

Structure of the Charge-Transfer Complex of (DBTTF)(BTDA-TCNQ)

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Abstract. 2-(1,3-Benzodithiol-2-ylidene)-1,3-benzodithiole-2,2'-(4,6,10,12-tetraaza-5,11-dithiatricyclo-[7.3.0.0^{3,7}]-dodeca-3,6,9,12-tetraene-2,8-diyldene)bispropanedinitrile, (DBTTF)(BTDA-TCNQ), C₁₄H₈S₄C₁₂N₈S₂, *M_r* = 624.8, orthorhombic, *Pnmm*, *a* = 12.940 (3), *b* = 13.551 (3), *c* = 7.440 (2) Å, *V* = 1304.6 (5) Å³, *Z* = 2, *D_m* = 1.60, *D_x* = 1.59 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 4.96 cm⁻¹, *F*(000) = 632, *T* = 293 K, *R* = 0.067 (*wR* = 0.062) for 1028 reflections. The components of the complex, DBTTF (donor) and BTDA-TCNQ (acceptor), form a mixed-stack column along the *c* axis. There are no intermolecular contacts shorter than the sum of the van der Waals radii within the molecular stack and between the stacks.

Introduction. BTDA-TCNQ forms a two-dimensional sheet-like network through S...N≡C interactions in the crystalline state (Kabuto, Suzuki, Yamashita & Mukai, 1986). Thus the charge-transfer complexes of BTDA-TCNQ with donor molecules containing S or Se atoms are expected to form a high-dimensional structure, which might stabilize the metallic state and induce high electrical conductivity along two or three mutually perpendicular directions. In fact, the (TTF)(BTDA-TCNQ) complex (Suzuki, Kabuto, Yamashita & Mukai, 1987) (TTF = tetrathiafulvalene) has a sheet-like network structure, but it shows a very low conductivity because of its mixed-stack structure. Recently, we have synthesized the charge-transfer complexes of (tetraselenotetracene)(BTDA-TCNQ), and found that one of the crystal modifications has a segregated-stack structure: this complex keeps a metallic state down to 1.5 K without undergoing a Peierls transition (Ugawa, Iwasaki, Kawamoto, Yamashita, Yakushi

& Suzuki, 1991). We have searched for a series of charge-transfer complexes containing BTDA-TCNQ as an electron acceptor. In this paper, we report the crystal structure of the charge-transfer complex (DBTTF)(BTDA-TCNQ).†

Experimental. Black needles of (DBTTF)(BTDA-TCNQ) were obtained by the diffusion method, using an H-shaped cell, from a 50 ml acetonitrile solution containing 10 mg of DBTTF and 10 mg of BTDA-TCNQ. *D_m* was determined by flotation in an aqueous solution of thallium(I) formate. A crystal 0.50 × 0.15 × 0.02 mm was mounted on a Rigaku AFC-5 four-circle diffractometer. Unit-cell dimensions were determined from 15 reflections (30 < 2θ < 36°). Data were collected using graphite-monochromated Mo *K*α radiation with the 2θ-ω scan mode. ω-scan speeds were (i) 8.0, (ii) 6.0 and (iii) 4.0° min⁻¹ in the 2θ range 0 < (i) < 35 < (ii) < 47 < (iii) < 55°. Three standard reflections measured after every 100 reflections showed no significant decay. 1571 independent reflections were obtained by averaging the equivalent ones from 1822 reflections (0 ≤ *h* ≤ 16, 0 ≤ *k* ≤ 17, 0 ≤ *l* ≤ 9), since *R_{int}* = 0.023 is significantly small. An analytical absorption correction (Katayama, 1986) was applied, the maximum and minimum correction factors being 1.281 and 1.010, respectively. 1028 reflections [|*F_o*| > 3σ(|*F_o*|)] were used for the refinement. The crystal structure was solved by the Monte Carlo direct method (Furusaki, 1979) with the aid of the *MULTAN*78 program system (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and was refined by the full-matrix least-squares method. All H atoms were found in the difference Fourier map, and their positional param-

† DBTTF = dibenzotetrathiafulvalene: 2-(1,3-benzodithiol-2-ylidene)-1,3-benzodithiole. BTDA-TCNQ = bis(1,2,5-thiadiazolo)tetracyanoquinodimethane: 4*H*,8*H*-4,8-bis(dicyanomethylene)-benzo[1,2-*c*:4',5'-*c'*]bis[1,2,5]thiadiazole.

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eters were refined with fixed isotropic temperature factors taken to be equal to those of the bonded C atoms. Only the space group *Pnmn* could bring about a reasonable structure (*Pnn2* could not). Finally, the values $R = 0.067$, $wR = 0.062$, $S = 1.66$, $(\Delta/\sigma)_{\max} = 0.18$ and $\Delta\rho_{\max}/\Delta\rho_{\min} = 0.55/-0.60$ were obtained by minimizing $\sum w(F_o^2 - F_c^2)^2$, where $w = [\sigma^2(F_o)]^{-1}$. The number of refined parameters in the final stage was 112. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations except the best planes of molecules were carried out using the *CRYSTAN* program system (Katayama & Honda, 1985) on a Hitachi M-680 computer at the Institute for Molecular Science; the best planes of molecules were calculated by use of the *UNICSIII* program system (Sakurai & Kobayashi, 1979). *ORTEP* (Johnson, 1965) was used to produce the illustrations of the crystal and molecular structures.

