An Isomeric Series of Thiophene-Fused Tetracyanoquinodimethanes. III. Crystal Structures of Charge-Transfer Complexes with TTF

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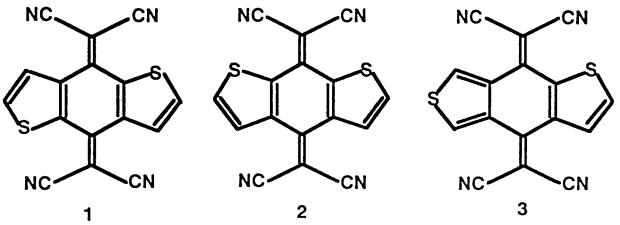
The crystal structures of the charge-transfer complexes of two isomeric thiophene-fused TCNQs, 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene (**1**), and [1,2-*b*:4,5-*c'*] isomer (**3**) with tetrathiafulvalene (TTF) have been determined by the X-ray method. For **1**–**TTF**, triclinic, $P\bar{1}$, a=10.458(2), b=9.852(2), c=11.292(8) Å, α=92.60(7), β=113.64(6), γ=97.38(6)°, V=1051(2) Å^3, Z=2, D_x=1.646 Mg m^{-3}. For **3**–**TTF**, triclinic, $P\bar{1}$, a=9.059(2), b=8.459(2), c=8.850(2) Å, α=103.36(2), β=115.76(2), γ=106.30(2)°, V=535.1(3) Å^3, Z=1, D_x=1.616 Mg m^{-3}. The final R values are 0.079 for 3437 observed reflections and 0.048 for 1937 observed reflections for **1**–**TTF** and **3**–**TTF**, respectively. The crystal structure of **1**–**TTF** complex is composed of TTF pairs and TCNQ pairs. These pairs stack alternately with each other. The mean distances between molecular planes are: 3.62 Å for **TTF**–**TTF**, 3.49 Å for **1**–**1** and 3.36 Å for **1**–**TTF**. In the crystals of **3**–**TTF** the molecules form mixed stacks with the separation of 3.59 Å. The molecular geometry of **TTF** in the **1**–**TTF** complex shows a TTF^+ character, while that in **3**–**TTF** shows a neutral type.

Thiophene-fused TCNQ compounds, 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene (**1**), [1,2-*b*:5,4-*b'*] isomer (**2**) and [1,2-*b*:4,5-*c'*] isomer (**3**) formed charge-transfer complexes with tetrathiafulvalene (TTF) in acetonitrile. Conductivities were measured at room temperature on compressed pellets. Extremely high values were observed for **1**–**TTF** (4.78 S cm^{-1}) and **2**–**TTF** (0.89 S cm^{-1}), while low value (less than 10^{-6} S cm^{-1}) was obtained for **3**–**TTF**.[1,2] Crystal structures of **1**–**TTF** and **3**–**TTF** have been determined in order to investigate the crystal structural variation associated with the conductivities and to compare the molecular structures of acceptors in the complexes to those in the neutral molecules.[3]



Scheme 1.

Table 1. Crystal Data, Details of Data Collection and Structure Refinement

	1–**TTF** ($C_6H_4S_4$) ($C_{16}H_4N_4S_2$)	**3**–**TTF** ($C_6H_4S_4$) ($C_{16}H_4N_4S_2$)
Color	Black red	Purple red
Crystal shape	Needles	Needles
Crystal size/mm	0.15×0.22×0.45	0.70×0.15×0.46
M_r	520.73	520.73
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.458(8)	9.059(2)
b/Å	9.852(8)	8.459(2)
c/Å	11.292(9)	8.850(2)
α/°	92.60(7)	103.36(2)
β/°	113.64(6)	115.76(2)
γ/°	97.38(6)	106.30(2)
V/Å^3	1051(2)	535.1(3)
Z	2	1
D_x/Mg m^{-3}	1.646	1.616
Radiation	Mo$K\alpha$	Mo$K\alpha$
λ/Å	0.71069	0.71069
μ/mm^{-1}	0.645	0.633
For cell parameters		
2θ range/°	30.3—35.0	29.4—34.9
No. of reflections	25	24

Table 1. (Continued)

