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The Crystal Structure of the Charge-transfer Complex of Dibenzotetrathiafulvalene-Tetracyanoquinodimethane, DBTTF-TCNQ

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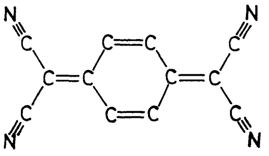
(Received September 29, 1980)

The crystal of the charge-transfer complex of dibenzotetrathiafulvalene–7,7,8,8-tetracyanoquinodimethane, DBTTF–TCNQ, belongs to the triclinic system; $a=10.309(8)$, $b=8.281(2)$, $c=7.727(3)$ Å, $\alpha=110.03(4)$, $\beta=109.80(4)$, $\gamma=72.05(3)°$, space group $P\bar{1}$ with $Z=1$. The structure has been determined by the X-ray method. DBTTF and TCNQ stack alternately along [011] to form mixed columns; this phenomenon is responsible for the low electrical conductivity of DBTTF–TCNQ. The intermolecular distance between DBTTF and TCNQ is 3.303 Å. The charge-transfer complexes of DBTTF with TNB, TCNE, DDQ, and fluoro-TCNQ were examined by means of X-ray photographs. It is shown that the DDQ complex, exhibiting a high conductivity, has segregated uniform columns of donors and acceptors, such as were not found in the other complexes.

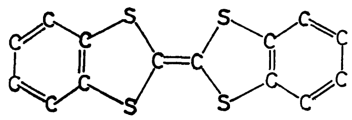
Since the discovery of the metallic conductivity of the organic compound, TTF–TCNQ (tetrathiafulvalene–tetracyanoquinodimethane), by Ferrais, Cowan, Walatka, and Perlstein, and by Coleman, Cohen, Sandman, Yamagishi, Garito, and Heeger in 1973,[1] many high-conducting organic materials have been reported. Recently, Jerome, Mazaud, Ribault, and Bechgaard have discovered an organic superconductor.[2]

High conductivity is associated with a crystal structure in which the planar donor and/or acceptor molecules are stacked to form columns.[3] Unlike TTF–TCNQ, however, DBTTF–TCNQ is insulating ($\sigma_{\mathrm{R.T.}}\approx 10^{-6}$ $(\Omega\,\mathrm{cm})^{-1}$ [4]). This paper will report the crystal and molecular structure of DBTTF–TCNQ and the molecular arrangements in the crystals of several DBTTF complexes.



TCNQ

7,7,8,8-Tetracyanoquinodimethane [2,2′-(2,5-Cyclohexadiene-1,4-diylidene)bis(propanedinitrile)]



DBTTF

Dibenzotetrathiafulvalene [2-(1,3-Benzodithiol-2-ylidene)-1,3-benzodithiole]

Experimental

Black lath-like crystals of DBTTF–TCNQ were prepared by a diffusion method, acetonitrile solutions of the two compounds being used. The lattice constants as determined by a Rigaku automated four-circle diffractometer are listed in Table 1. The crystals belongs to the triclinic system. The intensity data were collected with monochromated Mo K_α radiation by the ω-2θ scan technique up to $2\theta=60°$. The reflections were scanned at the rate of 4° min^{-1} in 2θ. Three standard reflections were measured after every 50 reflections. No significant intensity variation was observed during the course of the experiment. The crystal used had approximate dimensions of 0.3×0.3×0.06 mm. No corrections for absorption and extinction were made.

TABLE 1. CRYSTAL DATA OF DBTTF–TCNQ

Formula	$(C_{14}H_8S_4)(C_{12}H_4N_4)$	$F.W.=508.7$
Monoclinic	Space group $P\bar{1}$	
$a=10.309(8)$ Å	$b=8.281(2)$ Å	$c=7.727(3)$ Å
$\alpha=110.03(4)°$	$\beta=109.80(4)°$	$\gamma=72.05(3)°$
$V=573.7$ Å^3		
$D_c=1.474$ g cm^{-3}	$D_m=1.473$ g cm^{-3} (flotation method)	
$Z=1$	$\mu(\mathrm{Mo}\ K\alpha)=4.273$ cm^{-1}	

