Crystal Structures of Complexes between Hexacyanobutadiene and Tetramethyltetrathiafulvalene and Tetramethylthiotetrathiafulvalene

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Hexacyanobutadiene(HCBD) forms two kinds of molecular complexes with tetramethyltetrathiafulvalene (TMTTF) one kind with tetramethylthiotetrathiafulvalene(TTMTTF). The crystal structures of these complexes and neutral TTMTTF are determined by X-ray analyses. $(TMTTF)_2$·HCBD is composed of 2:1 donor and acceptor, and TMTTF exists as a dimer cation stacked along the c axis. HCBD anions are included in the cavity of the dimer stack directing their molecular planes parallel to the stacking axis. TMTTF·HCBD is composed of 1:1 donor and acceptor, and has segregated cation and anion stacks with the interplanar spacing of 3.61 Å in TMTTF and 3.43 Å in HCBD columns. TTMTTF·HCBD is shown to have a regular segregated column with a partial charge transfer. Neutral TTMTTF has a non-planar conformation. The C=C and C-S bond lengths of the donors in free and complexed states are correlated with the degree of the charge transfer in these four complexes, and linear relationships are found between these two quantities.

Hexacyanobutadiene (HCBD) is one of the strongest electron acceptors[1,2] and is expected to give charge-transfer complexes.[3] A weak or medium electron donor may form a nominally neutral, weak complex or a segregated mixed valence complex, and a good electron donor may crystallize as an ionic complex. Single crystals of HCBD complexes with tetramethyltetrathiafulvalene (TMTTF) and tetramethylthiotetrathiafulvalene (TTMTTF) were prepared and two complexes of TMTTF·HCBD were obtained; one is 2:1 and the other is 1:1 donor to acceptor ratio. TTMTTF·HCBD formed a crystal of 1:1 ratio.[4]

The crystal structures of these three complexes and that of free TTMTTF were analyzed and the molecular structures of the donors are discussed based on the structural data and the electronic structures of the complexes. This information will be used for the interpretation of the physical properties of these complexes in the succeeding paper.[5]

Experimental

Preparation of HCBD Complexes. HCBD was prepared by the method of Webster.[1] The product was identified by mass and infrared spectra. Molecular complexes of HCBD with TMTTF and TTMTTF were obtained by mixing hot acetonitrile solutions of the donor and the acceptor in the same flask. Complex crystals were grown in the refrigerator for overnight. Two complexes of TMTTF·HCBD were obtained; $(TMTTF)_2$·HCBD crystal is a hexagonal prism of dark green color with the (100), (001), and (20$\bar{1}$) faces and

TABLE 1. CRYSTALLOGRAPHIC DATA

	$(TMTTF)_2$·HCBD	TMTTF·HCBD	TTMTTF·HCBD	TTMTTF
Chemical formula	$C_{30}H_{24}N_6S_8$	$C_{20}H_{12}N_6S_4$	$C_{20}H_{12}N_6S_8$	$C_{10}H_{12}S_8$
$D:A$	2:1	1:1	1:1	—
FW	725.10	464.61	592.89	388.73
Space group	C2/m	C2/m	C2/c	$P2_1/n$
a/Å	18.266(2)	12.8016(10)	30.161(3)	15.668(1)
b/Å	9.813(1)	21.6196(9)	4.046(1)	7.804(1)
c/Å	9.501(1)	4.0223(3)	23.414(2)	14.010(2)
β/°	102.741(8)	108.062 (7)	117.48 (1)	106.16 (1)
V/Å^3	1661.0 (3)	1058.4 (2)	2534.7 (5)	1645.5 (4)
Z	2	2	4	4
d_{obd}/g/cm^3	1.46	1.46	1.53	1.56
d_{cald}/g/cm^3	1.45	1.46	1.55	1.57
R	0.042	0.049	0.051	0.053
$2\theta_{max}$/°	126	126	126	126
No. of non-zero unique data	1398	867	1954	2593
Crystal size/mm	0.15×0.16×0.35	0.18×0.03×0.38	0.09×0.02×1.11	0.15×0.15×0.75
μ(Cu $K\alpha$)/cm^{-1}	50.46	41.24	64.94	95.89
transmission factor	—	0.48—0.88	0.56—0.88	0.23—0.24
λ(Cu $K\alpha$)/Å	1.5418	1.5418	1.5418	1.5418
Diffractometer	Rigaku automated four-circle diffractometer			

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it is composed of two donor and one acceptor molecules. TMTTF·HCBD is a one to one complex and the crystal is a thin plate showing golden luster with the (010) face. TTMTTF·HCBD is a complex of 1:1 donor to acceptor ratio. The crystal is a black rod elongated along the b axis with the (100) and (001) faces. TTMTTF is a crystal of an orange color.