Discussion. Atomic coordinates of the title complex are listed in Table 1.* Fig. 1 gives the numbering of atoms, bond lengths and bond angles. The symmetry of both molecules is C_{2h} ; for BTDA-TCNQ a twofold axis passes through the two S atoms, and for DBTTF a twofold axis runs along the short molecular axis within the molecular plane. DBTTF and BTDA-TCNQ are each approximately planar; the maximum deviation from the molecular plane is 0.030 (3) Å for C(8) of DBTTF and 0.030 (3) Å for N(1) of BTDA-TCNQ. Table 2 shows the bond lengths of DBTTF in the present complex along with those of DBTTF itself, (DBTTF)(TCNQ) (TCNQ = tetracyanoquinodimethane), and (DBTTF)-(TCNQF₄) (TCNQF₄ = tetrafluorotetracyanoquinodimethane), which are not corrected for the libration of the molecules. From the geometries of DBTTF, Emge, Wiygul, Chappell, Bloch, Ferraris, Cowan & Kistenmacher (1982) estimated the degrees of charge transfer of (DBTTF)(TCNQ) and (DBTTF)-(TCNQF₄) as 0.25 and 1.00, respectively. The most significantly different bond lengths between DBTTF⁰ and DBTTF⁺ are the central C=C bond (bond *a*) and the C—S bond (bond *b*). These bonds *a* and *b* of the present complex are intermediate between DBTTF⁰ and DBTTF⁺. If we take account of the e.s.d.'s, bond *b* is more reliable for the judgement of the degree of charge transfer. If it is assumed that the bond length changes proportionally to the degree of charge transfer, the degree of charge transfer is

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55170 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0570]

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B _{eq}
S(1)	0.0	0.2564 (1)	0.0	3.86 (5)
N(1)	0.0875 (2)	0.1804 (2)	-0.0653 (4)	3.13 (8)
C(1)	0.0510 (2)	0.0898 (2)	-0.0372 (4)	2.54 (9)
C(2)	0.1090 (3)	0.0	-0.0792 (7)	2.37 (11)
C(3)	0.2073 (3)	0.0	-0.1463 (7)	2.77 (13)
C(4)	0.2655 (3)	-0.0873 (3)	-0.1846 (5)	3.39 (10)
N(2)	0.3202 (3)	-0.1511 (3)	-0.2193 (5)	5.20 (12)
S(2)	0.1148 (1)	-0.1101 (1)	0.4203 (1)	3.80 (4)
C(5)	0.0489 (4)	0.0	0.4651 (7)	3.12 (14)
C(6)	0.2267 (3)	-0.0515 (3)	0.3364 (5)	3.32 (10)
C(7)	0.3112 (3)	-0.1026 (4)	0.2757 (6)	4.34 (12)
C(8)	0.3967 (3)	-0.0515 (4)	0.2144 (6)	5.14 (14)

Table 2. Comparison of the average bond lengths (Å) in DBTTF with e.s.d.'s in parentheses

Bonds *a*–*g* are shown in Fig. 1.

	DBTTF ^{0*}	DBTTF ^{0.25+†}	DBTTF ^{1.0+‡}	BTDA-TCNQ§
<i>a</i>	1.336 (2)	1.358 (6)	1.393 (6)	1.369 (10)
<i>b</i>	1.759 (2)	1.747 (4)	1.718 (4)	1.750 (3)
<i>c</i>	1.748 (2)	1.751 (4)	1.742 (4)	1.766 (4)
<i>d</i>	1.399 (2)	1.398 (6)	1.396 (8)	1.394 (7)
<i>e</i>	1.384 (3)	1.386 (7)	1.387 (8)	1.371 (6)
<i>f</i>	1.379 (3)	1.378 (8)	1.378 (8)	1.382 (6)
<i>g</i>	1.383 (3)	1.368 (8)	1.370 (8)	1.396 (9)

* DBTTF (Emge, Wiygul, Chappell, Bloch, Ferraris, Cowan & Kistenmacher, 1982).

† (DBTTF)(TCNQ) complex (Emge, Wiygul, Chappell, Bloch, Ferraris, Cowan & Kistenmacher, 1982).

‡ (DBTTF)(tetrafluoroTCNQ) complex (Emge, Bryden, Wiygul, Cowan, Kistenmacher & Bloch (1982).

§ This work.

estimated at 0.22 (9) in the title complex and, thus, is close to the case of (DBTTF)(TCNQ). The molecular geometry of BTDA-TCNQ (Kabuto, Suzuki, Yamashita & Mukai, 1986) and radical salts of BTDA-TCNQ (Suzuki, Kabuto, Yamashita, Mukai, Miyashi & Saito, 1988) shows that the largest geometrical change accompanied by charge transfer is seen in the C=C bond of the C=C(CN)₂ group: 1.356 (4) Å for BTDA-TCNQ⁰ and 1.390 (6) Å for BTDA-TCNQ⁻. The corresponding value of 1.366 (6) Å in the title complex is intermediate between them. In the same way as DBTTF, we can estimate the degree of charge transfer at 0.29 (20), which is consistent with the geometrical change of DBTTF.