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method. Patterson maps were computed on the basis of 1415 independent reflections of $|F_o|\geqq 3\sigma$. A refinement of the structure was performed by the block-diagonal, least-squares method. Anisotropic temperature factors were used for non-hydrogen atoms, whiel isotropic ones were used for the hydrogen atoms found by the difference Fourier synthesis. The final R value was 0.089. The weighting scheme used was: $\omega=1/[a+b|F_o|+c|F_o|^2]$ for $|F_o|\geqq 6.19$ (absolute scale), $a=12.37$, $b=1.0$, $c=0.015$; $\omega=0.1$ otherwise. The atomic scattering factors were taken from

TABLE 2. FINAL ATOMIC PARAMETERS
(Values for fractional coordinates are multiplied by 10^4.)

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$ [a)]
S(1)	1684(3)	1415(4)	924(4)	8.9
S(2)	619(3)	−118(3)	2963(3)	12.5
N(1)	2429(12)	5386(15)	1430(14)	19.0
N(2)	4011(11)	7356(16)	8200(15)	18.7
C(1)	517(11)	265(13)	809(13)	11.7
C(2)	2600(9)	1500(12)	3309(13)	9.8
C(3)	2090(11)	797(13)	4280(14)	13.1
C(4)	3753(11)	2301(14)	4220(16)	14.5
C(5)	4394(11)	2288(14)	6154(16)	15.0
C(6)	3907(12)	1554(15)	7080(16)	15.0
C(7)	2737(12)	780(14)	6167(15)	14.7
C(8)	74(10)	4638(12)	6689(13)	9.7
C(9)	952(9)	5806(12)	4874(12)	9.0
C(10)	1090(8)	5436(11)	6631(12)	8.1
C(11)	2177(9)	5917(12)	8240(13)	9.7
C(12)	2300(11)	5607(13)	5(14)	11.7
C(13)	3167(11)	6726(15)	8216(14)	14.1

a) Equivalent isotropic temperature factor as defined by H. C. Hamilton (*Acta Crystallogr.*, **12**, 609 (1959)).

"International Tables for X-Ray Crystallography."[5] The final atomic parameters are presented in Table 2.[††]

Results and Discussion

Arrangement of Molecules. The crystal structure is shown in Fig. 1. The planar π-electron donors (DBTTF) and acceptors (TCNQ) stack alternately to form mixed columns along [011] (Fig. 2). The least-squares planes, as calculated through the DBTTF and TCNQ moieties, are listed in Table 3. The dihedral angle between these two planes is about 3.0°. TCNQ is almost planar: the largest deviation of the atoms from the TCNQ plane is 0.02 Å. DBTTF is slightly one-planar: the dihedral angle between the plane of the ethylenetetrathio group and that of the *o*-phenylene group is about 3°. The short intermolecular distance of 3.303 Å and the mode of intermolecular overlap suggest that the charge-transfer interaction is important. Figure 3 shows the projection of DBTTF onto the TCNQ plane. The charge-transfer interaction requires a large overlap integral between the electron-donating and -accepting orbitals.[6,7] Since the highest occupied molecular orbital of DBTTF and the lowest unocuupied molecular orbital of TCNQ are of different symmetries with respect to inversion (B_{1u}(DBTTF), B_{2g}(TCNQ)),[8] the direct overlap is unfavorable in DBTTF–TCNQ. This may be the reason why DBTTF is shifted from the position just above TCNQ.

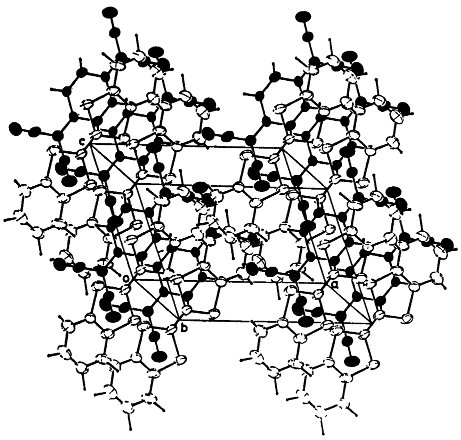


Fig. 1. Three-dimensional structure of DBTTF–TCNQ.