	1–TTF ($C_6H_4S_4$) ($C_{16}H_4N_4S_2$)	**3**–TTF ($C_6H_4S_4$) ($C_{16}H_4N_4S_2$)
Scan range $2\theta/°$	2—55	2—55
Scan width $\Delta\omega/°$	1.3+0.4tan θ	1.15+0.4tan θ
Scan speed $2\theta/°\,min^{-1}$	4	4
Scan mode	2θ–ω	2θ–ω
Monitored reflections	4 0 −3, 2 0 −5,	−2 4 −1, −2 1 2
(every 50 reflections)	1 −4 1	1 3 −1
Variation of intensities	0.994—1.002	0.992—1.019
Range of h,k,l	−13—13, 0—12, −14—13	−11—11, 0—11, −11—11
Time for back-ground/s	10	10
No. of reflections		
Measured	5119	2625
Observed ($\|F_o\|>3\sigma(F)$)	3437	1937
R	0.075	0.047
wR	0.075	0.047
$\Delta\rho_{max}$—$\Delta\rho_{min}$/eÅ^{-3}	0.696—−0.689	0.372—−0.478

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors (B_{eq}) for Non-H Atoms

$$B_{eq}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$$

(**1**) (×10^4) Atom	x	y	z	B_{eq}/Å^2
S(1A)	3512(6)	1420(7)	1532(7)	4.10(9)
C(2A)	3388(13)	2524(13)	387(12)	3.05(12)
C(3A)	4529(17)	2658(17)	106(17)	2.80(13)
S(5A)	9297(5)	318(7)	1755(7)	4.13(9)
C(6A)	9404(14)	−770(13)	2917(12)	3.15(12)
C(7A)	8298(17)	−914(18)	3238(16)	2.85(13)
C(1B)	3657(17)	1412(18)	1559(18)	2.68(13)
C(2B)	3338(12)	2342(13)	713(12)	2.95(12)
S(3B)	4464(5)	2829(5)	−16(5)	3.33(9)
C(5B)	9131(16)	358(18)	1769(17)	3.03(13)
C(6B)	9468(12)	−567(13)	2626(12)	2.89(12)
S(7B)	8368(5)	−1011(6)	3406(6)	3.99(9)
N(1)	2898(7)	−920(8)	3288(8)	5.35(11)
N(2)	6609(7)	−2209(8)	4997(7)	5.23(11)
N(3)	6138(7)	3902(8)	−1736(7)	4.64(11)
N(4)	9794(7)	2403(8)	−193(7)	4.99(11)
C(4)	6941(6)	1653(7)	808(6)	2.54(10)
C(8)	5882(6)	146(7)	2549(6)	2.62(10)
C(9)	5383(7)	−624(7)	3302(7)	3.03(10)
C(10)	7418(6)	2367(7)	−14(7)	2.82(10)
C(11)	5107(6)	1073(7)	1684(7)	2.67(10)
C(12)	5583(6)	1772(7)	865(6)	2.58(10)
C(13)	7730(6)	725(7)	1673(7)	2.67(10)
C(14)	7260(6)	31(7)	2497(6)	2.65(10)
C(15)	3967(7)	−715(8)	3249(7)	3.47(11)
C(16)	6134(7)	−1493(8)	4224(8)	3.73(11)
C(17)	6653(7)	3219(8)	−944(7)	3.23(11)
C(18)	8770(7)	2323(8)	−70(7)	3.53(11)
S(1T)	775(2)	4791(2)	−1975(2)	3.75(6)
S(2T)	−607(2)	6699(2)	−3820(2)	3.37(5)
S(3T)	2091(2)	7114(2)	−4600(2)	3.31(5)
S(4T)	3336(2)	5062(2)	−2870(2)	3.31(5)
C(3T)	841(7)	5867(7)	−3116(7)	2.96(10)
C(4T)	−894(8)	5076(9)	−2139(8)	4.47(11)
C(5T)	−1497(7)	5926(9)	−2962(8)	4.05(11)
C(6T)	1994(7)	6032(7)	−3484(7)	2.97(11)
C(7T)	3609(7)	6594(8)	−4613(8)	3.89(11)
C(8T)	4175(7)	5693(8)	−3824(8)	3.82(11)

Occupancy factor: A 0.484(2), B 0.516(2).