Crystal Structure Analysis. The X-ray diffraction data were collected by use of an automated four-circle diffractometer, Rigaku AFC-5, set on a rotating anode X-ray generator, Rigaku RU-200, with a graphite monochromated Cu radiation (Cu $K\alpha$=1.5418 Å). Composition of the complexes and crystallographic data are listed in Table 1 together with experimental results. Crystal structures were solved by the Monte-Carlo direct method[6] using MULTAN 78 program system[7] and were refined on F^2 by the full-matrix least-squares program with the analytical absorption correction.[8] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[9] ORTEP[10] was used for drawing of the molecular and crystal structures. Anisotropic temperature factors were used for the refinement of the non-H atoms. All H atoms were located from difference Fourier maps and were refined with the isotropic temperature factors equivalent to that of the bonded carbon atoms.

TABLE 2. POSITIONAL PARAMETERS ($\times 10^5$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS WITH *e.s.d.*·*s* IN PARENTHESES

$B_{eq}=8/3\pi^2\,\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\boldsymbol{a}_j$

$(TMTTF)_2$·HCBD	*x*	*y*	*z*	B_{eq}/10²Å²
S(1T)	96259(2)	14820(5)	18134(5)	361(1)
S(1S)	110011(2)	14838(5)	46333(5)	363(1)
C(2T)	100197(14)	0	26349(29)	332(5)
C(2S)	105983(14)	0	38324(29)	331(5)
C(5T)	89724(10)	6802(23)	4445(19)	373(4)
C(5S)	116945(9)	6788(20)	59327(19)	353(4)
C(7T)	84727(15)	15830(32)	−6179(29)	506(6)
C(7S)	122269(11)	15963(28)	69202(25)	456(5)
C(1H)	47425(31)	0	29424(52)	672(13)
C(2H)	46652(37)	0	43994(95)	368(20)
C(3H)	51840(86)	0	44859(156)	668(42)
C(4H)	40245(34)	0	20302(65)	748(16)
N(5H)	34378(31)	0	13096(68)	1009(20)
C(6H)	39600(20)	0	48834(53)	604(11)
N(7H)	33436(19)	0	48574(46)	703(11)
C(8H)	53331(31)	0	22304(62)	727(14)
N(9H)	58042(29)	0	16119(71)	1075(21)
H(7TA)	80186(206)	16151(340)	−4435(368)	506(*)
H(7TB)	85438(203)	14584(352)	−13482(417)	506(*)
H(7TC)	85130(179)	24481(359)	−3186(361)	506(*)
H(7SA)	125490(185)	11348(334)	76103(371)	456(*)
H(7SB)	119961(173)	21975(326)	74169(337)	456(*)
H(7SC)	125284(173)	20557(319)	64045(344)	456(*)

TMTTF·HCBD	*x*	*y*	*z*	B_{eq}/10²Å²
S(1T)	60682(5)	7525(2)	44756(19)	439(12)
C(2T)	50000	3252(15)	50000	387(14)
C(5T)	54966(20)	14739(10)	47499(71)	416(13)
C(7T)	61570(28)	20240(13)	44037(99)	546(14)
C(1H)	100000	8854(18)	100000	579(17)
C(2H)	103272(34)	2408(20)	97292(123)	371(16)
C(4H)	108346(32)	12375(15)	93115(99)	648(16)
N(5H)	114953(34)	15415(19)	87695(123)	959(18)
C(6H)	113099(32)	0	88601(114)	545(17)
N(7H)	120839(29)	0	81156(120)	660(18)
H(7TA)	57603(282)	24047(167)	40748(927)	546(*)
H(7TB)	64115(286)	19878(182)	26558(1005)	546(*)
H(7TC)	667571(291)	20795(167)	63197(1007)	546(*)

