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The Crystal Structure and Physical Properties of the 3:2 Charge Transfer Complex of Bis(ethylenedithio)dithiapyrene (ETDTPY) and Dibenzobarrelenotetracyanoquinodimethane (DBBTCNQ)

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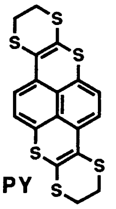
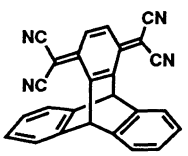
The V-shape correlation between $h\nu_{CT}$ and $\Delta E^{o,r}$ of the charge transfer complexes is convenient to judge the gross features of the solid state properties. Using this correlation, we found the 3:2 charge transfer complex of bis(ethylenedithio)dithiapyrene (ETDTPY) and dibenzobarrelenotetracyanoquinodimethane (DBBTCNQ) which showed the columnar structure of alternating trimeric stack of the donor and dimeric stack of the acceptor.

Recently, we have designed and synthesized the peri-condensed Weitz-type donors, such as dithiaperylene (DTPR), dithiapyrene (DTPY), and their alkylthio substituted derivatives.1) These donors produced a variety of electrically conducting charge transfer (CT) complexes and salts, including organic molecular metals and highly conducting semi-conductors. During these studies, we found a convenient utility of the V-shape correlation, reported by Torrance, *et al.*,2) between $h\nu_{CT}$ and $\Delta E^{o,r}$ to judge the gross features of the solid state properties of the CT complexes.3) Here, $h\nu_{CT}$ and $\Delta E^{o,r}$ denote the CT transition energies and the difference between the oxidation potential of donor and the reduction potential of acceptor, respectively. By using the V-shape correlation, we can simply classify the CT complexes into three groups, neutral, ionic, and non-V-shape group.3a) The non-V-shape group has high possibility to show high conductivity or even metallic conductivity having a segregated stacking structure, or to possess a different crystal structure from usual alternated stacking structures. The former examples have already been reported.3a) As a latter example, we now present the crystal structure of the 3:2 charge transfer complex of bis(ethylenedithio)dithiapyrene (ETDTPY)1b) and dibenzobarrelenotetracyanoquinodimethane (DBBTCNQ).3c, 4)