(**2**) (×10^4) Atom	x	y	z	B_{eq}/Å^2
S(1A)	3480(5)	2681(5)	576(6)	4.75(6)
C(2A)	4768(7)	1703(8)	1654(8)	6.22(7)
C(3A)	3627(7)	263(7)	1739(8)	3.05(7)
C(1B)	3276(6)	2371(6)	434(7)	3.49(7)
S(2B)	4866(3)	1672(3)	1536(4)	5.89(5)
C(3B)	3420(6)	−171(6)	1435(7)	4.21(7)
C(1C)	3486(7)	2285(7)	721(8)	3.49(7)
C(2C)	4833(7)	1741(8)	1608(8)	6.19(7)
S(3C)	3735(4)	20(5)	1971(5)	4.83(6)
N(1)	2302(4)	5284(4)	−1149(4)	5.57(6)
N(2)	−3143(4)	3070(4)	−3334(4)	5.68(6)
C(8)	−127(4)	1422(4)	−718(4)	3.15(6)
C(9)	−267(4)	2700(4)	−1435(4)	3.40(6)
C(11)	1567(3)	1275(4)	222(4)	3.28(6)
C(12)	1681(3)	−84(4)	888(4)	3.41(6)
C(15)	1227(4)	4106(4)	−1248(4)	3.93(6)
C(16)	−1929(4)	2826(4)	−2498(4)	4.11(6)
S(1T)	2779(1)	1569(1)	5750(1)	4.40(3)
S(2T)	−612(1)	2007(1)	3978(1)	4.54(3)
C(3T)	453(4)	741(4)	4950(4)	3.33(6)
C(4T)	2850(5)	3358(4)	5103(5)	5.49(6)
C(5T)	1348(5)	3552(4)	4328(5)	5.63(6)

Occupancy factor: A 0.25, B 0.50, C 0.25.

Experimental

Crystal data, details of data collection and structure refinement are listed in Table 1. Intensity data were collected using a Rigaku diffractometer with graphite monochromator. No absorption corrections were applied. The structure of **1**–**TTF** was solved by the direct method with the program MULTAN78.[4] During the refinements the molecule of **1** showed an orientational disorder with an approximate symmetry of mm. The disordered mode is very similar to that in the crystal structure of the uncomplexed **1**.[3] In the present case only peripheral atoms of thiophene rings were treated to be disordered with the preliminary occupancy factors estimated to be 0.5 : 0.5 from the peak heights of the D-maps. TCNQ framework was treated as ordered, i.e. with a unit occupancy factor. H atoms were located from the calculation. The final refinement was carried out by the full-matrix least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H using SHELX76.[5] The occupancy factors for the disordered structures were also refined to be 0.484(2) : 0.516(2) for the molecules **A** : **B**. The final R value was 0.075 for 3437 observed reflections. $\Sigma w(|F_c|-k^{-1}|F_o|)^2$ was minimized with a unit weight for all reflections.

The structure of **3**–**TTF** was solved by the direct method. The structure of **3** in the complex was also revealed to be disordered in the same manner as in the crystals of the uncomplexed **3**. In the present case occupancy factors are 0.25 : 0.25 : 0.25 : 0.25 for each disordered molecule, since the molecules of **3** and **TTF** were located on the centered symmetry of the space group $P\bar{1}$. Thus the set of peripheral atoms of thiophene rings were classified to three types, S(1A)–C(2A)–C(3A), C(1B)–S(2B)–C(3B), and C(1C)–C(2C)–S(3C), with occupancy factors of 0.25, 0.50, and 0.25, respectively. The other atoms were treated with occupancy factor of 1.0. H atoms were located from the calculation. Full-matrix least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H reduced R value to 0.047 for 1937 observed reflections. w=1 for all reflections. The refinement with the space group $P\bar{1}$ could not be converged.

Atomic scattering factors were used from International Tables for X-Ray Crystallography.[6] All computations were performed on a HITAC M260D and an IBM ES/3090-180S Computers of Information Processing Center of the University of Electro-Communications with the programs MULTAN78, SHELX76, UNICS III,[7] ORTEP II.[8] The final atomic parameters are given in Table 2.[9]

Discussions

The molecular structures with the atomic numbering are shown in Fig. 1. Bond distances and angles are listed in Table 3. The dihedral angles between selected planes are listed in Table 4.