TTMTTF·HCBD	*x*	*y*	*z*	B_{eq}/10²Å²
S(1T)	71636(2)	4812(25)	5681(2)	441(6)
C(2T)	75781(10)	17452(92)	2956(13)	423(10)
S(3T)	81991(2)	9580(25)	8075(2)	467(6)
C(4T)	80996(10)	−6435(87)	14264(11)	417(10)
C(5T)	76137(10)	−9137(81)	13073(13)	397(10)
S(6T)	85864(2)	−19848(32)	21441(3)	585(6)
C(7T)	91302(16)	−5853(175)	21057(31)	820(19)
S(8T)	74547(2)	−27064(23)	18628(2)	479(6)
C(9T)	68145(14)	−14583(111)	15845(19)	529(12)
C(1H)	96597(15)	32813(120)	4486(22)	672(15)
C(2H)	97823(22)	40292(166)	−666(40)	354(19)
C(3H)	100246(38)	50158(252)	3042(40)	521(27)
C(4H)	92272(15)	13140(130)	1787(19)	656(15)
N(5H)	88842(15)	−3543(139)	−82(22)	878(18)
C(6H)	95059(13)	30266(117)	−7507(19)	595(13)
N(7H)	92192(11)	18758(114)	−12022(15)	701(13)
C(8H)	98246(18)	40467(139)	11038(26)	766(18)
N(9H)	99356(22)	46245(175)	16244(28)	1212(27)
H(7TA)	93702(218)	−14596(1519)	24433(285)	820(*)
H(7TB)	91220(219)	14855(1617)	20224(301)	820(*)
H(7TC)	91485(209)	−12314(1593)	16872(279)	820(*)
H(9TA)	66996(167)	−26332(1239)	18392(230)	529(*)
H(9TB)	68022(175)	8788(1331)	15671(231)	529(*)
H(9TC)	66353(169)	−24514(1292)	11843(239)	529(*)

TTMTTF	*x*	*y*	*z*	B_{eq}/10²Å²
S(1T)	39724(6)	23842(13)	38353(6)	451(6)
S(1S)	24083(6)	25540(10)	49006(6)	386(6)
C(2T)	31612(22)	39841(46)	35640(23)	341(10)
C(2S)	25140(22)	40872(44)	40250(23)	326(10)
S(3T)	32809(6)	54067(14)	26398(6)	425(6)
S(3S)	17043(6)	56958(11)	38157(6)	377(6)
C(4T)	44253(25)	49656(53)	28540(26)	427(11)
C(4S)	14590(19)	53447(41)	49568(23)	291(9)
C(5T)	47454(25)	35967(56)	34091(29)	444(12)
C(5S)	17739(19)	39035(43)	54491(22)	292(9)
S(6T)	50307(7)	62301(15)	22418(7)	552(7)
S(6S)	7194(5)	67389(11)	52944(6)	378(6)
C(7T)	51368(34)	82070(65)	29217(40)	530(14)
C(7S)	11845(43)	87948(60)	51112(44)	599(17)
S(8T)	58328(7)	28321(23)	36560(10)	706(7)
S(8S)	14824(5)	31580(11)	64922(6)	345(6)
C(9T)	60759(38)	20495(99)	48926(47)	669(18)
C(9S)	25413(29)	24609(80)	72705(34)	551(14)
H(7TA)	51446(368)	88533(905)	23555(457)	530(*)
H(7TB)	55284(394)	80184(857)	35902(459)	530(*)
H(7TC)	45726(403)	86923(869)	28828(425)	530(*)
H(7SA)	8786(394)	93550(879)	53160(446)	599(*)
H(7SB)	9245(358)	88295(845)	44091(439)	599(*)
H(7SC)	18573(395)	87813(837)	53580(408)	599(*)
H(9TA)	66091(481)	17677(1032)	50768(538)	669(*)
H(9TB)	60311(510)	30263(1071)	51073(581)	669(*)
H(9TC)	57379(476)	10515(1104)	49221(518)	669(*)
H(9SA)	27525(384)	14515(911)	68986(439)	551(*)
H(9SB)	24593(400)	19582(883)	77948(499)	551(*)
H(9SC)	29532(394)	33655(925)	73350(445)	551(*)

* The B_{eq} of hydrogen atoms were assumed to be the same with the values for the attached C atoms.