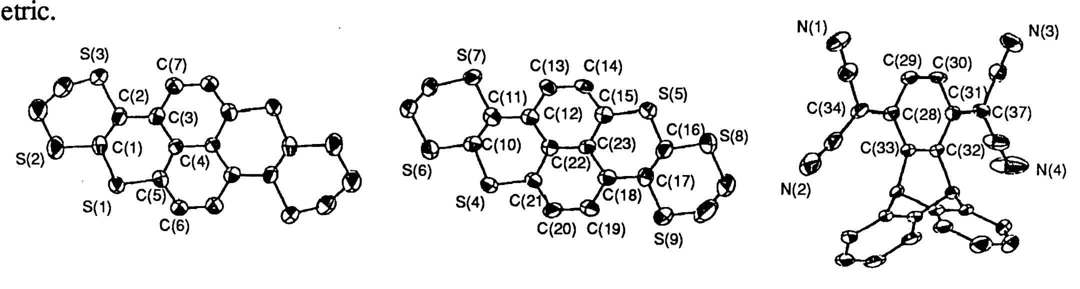

ETDTPY


DBBTCNQ

Peri-condensed Weitz-type donor, ETDTPY, is designed so as to increase the number of chalcogen sites responsible for interstack interactions in the solid state, like bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF). We found some resemblance in physical properties, such as the oxidation potentials (0.48 and 0.83 V)1b) and the crystal structure,5) between the two donors. It's, however, difficult to obtain single crystals of CT complexes of ETDTPY suitable for measurements of the solid state properties and X-ray crystal structure analysis. In such situation, we recently obtained the CT complex with DBBTCNQ.3b) The $\Delta E^{o,r}$ value for the donor and acceptor combination is 0.25 V, since the oxidation potential of the donor and the reduction potential of the acceptor are 0.48 V and 0.23 V,[3c)] respectively. The solid state electronic absorption spectrum of the complex showed a low energy band at 0.50 eV. The V-shape correlation is expressed by the following two equations: for $\Delta E^{o,r} > 0.13$, $h\upsilon_{CT} = \Delta E^{o,r} + 0.5$, and for $\Delta E^{o,r} < 0.13$, $h\upsilon_{CT} = 0.83 - \Delta E^{o,r}$ In the present case, we obtain 0.75 eV as the calculated $h\upsilon_{CT}$ using the former equation. Therefore, the observed $h\upsilon_{CT}$, 0.5 eV, deviates from the correlation to the lower energy side by 0.25 eV. We classify such a complex to the non-V-shape group. Taking into consideration of the the value of conductivity of a single crystal, 3.7×10^{-3} Scm^{-1}, which is not so high value, we can expect this complex might have a different crystal structure from those of the usual CT complexes having the alternated stacking donor and acceptor component.

The single crystals of the CT complex, (ETDTPY)$_3$(DBBTCNQ)$_2$, were prepared as black needles by slow evaporation by standing of a solution of the donor and the acceptor in 1:1 mixture of methylenechloride and *n*-hexane. The stoichiometry was determined by both elemental analysis[6)] and crystal structure analysis. Crystal data[7)]: $C_{106}H_{60}N_8S_{18}$, P1, a = 14.282 (4), b = 14.900 (4), c = 11.783 (3) Å, α = 110.72 (2), β = 100.35 (2), γ = 98.91 (2)° , V = 2241 (1) Å^3, D_c = 1.50 g/cm^3, Z = 1.

The atomic numbering scheme and the selected bond lengths of the donor and acceptor components of (ETDTPY)$_3$(DBBTCNQ)$_2$ are shown in Fig. 1. The crystal structures viewed along the c and b axes are shown in Fig. 2. The donor molecules, A, B, and C, form the trimeric stacks rotating the long axis by around 60°, to avoid the steric repulsion between the non-planar and bulky ethylenedithio moieties (Figs. 2 and 3 (a)). The trimeric stack contains a center of symmetry. The planarity of the centrosymmetric molecule (B) is higher than the others (A and C). The deviations from the mean plane of the dithiapyrene skeleton are as follow: for the molecule B, S(1); -0.032, C(1); 0.035, C(4); 0.020, and C(2); -0.015, and for the molecule A (and C), S(4); -0.145, S(5); -0.258, C(10); 0.184, C(11); 0.120, C(16); 0.159, C(17); 0.254, C(20); -0.115, C(21); 0.081 Å. The overlap mode between the donors is shown in Fig. 4 (a). The distances of S···S contacts in an intratrimeric stack, d_1 and d_2 (Fig.2 (a)), are 3.69 and 3.83 Å, respectively. The distances of those between intertrimeric stacks, d_4 and d_5 (Fig.2 (b)), are 3.66 and 3.77 Å, respectively. Therefore, the trimeric stacks contain no strong contacts between the stacks. The acceptor molecules, E and F for example, form the dimeric stacks which are also centro-symmetric.



Donor (B) Donor (A or C) Acceptor (E or F)

Fig. 1. The numbering scheme the donor and the acceptor components of (ETDTPY)$_3$(DBBTCNQ)$_2$: (a) the centrosymmetric donor (B) and (b) the noncentrosymmetric donor (A or C), and (c) the acceptor (E or F). The selected bond lengths (Å): S(1)-C(1); 1.707, C(1)-C(2); 1.375, C(3)-C(4); 1.416, C(4)-C(5); 1.450, C(5)-S(1); 1.727, S(4)-C(10); 1.757, C(10)-C(11); 1.323, C(11)-C(12); 1.474, C(12)-C(13); 1.384, C(13)-C(14); 1.392, C(14)-C(15); 1.381, C(15)-S(5); 1.724, S(5)-C(16); 1.739, C(16)-C(17); 1.339, C(17)-C(18); 1.485, C(18)-C(19); 1.379, C(19)-C(20); 1.416, C(20)-C(21); 1.372, C(21)-S(4); 1.734, C(28)-C(29); 1.437, C(29)-C(30); 1.330, C(30)-C(31); 1.434, C(31)-C(32); 1.437, C(32)-C(33); 1.382, C(33)-C(28); 1.443, C(28)-C(34); 1.403, C(31)-C(37); 1.409, C-N(1); 1.155, C-N(2); 1.150, C-N(3); 1.145, C-N(4); 1.146.