Structure of 1-TTF. Figure 2 shows the crystal structure of **1**–**TTF** viewed along the c axis. The crystal structure of **1**–**TTF** complex is composed of TTF pairs and TCNQ pairs as shown in Fig. 2. These pairs stack alternately with each other. The mean distances between molecular planes are: 3.62 Å for **TTF**–**TTF**, 3.49 Å for **1**–**1** and 3.36 Å for **1**–**TTF**. The intermolec-

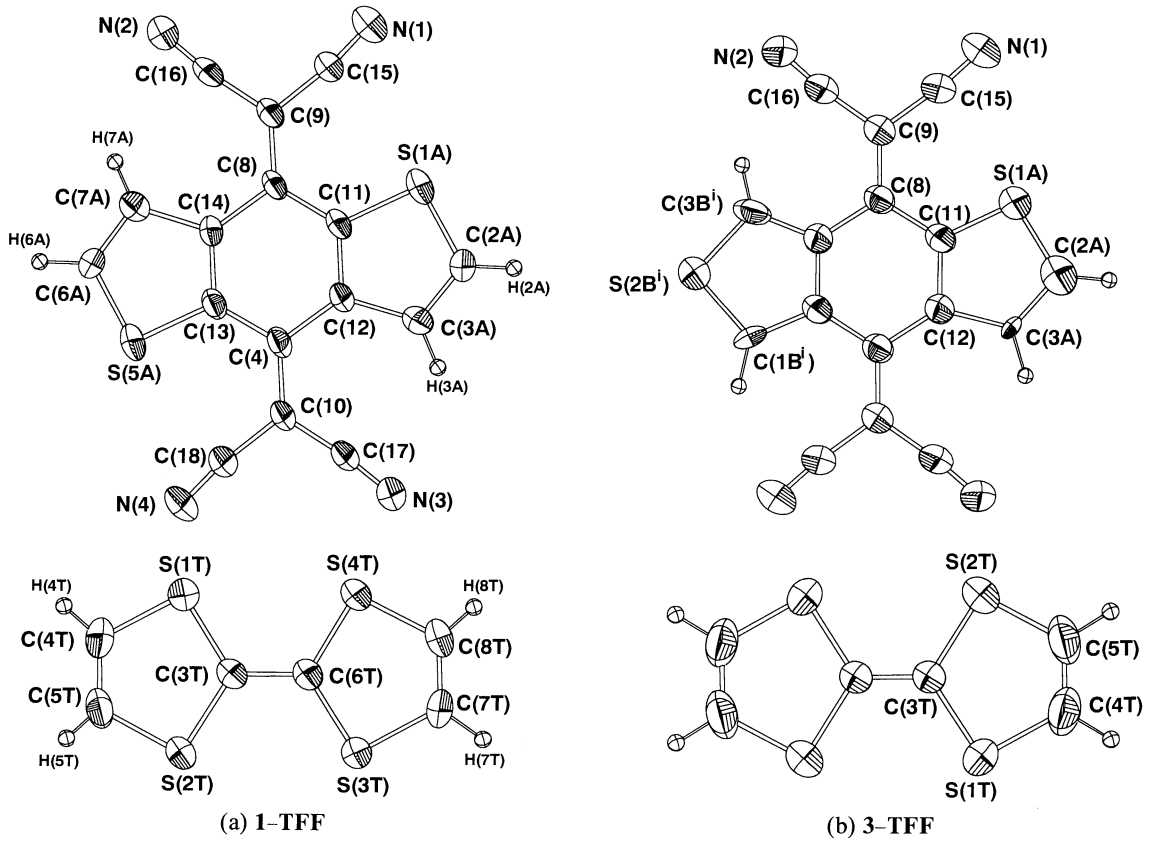


Fig. 1. ORTEPII drawings with atom numbering. (a) **1**–**TTF** and (b) **3**–**TTF**.