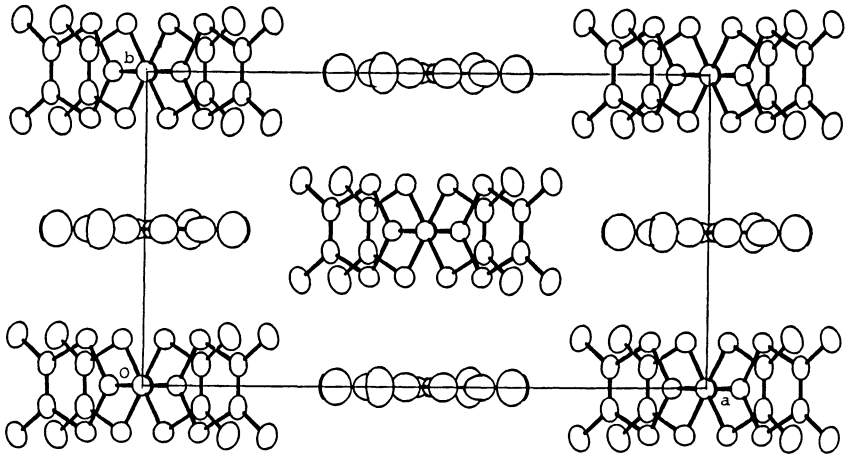


Fig. 1. Crystal structure of $(TMTTF)_2 \cdot HCBD$ projected along the c axis.

The final atomic parameters are listed in Table 2. All computations were carried out at the Computation Center of Nagoya University. The complete F_o—F_c data and the anisotropic temperature parameters are deposited as Document No. 8535 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Crystal Structure. $(TMTTF)_2 \cdot HCBD$: Crystal of $(TMTTF)_2 \cdot HCBD$ is composed of two donor and one acceptor molecules. The TMTTF molecules form a dimer, and the stacking axis is parallel to the c axis as shown in Fig. 1. HCBD molecules are included in the channels surrounded by the TMTTF columns and they are lined up without face to face stacking. A crystallographic two-fold axis penetrates the center of HCBD molecule and the molecules are disordered with a pseudo D_{2h} symmetry. The molecular plane of HCBD, which lies on a crystallographic mirror plane, is perpendicular to the plane of TMTTF molecule. The other mirror plane bisects the TMTTF molecule through the long axis.

In most donor-acceptor complexes having a segregated column, the stacking of both donor and acceptor molecules occur along the same direction; however, the present crystal shows different arrangement. It is conceivable that a large polarizability of HCBD parallel to the molecular plane may stabilize the charge resonance interaction in the dimer column of TMTTF. In the literature there are several examples in which the aromatic ring planes are arranged in the crystal parallel to the stacking axis of organic radicals.[11] From the bond length of the central C=C bond of TMTTF and the band position of the electronic spectra,[5] it is suggested that an oxidation occurs by transferring an electron in the ground state from one of the TMTTF dimer to the HCBD molecule. Accordingly the crystal is composed of $(TMTTF_2)^+ \cdot (HCBD)^-$. The interplanar spacing in the dimer is 3.53 Å and that between the dimer is 3.69 Å.

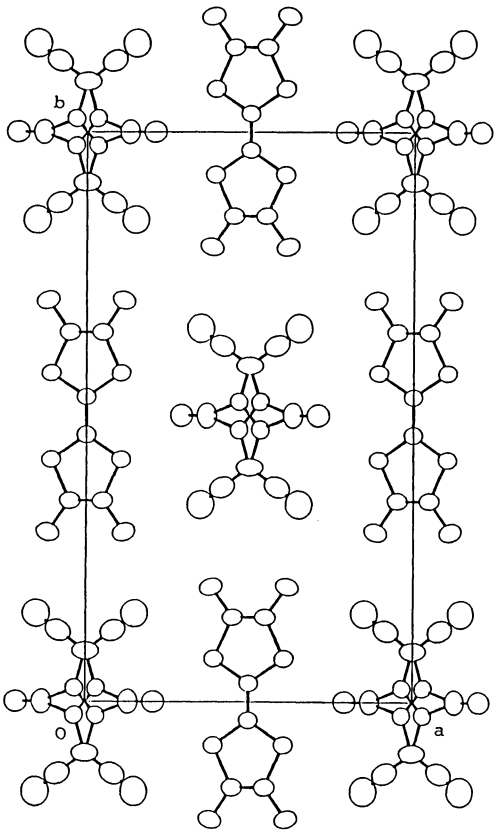


Fig. 2. Crystal structure of TMTTF·HCBD projected along the c axis.