Table 3. Least-squares planes and deviations (Å).
(In each of the equations of the planes X, Y, and Z are coordinates (Å) referred to the a, b, and c crystal axes respectively.)

DBTTF molecular plane							
$0.4781X-0.6482Y-0.1959Z=0.0$							
S(1)	0.066	S(2)	0.078	C(1)	0.003	C(2)	0.021
C(3)	0.044	C(4)	−0.001	C(5)	−0.035	C(6)	−0.029
C(7)	−0.009						
TCNQ molecular plane							
$0.4324X-0.6842(Y-b/2)-0.1791(Z-c/2)=0.0$							
N(1)	−0.006	N(2)	0.014	C(8)	0.014	C(9)	−0.012
C(10)	0.016	C(11)	0.012	C(12)	−0.009	C(13)	−0.018

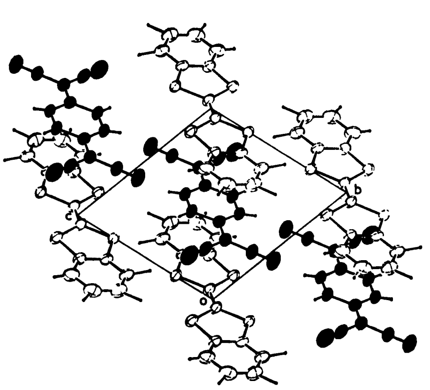


Fig. 2. The projection of the structure.

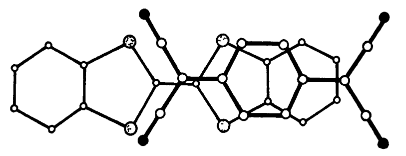


Fig. 3. Projection of DBTTF onto the plane of TCNQ.

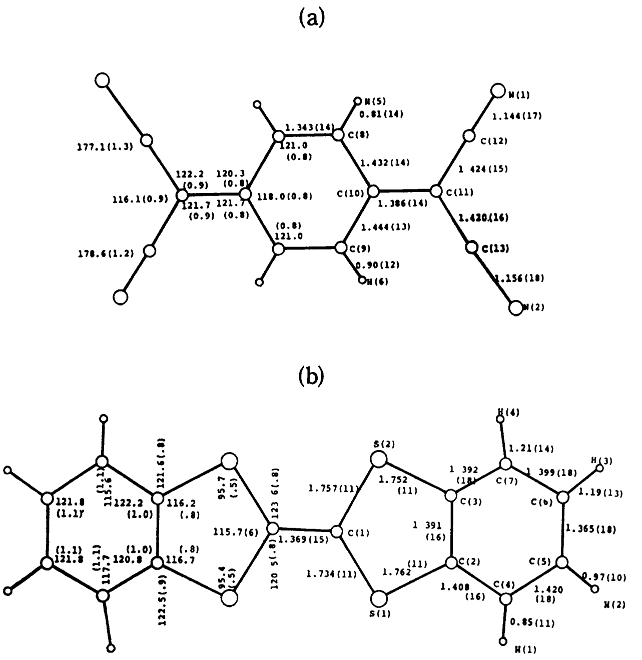


Fig. 4. Bond lengths and angles (e.s.d.'s in parentheses). (a): TCNQ, (b): DBTTF.

Molecular Geometry. The bond lengths and angles are shown in Fig. 4. It is well-known that the bond lengths of TCNQ depend on the size of the negative charge of the molecule (TCNQ$^{-\rho}$).[9,10] In Table 4, the bond lengths of TCNQ in DBTTF–TCNQ are compared with those of TCNQ° (neutral molecule)[11] and TCNQ$^-$ (alkali-TCNQ).[12] The averaged bond lengths

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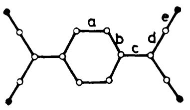
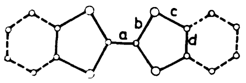
[††] A list of the observed and calculated structure factors and tables of the anisotropic thermal parameters for the non-hydrogen atoms and the atomic parameters for the hydrogen atoms are kept as Document No. 8133 at the Chemical Society of Japan.

Table 4. Comparison of average bond lengths (Å)
(The values are averaged by assuming D_{2h} symmetry. The distances are not corrected for rigid-body motions.)