Table 3. Bond Lengths (l) and Angles (θ) of Non-H Atoms

Length	l/Å	Length	l/Å	Angle	θ/°	Angle	θ/°
(1–TTF)							
S(1A)–C(2A)	1.704(16)	C(1B)–C(2B)	1.329(24)	C(2A)–S(1A)–C(11)	94.1(7)	C(2B)–C(1B)–C(11)	105.8(14)
S(1A)–C(11)	1.689(11)	C(1B)–C(11)	1.547(21)	S(1A)–C(2A)–C(3A)	112.1(12)	C(1B)–C(2B)–S(3B)	119.1(12)
C(2A)–C(3A)	1.345(24)	C(2B)–S(3B)	1.721(15)	C(2A)–C(3A)–C(12)	111.9(15)	C(2B)–S(3B)–C(12)	90.0(6)
C(3A)–C(12)	1.507(21)	S(3B)–C(12)	1.708(9)	C(6A)–S(5A)–C(13)	92.5(7)	C(6B)–C(5B)–C(13)	106.5(14)
S(5A)–C(6A)	1.710(16)	C(5B)–C(6B)	1.334(23)	S(5A)–C(6A)–C(7A)	114.8(12)	C(5B)–C(6B)–S(7B)	118.6(12)
S(5A)–C(13)	1.703(11)	C(5B)–C(13)	1.517(21)	C(6A)–C(7A)–C(14)	109.6(14)	C(6B)–S(7B)–C(14)	88.8(6)
C(6A)–C(7A)	1.337(23)	C(6B)–S(7B)	1.734(15)	S(1A)–C(11)–C(8)	124.4(6)	C(1B)–C(11)–C(8)	124.6(9)
C(7A)–C(14)	1.532(20)	S(7B)–C(14)	1.702(10)	S(1A)–C(11)–C(12)	112.0(6)	C(1B)–C(11)–C(12)	111.8(9)
				C(3A)–C(12)–C(4)	127.0(9)	S(3B)–C(12)–C(4)	123.8(6)
N(1)–C(15)	1.130(12)	C(8)–C(11)	1.442(10)	C(3A)–C(12)–C(11)	110.0(9)	S(3B)–C(12)–C(11)	113.2(6)
N(2)–C(16)	1.142(12)	C(8)–C(14)	1.485(10)	S(5A)–C(13)–C(4)	124.4(6)	C(5B)–C(13)–C(4)	125.2(9)
N(3)–C(17)	1.142(11)	C(9)–C(15)	1.449(11)	S(5A)–C(13)–C(14)	112.5(6)	C(5B)–C(13)–C(14)	111.6(9)
N(4)–C(18)	1.127(11)	C(9)–C(16)	1.425(12)	C(7A)–C(14)–C(8)	126.5(9)	S(7B)–C(14)–C(8)	122.8(6)
C(4)–C(10)	1.395(10)	C(10)–C(17)	1.424(11)	C(7A)–C(14)–C(13)	110.5(9)	S(7B)–C(14)–C(13)	114.3(6)
C(4)–C(12)	1.466(10)	C(10)–C(18)	1.447(11)				
C(4)–C(13)	1.450(10)	C(11)–C(12)	1.385(10)	C(10)–C(4)–C(12)	122.7(6)	C(4)–C(10)–C(18)	124.7(7)
C(8)–C(9)	1.372(11)	C(13)–C(14)	1.383(10)	C(10)–C(4)–C(13)	123.3(7)	C(17)–C(10)–C(18)	109.4(7)
				C(12)–C(4)–C(13)	114.0(6)	C(8)–C(11)–C(12)	123.6(7)
S(1T)–C(3T)	1.722(8)	S(4T)–C(6T)	1.729(8)	C(9)–C(8)–C(11)	124.3(7)	C(4)–C(12)–C(11)	123.0(6)
S(1T)–C(4T)	1.741(10)	S(4T)–C(8T)	1.730(9)	C(9)–C(8)–C(14)	122.1(7)	C(4)–C(13)–C(14)	123.1(7)
S(2T)–C(3T)	1.735(8)	C(3T)–C(6T)	1.418(11)	C(11)–C(8)–C(14)	113.5(6)	C(8)–C(14)–C(13)	122.8(7)
S(2T)–C(5T)	1.729(9)	C(4T)–C(5T)	1.304(13)	C(8)–C(9)–C(15)	124.7(7)	N(1)–C(15)–C(9)	171.7(9)
S(3T)–C(6T)	1.712(8)	C(7T)–C(8T)	1.310(12)	C(8)–C(9)–C(16)	126.6(7)	N(2)–C(16)–C(9)	172.4(10)