TMTTF·HCBD: The crystal composition is one donor and the one acceptor. They are stacked in segregated columns extending along the c axis (Fig. 2). A mirror plane parallel to the (010) bisects the central C–C bonds of TMTTF and HCBD. A crystallographic two-fold axis penetrates the center of these molecules. The HCBD molecule is disordered in the positions of carbon atoms of the central C–C bond. As will be discussed in the next section, the charge transfer from TMTTF to HCBD seems to be complete, therefore this crystal has segregated columns com-

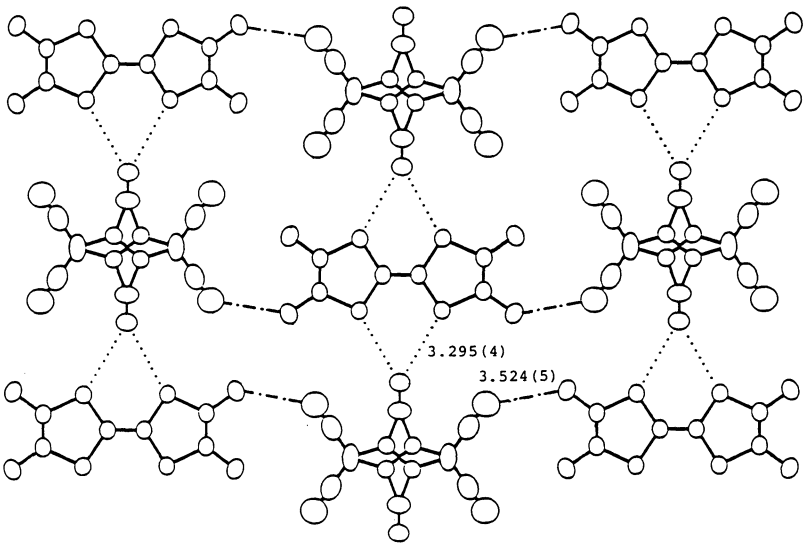


Fig. 3. The network of TMTTF and HCBD molecules projected onto the (101) plane. Close intermolecular distances are illustrated.

posed of ionic constituents. Such a structure of DA complex is known in the case of HMTTF·$TCNQF_4$.[12] The interplanar distance is 3.61 Å in the TMTTF cation column, which is a mean value of the inter- and intra-dimer distances in $(TMTTF)_2$·HCBD. The corresponding distance for HCBD anion is 3.43 Å. The Coulomb force between the charges of the same sign is repulsive for close contact of the same molecules; however, the covalent or the charge resonance interaction will favour a short interplanar distance. The actual molecular packing is determined by a balance of these repulsive and attractive interactions. The inter-column interaction between HCBD and TMTTF molecules is evident in the composite diagram of the (101) plane (Fig. 3). The closest contact is that between S···N with the distance of 3.295 (4) Å, which is shorter than the van der Waals distance of 3.35 Å, and two-dimensional network is formed.

TTMTTF·HCBD: The complex is made of the donor and the acceptor with 1:1 ratio, and they form segregated stacks along the b axis as shown in Fig. 4. Both the donor and the acceptor are stacked in one-dimensional regular lattice, and the spacing between the planes of adjacent TTMTTF molecules is 3.63 Å. The degree of the charge transfer from the donor to the acceptor is a partial one as will be discussed in the next section from the bond lengths. It is inferred that both the donor and the acceptor columns are in mixed valence state. The centers of the molecules are coincident with a center of symmetry of the crystal. The central carbon atoms in HCBD are disordered around the inversion center. There are several close distances between TTMTTF and HCBD in different columns, and they are S···S 3.510(1) Å where the van der Waals distance is 3.70 Å. In the polarized reflection spectra, there is some indication of the inter-column interaction.[5]