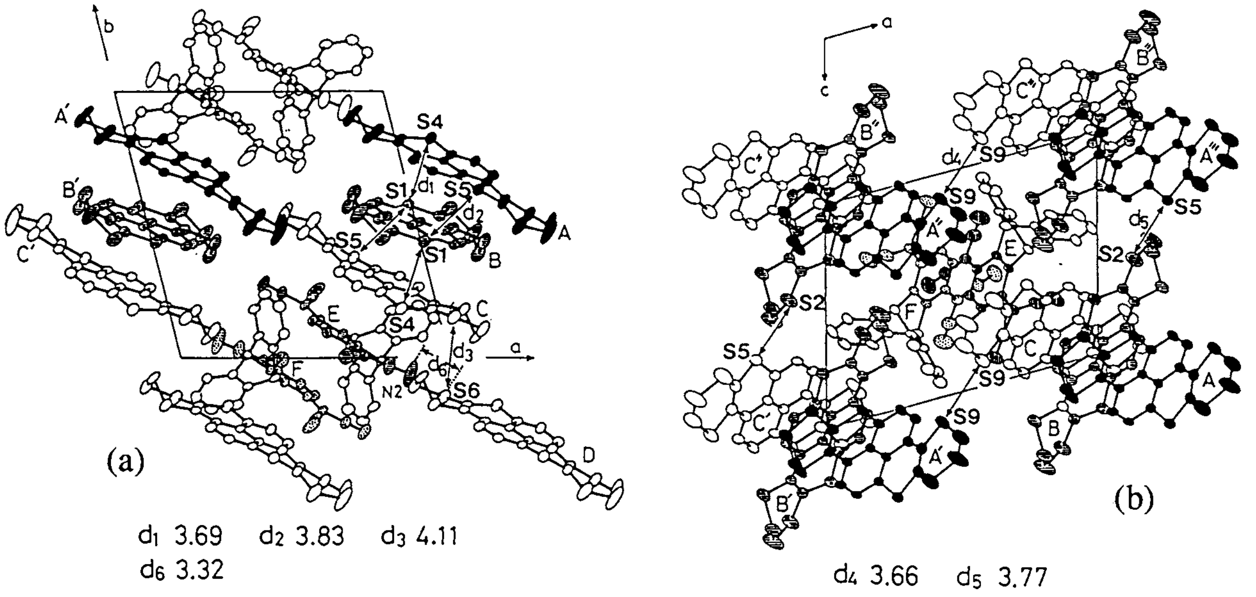


Fig. 2. The crystal structure of $(ETDTPY)_3(DBBTCNQ)_2$: View (a) along the *c* axis and (b) the *b* axis.

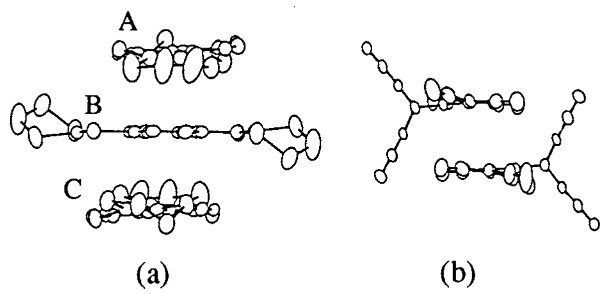


Fig. 3. The view of (a) the trimeric stack of the donor and (b) the dimeric stack of the acceptor.