S(3T)–C(7T)	1.734(9)			C(15)–C(9)–C(16)	108.7(7)	N(3)–C(17)–C(10)	173.3(9)
				C(4)–C(10)–C(17)	125.9(7)	N(4)–C(18)–C(10)	172.6(9)
				C(3T)–S(1T)–C(4T)	94.2(4)	S(1T)–C(4T)–C(5T)	117.3(7)
				C(3T)–S(2T)–C(5T)	93.7(4)	S(2T)–C(5T)–C(4T)	118.7(7)
				C(6T)–S(3T)–C(7T)	93.8(4)	S(3T)–C(6T)–S(4T)	116.8(4)
				C(6T)–S(4T)–C(8T)	93.5(4)	S(3T)–C(6T)–C(3T)	122.6(6)
				S(1T)–C(3T)–S(2T)	116.1(4)	S(4T)–C(6T)–C(3T)	120.5(6)
				S(1T)–C(3T)–C(6T)	121.9(6)	S(3T)–C(7T)–C(8T)	117.7(7)
				S(2T)–C(3T)–C(6T)	122.0(6)	S(4T)–C(8T)–C(7T)	118.1(7)
(3–TTF)							
S(1A)–C(2A)	1.701(9)	N(1)–C(15)	1.136(5)	C(2A)–S(1A)–C(11)	95.5(4)	C(3A)–C(12)–C(8^{i})	132.5(4)
S(1A)–C(11)	1.647(6)	N(2)–C(16)	1.136(5)	S(1A)–C(2A)–C(3A)	107.2(6)	C(3B)–C(12)–C(8^{i})	124.6(4)
C(2A)–C(3A)	1.400(10)	C(8)–C(9)	1.382(5)	C(2A)–C(3A)–C(12)	117.0(6)	S(3C)–C(12)–C(8^{i})	122.1(3)
C(3A)–C(12)	1.488(8)	C(8)–C(11)	1.453(5)	S(2B)–C(1B)–C(11)	108.4(4)	C(9)–C(8)–C(11)	122.7(3)
C(1B)–S(2B)	1.703(7)	C(8^{i})–C(12)	1.459(5)	C(1B)–S(2B)–C(3B)	96.2(3)	C(9)–C(8)–C(12^{i})	122.7(3)
C(1B)–C(11)	1.467(7)	C(9)–C(15)	1.443(5)	S(2B)–C(3B)–C(12)	109.4(4)	C(11)–C(8)–C(12^{i})	114.6(3)
S(2B)–C(3B)	1.686(7)	C(9)–C(16)	1.438(5)	C(2C)–C(1C)–C(11)	120.5(6)	C(8)–C(9)–C(15)	125.4(3)
C(3B)–C(12)	1.463(7)	C(11)–C(12)	1.416(5)	C(1C)–C(2C)–S(3C)	103.2(5)	C(8)–C(9)–C(16)	125.2(3)
C(1C)–C(2C)	1.402(10)			C(2C)–S(3C)–C(12)	98.5(4)	C(15)–C(9)–C(16)	109.3(3)
C(1C)–C(11)	1.507(8)			S(1A)–C(11)–C(8)	121.9(3)	C(8)–C(11)–C(12)	122.3(3)
C(2C)–S(3C)	1.701(9)			S(1A)–C(11)–C(12)	115.8(3)	C(11)–C(12)–C(8^{i})	123.1(3)
S(3C)–C(12)	1.645(6)			C(1B)–C(11)–C(8)	124.7(4)	N(1)–C(15)–C(9)	173.9(4)
				C(1B)–C(11)–C(12)	112.8(4)	N(2)–C(16)–C(9)	173.6(4)
S(1T)–C(3T)	1.755(4)	S(2T)–C(5T)	1.729(5)	C(1C)–C(11)–C(8)	135.0(4)		
S(1T)–C(4T)	1.732(5)	C(3T)–C(3T^{ii})	1.338(7)	C(1C)–C(11)–C(12)	102.8(4)		
S(2T)–C(3T)	1.761(4)	C(4T)–C(5T)	1.309(6)	C(3A)–C(12)–C(11)	104.4(4)		
				C(3B)–C(12)–C(11)	111.4(4)		
				S(3C)–C(12)–C(11)	114.8(3)		
				C(3T)–S(1T)–C(4T)	94.4(2)	S(2T)–C(3T)–C(3T^{ii})	122.4(3)
				C(3T)–S(2T)–C(5T)	94.1(2)	S(1T)–C(4T)–C(5T)	118.2(4)
				S(1T)–C(3T)–S(2T)	114.6(2)	S(2T)–C(5T)–C(4T)	118.7(4)
				S(1T)–C(3T)–C(3T^{ii})	123.0(3)		

i=$-x$, $-y$, $-z$; ii=$-x$, $-y$, 1$-z$.