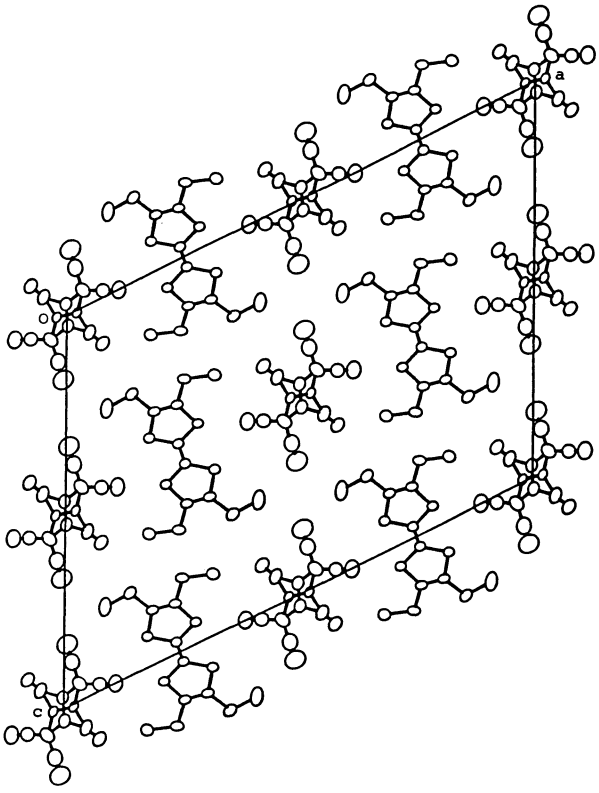


Fig. 4. Crystal structure of TTMTTF·HCBD projected onto the (010) plane.

TTMTTF: The arrangement of the molecules is projected onto the (010) plane as shown in Fig. 5. There are close contacts between S atoms of methylthio groups arranged along $[10\bar{1}]$ ranging about 3.54—3.57 Å.

Molecular Structure. ORTEP drawings and important bond lengths are shown for the donor molecules in different crystals in Figs. 6—10. Several papers have been published in which the bond lengths

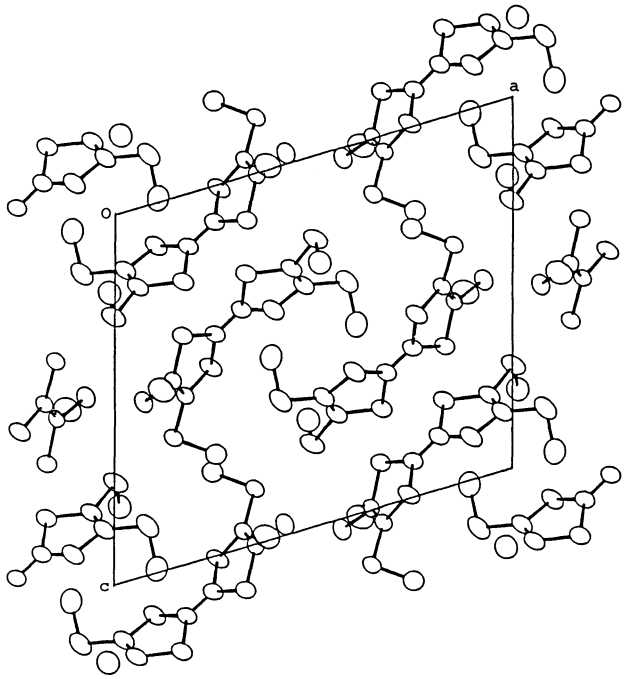


Fig. 5. Crystal structure of TTMTTF projected onto the (010) plane.

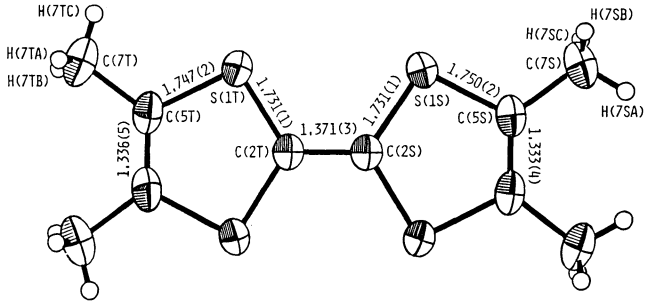


Fig. 6. Molecular structure of TMTTF in $(TMTTF)_2$ ·HCBD crystal.