	Ref.	*a*	*b*	*c*	*d*	*e*
$TCNQ^{\circ}$	11	1.344	1.443	1.373	1.436	1.138
$TCNQ^{-}$	12	1.358	1.422	1.410	1.416	1.155
$TCNQ^{-0.59}$	13, 17	1.356	1.433	1.402	1.423	1.151
TCNQ	This work	1.343	1.438	1.386	1.422	1.150



	Ref.	*a*	*b*	c	*d*
TTF°	15	1.349	1.757	1.730	1.314
TTF^{+}	16	1.404	1.713	1.725	1.306
$TTF^{+0.59}$	13, 17	1.369	1.743	1.736	1.323
DBTTF	This work	1.369	1.746	1.757	1.391

of TCNQ in the present complex resemble those of $TCNQ^{\circ}$ rather than those of $TCNQ^{-}$. If we assume that the bond length (l) and the formal charge (ρ) are linearly related, ρ can be estimated to be $|l_i(\rho)-l_i(0)|/|l_i(1)-l_i(0)|$ (i=a,b,..(Table 4)), where $l_i(\rho)$ is the bond length of $TCNQ^{-\rho}$. The values of ρ were calculated for TTF–TCNQ[13] in order to confirm the validity of this assumption; the terminal C–N bond was not used. The mean value of ρ (0.6) is consistent with the degree of charge transfer determined by X-ray diffuse-scattering experiments ($\rho=0.59$[14]). For TCNQ in the present complex, the mean value of ρ is 0.25, which indicates that DBTTF–TCNQ is a non-ionic complex.

The bond lengths of the TTF skeleton in DBTTF are compared with those of TTF°, TTF^{+}, and $TTF^{+0.59}$ in Table 4. No simple correlation between l and ρ, as in TCNQ, is observed. The a bond tends to elongate, while the b bond tends to contract, with an increase in the positive charge on TTF. This change accords with the variation in bond orders estimated on the basis of the wave function of TTF.[8] The lengths of the a and b of DBTTF are intermediate between those of TTF° and TTF^{+}. The d length of TTF is approximately equal to the length of typical C=C double bonds. The d bond of DBTTF is much longer, however, its length is almost equal to the C–C bond length of the benzene molecule. In addition, the c bond of DBTTF is fairly long. Consequently, DBTTF may be regarded as a "composite molecule" comprised of ethylenetetrathio and o-phenylene groups.

Molecular Arrangements in Some DBTTF Complexes. Many charge-transfer complexes containing TTF and/or TCNQ (or their analogues) exhibit high electrical conductivities.[18,19] Some of them are regarded as "organic metals." High-conducting complexes hitherto known crystallize in segregated uniform stacks, in which donors and acceptors stack separately to form parallel columns. As has been described in the preceding section, the molecular arrangement in DBTTF–TCNQ differs from those in organic metals. The mixed-column structure of DBTTF–TCNQ well interprets the low conductivity ($\sigma_{R.T.}\approx 10^{-6}$ $(\Omega\ \mathrm{cm})^{-1}$).[4]

Besides DBTTF–TCNQ, several DBTTF complexes were prepared in order to examine the relationship between the structure and the conductive properties. The acceptors used were tetracyanoethylene (TCNE), 1,3,5-trinitrobenzene (TNB), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), and 2,2′-(2-fluoro-2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile) (TCNQ(F)). The preliminary crystal data are: DBTTF–TCNE, monoclinic, $P2_1/c$, $a=6.92$, $b=6.61$, $c=20.81$ Å, $\beta=99.6°$; DBTTF–TNB, monoclinic, $P2_1/c$, $a=7.44$, $b=13.91$, $c=14.47$ Å, $\beta=90.1°$. The crystal habits and the diffraction patterns of these black crystals suggest that donors and acceptors stack alternately to form mixed columns and that the columns in DBTTF–TCNE and DBTTF–TNB are parallel to the b and a axes respectively. The crystal of DBTTF–TCNQ(F) has a lattice period of about 9.3 Å along the needle axis, indicating that this crystal also does not have segregated uniform columns. The electrical conductivities of these DBTTF complexes are very low ($\sigma_{R.T.}<10^{-4}$ $(\Omega\ \mathrm{cm})^{-1}$).[20] In contrast, DBTTF–DDQ is highly conducting ($\sigma_{R.T.}\approx$ 70 $(\Omega\ \mathrm{cm})^{-1}$).[20] Oscillation photographs around the needle axis show a lattice spacing of about 3.7 Å, indicative of segregated uniform columns of DDQ and DBTTF.