ular distance of 3.36 Å between **TTF** and **1** indicates that there is a significant interaction between the donor and the acceptor molecules. Significant short contacts are observed between S atoms of **1–TTF** pair [S(5A)···S(2T^{i})=3.425(8) Å, i=1$-x$, 1$-y$, $-z$); S(3B)···S(4T^{i})=3.518(6) Å]. The molecular overlappings are shown in

Table 4. Dihedral Angles of Selected Planes

Planes		1–TTF ϕ/°	3–TTF ϕ/°
I	II	0.2(5)	0.4(1)
I	III	2.5(3)	3.8(1)
I	IV	2.0(3)	0.9(1)
I	V	2.6(4)	
I	VI	8.8(2)	175.6(1)
I	VII	176.1(2)	
I	VIII	2.1(2)	

For **1**–**TTF** I C(11), C(12), C(13), C(14), C(4), C(8)
II S(1A), C(2A), C(3A), C(11), C(12)
III S(5A), C(6A), C(7A), C(13), C(14)
IV C(1B), C(2B), S(3B), C(11), C(12)
V C(5B), C(6B), S(7B), C(13), C(14)
VI N(1), N(2), C(8), C(9), C(15), C(16)
VII N(3), N(4), C(4), C(10), C(17), C(18)
VIII S(1T), S(2T), S(3T), S(4T), C(3T), C(6T)

For **3**–**TTF** I C(11), C(12), C(11^{i}), C(12^{i}), C(8), C(8^{i})
II S(1A), C(2A), C(3A), C(11), C(12)
III C(1B), S(2B), C(3B), C(11), C(12)
IV C(1C), C(2C), S(3C), C(11), C(12)
VI N(1), N(2), C(8), C(9), C(15), C(16)
VIII S(1T), S(2T), S(1T^{ii}), S(2T^{ii}), C(3T), C(3T^{ii})

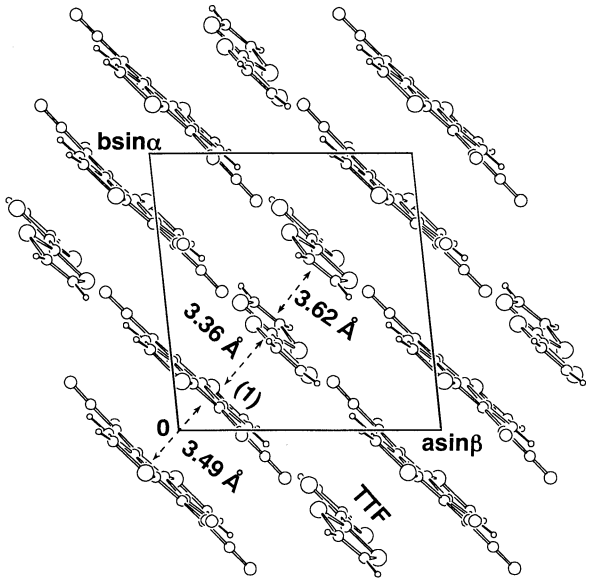


Fig. 2. Projection of the crystal structure of **1**–**TTF** viewed along the *c* axis.

Fig. 3. The molecular network of **1**–**TTF** is shown in Fig. 4. There are no short contacts between acceptor molecules within the network, while some significantly short contacts [S(2T)···N(2^{ii})=3.038(9), ii=$x-1$, y, $z-1$; S(4T)···N(3)=3.085 Å)] are observed between S of **TTF** and N of **1**.