DBTTF and BTDA-TCNQ are alternately stacked to form a mixed-stacked column along the *c* axis as shown in Fig. 2. The molecular planes of DBTTF and BTDA-TCNQ are almost parallel to each other with a dihedral angle of 0.35 (2)°. Fig. 3 shows the overlapping mode of DBTTF and BTDA-TCNQ. There are no intra- or interstack contacts shorter than the sum of the van der Waals radii of the

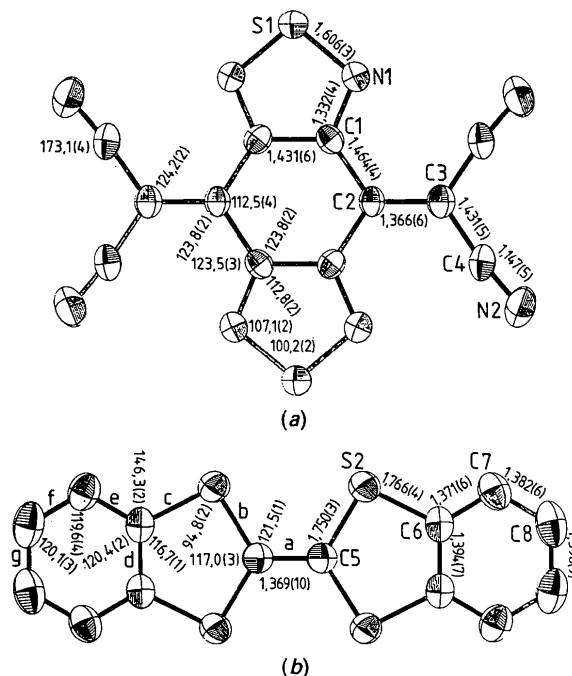


Fig. 1. ORTEP representation of each molecule, (a) BTDA-TCNQ and (b) DBTTF, showing the atomic numbering scheme. Bond lengths (Å) and bond angles (°) are also shown with e.s.d.'s in parentheses.

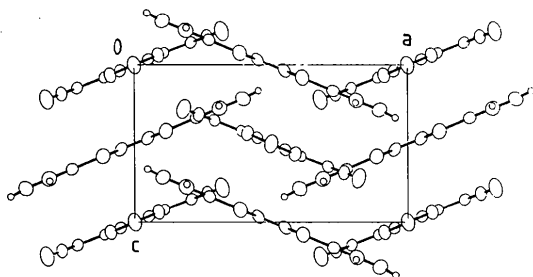


Fig. 2. View of the crystal packing projected along the *b* axis.

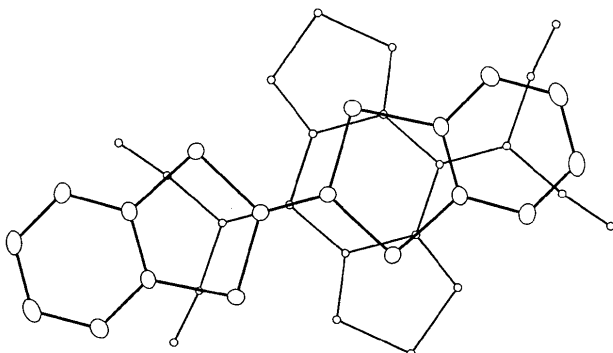


Fig. 3. Overlapping mode of DBTTF and BTDA-TCNQ molecules.

corresponding atoms. Only the distance [3.369 (4) Å] of S(1)···N(2) ($x - \frac{1}{2}, y + \frac{1}{2}, -z - \frac{1}{2}$) is comparable with the sum of the van der Waals radii (3.35 Å). This weak intermolecular interaction is in contrast to that found in the structure of the (TTF)(BTDA-TCNQ) complex, in which TTF molecules are surrounded by a network of BTDA-TCNQ to form an inclusion compound. Probably DBTTF is too large to be included in the network of BTDA-TCNQ molecules. Such structural characteristics of (DBTTF)(BTDA-TCNQ) lead to the view that the charge-transfer interaction between DBTTF and BTDA-TCNQ is extremely weak. The polarized reflection spectrum of this crystal also indicates a weak charge-transfer interaction; although a charge-transfer transition is observable in the *c*-polarized spectrum, the reflectivity (9%) and thus the oscillator strength of this charge-transfer band are very small ($f = 0.1$) (Iwasaki, Ugawa, Kawamoto, Ida, Yamashita, Yakushi & Suzuki, 1991). According to the bond-length comparison of DBTTF and BTDA-TCNQ as made above, the degree of charge transfer is estimated at about 0.25, which is too large for such a weak charge-transfer complex (Ida, Yakushi & Kuroda, 1989). Taking account of the e.s.d.'s shown in parentheses, we consider that the degree of charge transfer is less than 0.25.

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