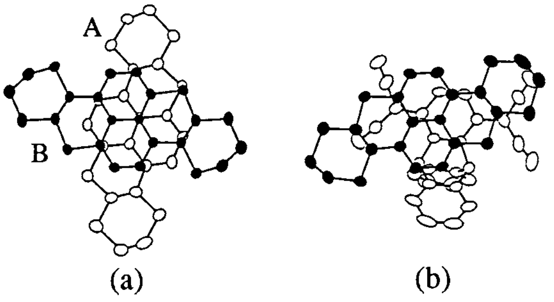


Fig. 4. The overlap mode (a) between the donors and (b) between the donor and the acceptor.

The bulky two benzo groups are arranged in the opposite directions to reduce their intermolecular steric repulsion (Figs. 2 and 3 (b)). The TCNQ moieties overlap with a lateral shift mode. The CN groups directed to methine hydrogens are tilted to avoid the steric repulsion. The deviation of the nitrogen atoms from the benzene moiety in the TCNQ group are as follow: N(1); -0.087, N(2); 0.495, N(3); 0.044, N(4); 0.718 Å. The trimeric and the dimeric stacks pack alternately along the [110] direction. *Therefore, this complex is characterized as the columnar structure of the alternating trimeric stack of the donor and dimeric stack of the acceptor.* The overlap mode between the donor and the acceptor stacks is shown in Fig. 4 (b). The ionicity of the CT complexes can conveniently be estimated by CN stretching frequencies of the TCNQ moieties.[3c, 11] The complex, $(ETDTPY)_3(DBBTCNQ)_2$, shows the broad absorption band at 2174 cm^{-1} in the CN stretching region, which is nearly same value with that of the $K^+DBBTCNQ^-$. The molecular structures of the trimeric donor components show the higher planarity of the central molecule B. This suggests that B exists as cation radical and A and C as neutral. Although both simple considerations indicate that the complex is not neutral but ionic, more data are needed to make this argument conclusive. Utilizing the V-shape correlation to estimate the gross features of the solid state properties for CT complexes, we are now in progress to produce single crystals of potentially highly conducting CT complexes of ETDTPY as our important next step.

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6) The elemental analysis data for $(ETDTPY)_3(DBBTCNQ)_2$. Anal Found: C, 62.70; H, 3.02; N, 5.58%. Calcd for $C_{106}H_{60}N_8S_{18}$: C, 62.94; H, 2.99; N, 5.54%.

7) The crystal structure analysis: Crystal dimensions 0.6 x 0.15 x 0.10 mm^3. Rigaku AFC-5R diffractometer, graphite monochrometer. Cell parameters refined by least-square method by use of 20 reflections ($53° < 2\theta < 59.9°$). Intensity measurement preformed up to 126°, range of *hkl*, -15 to 15, 0 to 16 and 0 to 9, ω-2θ scan, scan speed 8° min^{-1} ($0° < 2\theta < 126°$), scan width $(1.3 + 0.14\tan\theta)°$. Three standard reflections monitored every 100 reflections, decay less than 2%, 7226 reflections measured. Independent 5500 ($|F_o| > 3\sigma(|F_o|)$) reflections used for structure determination. Data corrected for Lorentz and polarization factors. Monte-Carlo direct method[8)] using *MULTAN78*[9)] program system. Full matrix least-squares on $\Sigma\omega(|F_o|^2 - |F_c|^2)$ with analytical absorption correction.[10)] Anisotropic temperature factors used for refinement of non-H atoms. All H atoms located from difference Fourier map and refined with isotropic temperature factors equivalent to that for the bonded carbon atoms. Final $R = 0.11$ and $R_w = 0.12$. Atomic scattering factors from *International Tables for X-Ray Crystallography* (1974). Calculation carried out on FACOM M780 computer at the Computer Center of Nagoya University.

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