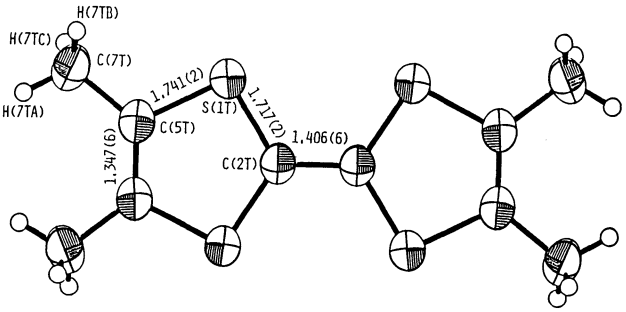


Fig. 7. Molecular structure of TMTTF in (TMTTF)·HCBD crystal.

of TTF analogues are discussed with reference to charges in the molecule.[11] We take the bond lengths of TTF[13] and TTMTTF and their salts TTF perchlorate,[14] and TTMTTF·AsF_6[15] as standards of the neutral and ionic species and draw the correlation diagram between the bond length and the degree of charge transfer as shown in Figs. 11 and 12. The results

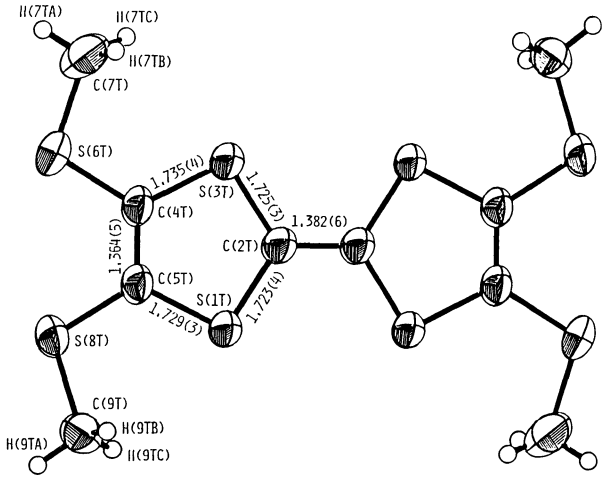
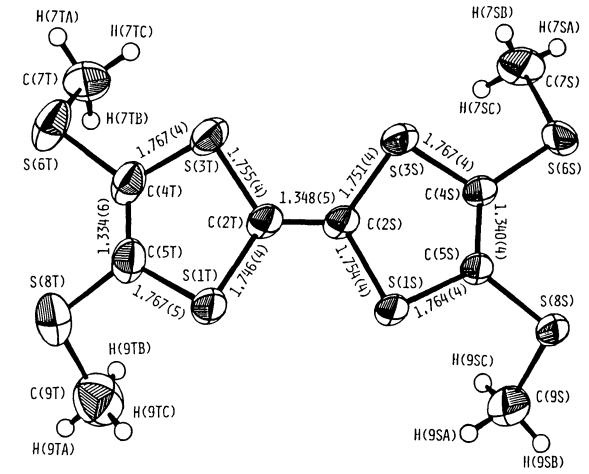


Fig. 8. Molecular structure of TTMTTF in (TTMTTF)·HCBD crystal.



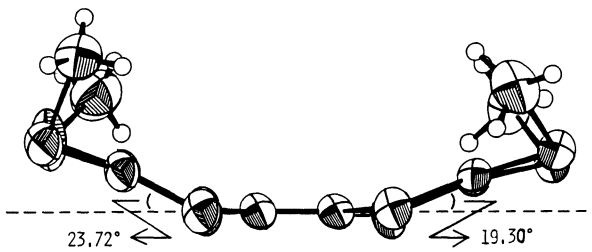


Fig. 9. Molecular structure of neutral TTMTTF (a) and the side view (b).

of the present crystal analysis clearly show that the charges of TMTTF in TMTTF·HCBD is one (ρ=1.0) and that of in $(TMTTF)_2$·HCBD is a half (ρ=0.5) and the value in TTMTTF·HCBD is ρ=0.4—0.6. The standard deviations of the present results are rather small as compared to the published data. We quote here the values for the crystals in which the ρ value is well established by chemical stoichiometry and by other means. They are TTF·TCNQ[16] $(TMTTF)_2$·Br,[17] $(TMTTF)_2$·BF_4 (at 100 K),[18] $(TMTTF)_2$·SCN,[19] HMTTF·TCNQ.[20] The strain caused by substituent groups or benzene ring fusion might be significant in

