-S(1)	1.715(6)	C(1′)-C(1)-S(2)	122.0(4)
C(1)-S(2)	1.716(6)	S(1)-C(1)-S(2)	114.6(3)
S(1)-C(2)	1.724(6)	C(1)-S(1)-C(2)	96.6(3)
S(2)-C(3)	1.745(7)	C(1)-S(2)-C(3)	95.4(3)
C(2)-C(3)	1.329(9)	S(1)-C(2)-C(3)	116.2(5)
		S(2)-C(3)-C(2)	117.1(5)
C(8)-C(8′)	1.377(7)	C(8′)-C(8)-C(9)	122.3(4)
C(8)-C(9)	1.418(7)	C(8′)-C(8)-C(14)	112.9(4)
C(9)-C(10)	1.431(7)	C(9)-C(8)-C(14)	124.8(4)
C(9)-C(11)	1.416(7)	C(8)-C(9)-C(10)	115.2(5)
C(10)-C(10′)	1.356(8)	C(8)-C(9)-C(11)	127.3(5)
C(11)-C(13)	1.408(8)	C(10)-C(9)-C(11)	117.5(5)
C(11)-C(12)	1.393(9)	C(9)-C(10)-C(10′)	122.5(5)
N(1)-C(13)	1.149(9)	C(9)-C(11)-C(12)	127.5(5)
N(2)-C(12)	1.170(10)	C(9)-C(11)-C(13)	119.6(5)
		C(12)-C(11)-C(13)	112.9(5)
		C(11)-C(12)-N(2)	175.7(7)
		C(11)-C(13)-N(1)	179.6(7)

mixing solutions of donors and acceptors at 20—40 °C. The complexes usually precipitated out immediately. The 1:1 stoichiometries of donors and acceptors were determined by elemental analyses which agree with calculated values within ±0.4% for C, H, N, and S. In the case of OMTTF-DBBTCNQ, solvent molecule, benzene, was included in the crystals; elemental analysis and crystal-structure analysis indicated the molecular ratio of the components, OMTTF:DBBTCNQ:benzene, to be 1:1:1. The solvents used for the preparation of the complexes and their properties are summarized in Table 8.

Crystal Structure Analysis of OMTTF-DBBTCNQ. X-Ray data were collected on a Rigaku four-circle diffractometer of the Crystallographic Research Center, Institute for Protein Research, Osaka University. Ni-filtered Cu *Kα* radiation was provided by a Rigaku rotating anode X-ray generator operated at 40 kV and 200 mV. Crystallographic data are given in Table 9. The structure was solved by direct method, using the program MULTAN 78, and refined by the block-diagonal anisotropic least-squares methods to final *R* value of 0.091. The hydrogen atoms were not included in the refinement. The atomic numbering scheme, bond lengths, and bond angles are shown in Fig. 4 and Table 10, respectively. Tables of structure factors, atomic and thermal parameters, bond lengths and angles are deposited as Document No. 8605 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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