The authors are grateful to Dr. G. Saito for his gift of TCNQ(F).

References

1) J. Ferraris, D. O. Cowan, V. V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).

2) D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, *J. Phys. Lett.* **41**, 95 (1980).

3) I. F. Shchegolev, *Phys. Status Solidi, A*, **12**, 9 (1972); J. J. Andre, A. Bieber, and F. Gautier, *Ann. Phys.*, **1976**, 145; T. J. Kistenmacher, "Synthesis and Properties of Low-Dimensional Materials (Annals of the New York Academy of Sciences, Vol. 313)," ed by J. S. Miller and A. J. Epstein, The New York Academy of Sciences, New York (1978), pp. 333—342.

4) G. S. Bajwa, K. D. Berlin, and H. A. Pohl, *J. Org. Chem.*, **41**, 145 (1976).

5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, (1974), Vol. IV.

6) J. B. Torrance, J. J. Mayerrle, V. Y. Lee, and K. Bechaard, *J. Am. Chem. Soc.*, **101**, 4747 (1979).

7) H. Kuroda, I. Ikemoto, and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **39**, 1842 (1966); H. Kuroda, T. Amano, I. Ikemoto, and H. Akamatu, *J. Am. Chem. Soc.*, **89**, 6056 (1967).

8) A. J. Berinsky, J. F. Carolan, and L. Weiler, *Solid State Commun.*, **15**, 795 (1974); D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971).

9) C. J. Fritchie and P. Arthur *Acta Crystallogr.*, **21**, 1939 (1966); T. Sundaresan and S. C. Wallwork, *Acta Crystallogr., Sect. B*, **28**, 491 (1972); P. S. Flandrois and D. Chasseau, *Acta Crystallogr., Sect. B*, **33**, 2744 (1977); P. Coppens and T. N. G. Row, "Synthesis and Properties of Low-Dimensional Materials (Annals of the New York Academy of Science, Vol. 313)," ed by J. S. Miller and A. J. Epstein, New York Academy

of Sciences, New York (1978), pp. 244—255.

10) H. Kobayashi, T. Danno, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 2693 (1973).

11) R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, **18**, 932 (1965).

12) M. Konno and Y. Saito, *Acta Crystallogr., Sect. B*, **31**, 2007 (1975); H. Kobayashi, to be published; T. Sundaresan and S. C. Wallwork, *Acta Crystallogr., Sect. B*, **28**, 2474 (1972).

13) T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **30**, 763 (1974).

14) S. Kagoshima, H. Anzai, K. Kajimura, and T. Ishiguro, *J. Phys. Soc. Jpn.*, **39**, 1143 (1975); R. Comes," Chemistry and Physics of One-Dimensional Metals," ed by H. J. Keller, Plenum Press, New York and London (1977), pp. 315—339; R. Comes and G. Shirane, "Highly Conducting One-Dimensional Solids," ed by J. T. Devreese, R. P. Evrard, and V. E. van Doren, Plenum Press, New York and London (1979).

15) W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, *J. Chem. Soc., Chem. Commun.*, **1971**, 889.

16) K. Yakushi, S. Nishimura, T. Sugano, H. Kuroda, and I. Ikemoto, *Acta Crystallogr., Sect. B*, **36**, 358 (1980).

17) A. J. Schultz, G. D. Stuky, R. H. Blessing, and P. Coppens, *J. Am. Chem. Soc.*, **98**, 3194 (1976).

18) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974); K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, *Solid State Commun.*, **33**, 1119 (1980).

19) G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, **53**, 2141 (1980).

20) H. Kobayashi, T. Yamamoto, T. Danno, and J. Nakayama, Paper Presented at the Symposium on Molecular Structure, Tokyo, Japan (1979), p. 22.