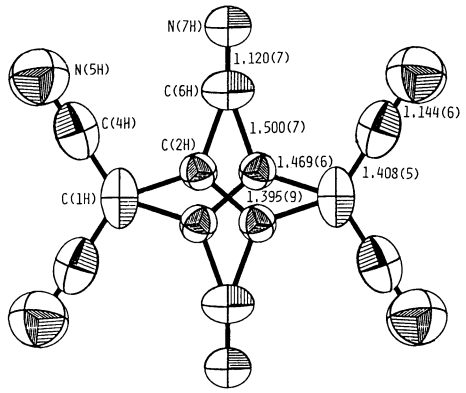


Fig. 10. Molecular structure of HCBD in (TMTTF)·HCBD crystal.

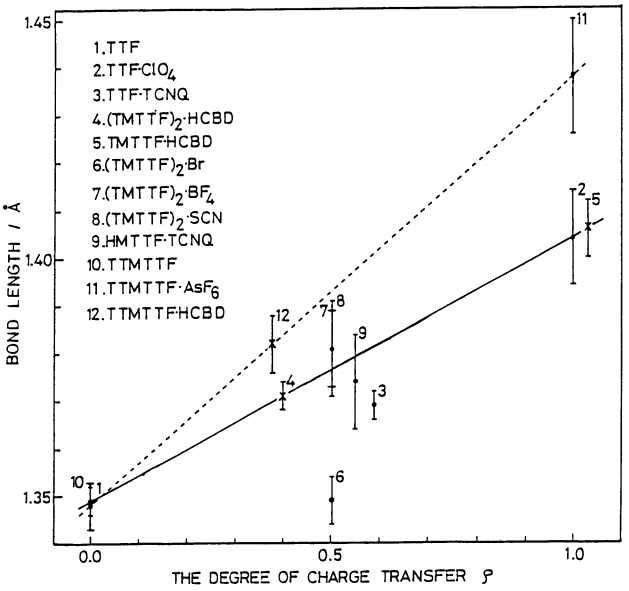


Fig. 11. The relation between the length of the central C=C bond and the degree of cherge transfer in TMTTF complexes (——) and TTMTTF complexes (---). The vertical line at each point illustrates the standard deviation.

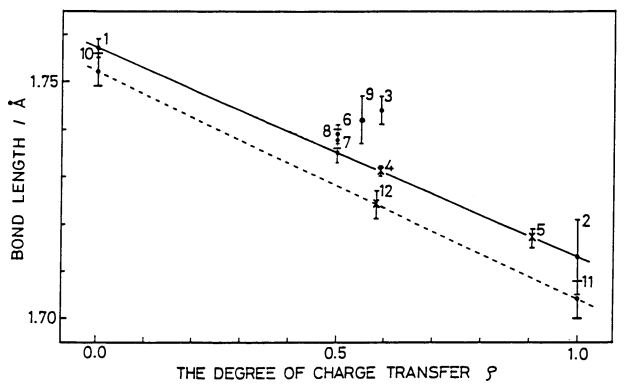


Fig. 12. The relation between the bond length (C–S) and the degree of charge transfer in TMTTF complexes (——) and TTMTTF complexes (----). The vertical line at each point illustrates the standard deviation.

changing the central C=C bond distance in dibenzotetrathiafulvalene series. In spite of this, the correlation between the bond lengths and the charge density seems to be useful for assessment of the electronic structure of the TTF type donors when the accuracy of structural analysis is sufficiently high.

The molecular structure of HCBD in the crystal of TMTTF·HCBD is illustrated in Fig. 10. However, the precise structure of HCBD is difficult to ascertain because the molecule is disordered in all complexes. It is remarkable that all C–C bond lengths in butadiene skelton are longer than normal values, presumably because all cyano groups will take electrons from the central carbon bonds.

The free TTMTTF molecule has a bent structure (Fig. 9b), in which all methylthio groups and the attached carbon atoms are displaced significantly from the central ring plane. The tilt angles are about 20° in both ends. The terminal C–S–C bonds are strongly bent, and the bond angles are in the range of 101—104°. It is of interest that the molecule is planar in the partial ionic column of TTMTTF·HCBD complex, because the planar conformation will be favoured by the charge resonance interaction.

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