A side view of the molecule **1** in the complex is depicted in Fig. 5 to represent the molecular planarity. The molecule **1** in the complex is more planar than that of the uncomplexed **1**. Six atoms of the quinonoid ring

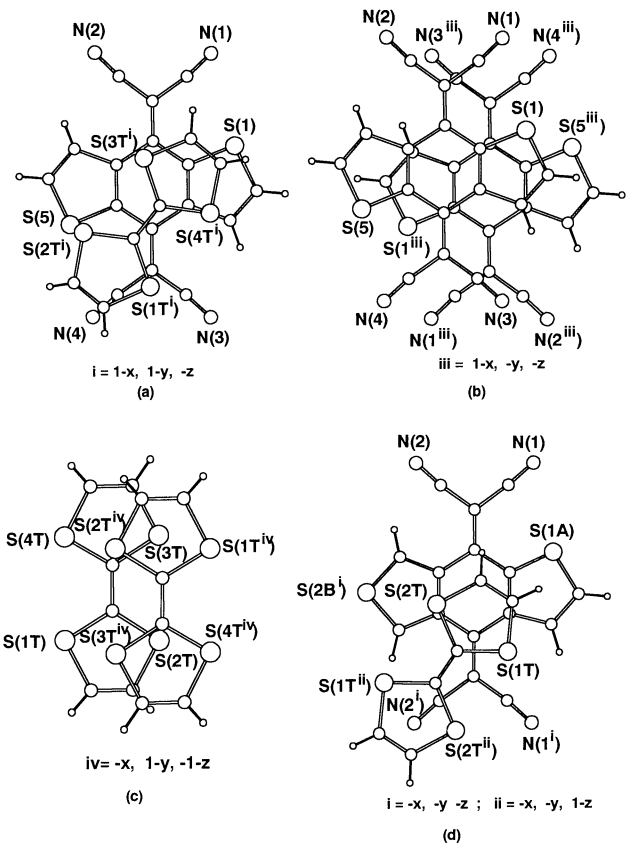
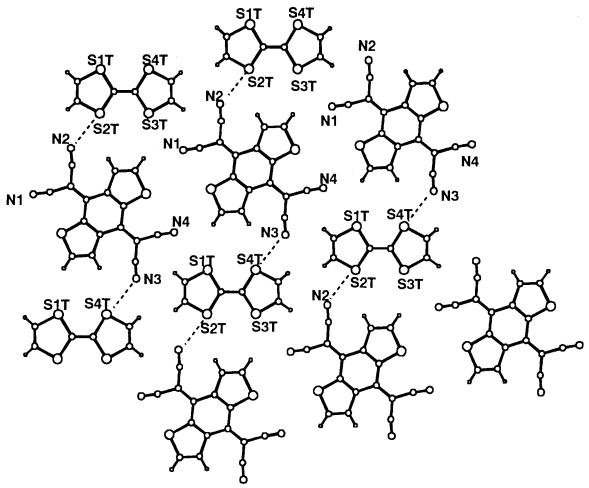


Fig. 3. Molecular overlappings of (a) **1**–**TTF**, (b) **1**–**1**, (c) **TTF**–**TTF** in **1**–**TTF**, and (d) **3**–**TTF**.

(plane **I**) are in one plane with the maximum deviation of 0.007(5) Å. The dihedral angles between the plane **I** and the thiophene ring are 0.5(5) and 2.5(3)° for molecule **A** and 2.0(3) and 2.6(4)° for **B**. Those between the plane **I** and dicyanomethylene groups are 8.8(2) and 176.1(2)°. On the other hand the shape of the uncomplexed molecule is a butterfly shape with a boat conformation of the quinonoid ring and with bent thiophene rings and dicyanomethylene groups from the quinonoid plane. However, it is very interesting that the planarity of the molecule is not so disadvantageous against the deformed structure of the uncomplexed molecule. The mean values of nonbonding intramolecular S···C, S···N, and C···C distances between the peri-atoms of thiophene rings and the cyano groups are 2.861, 3.232, and 2.881 Å, respectively, which are comparable with the corresponding distances of the uncomplexed **1**.

Bond lengths of TCNQ framework of the molecule **1** in the complex is similar to those of the uncomplexed **1**. Slight changes from the uncomplexed state are observed in the geometry of the thiophene rings. The mean value (1.717 Å) of S–C (thiophene) is longer than that of S–C (fused) (1.701 Å). The situation is opposite in the uncomplexed molecule, that is, the mean value of S–C (thiophene), 1.676 Å is shorter than that of S–C (fused), 1.709 Å. The bond angles are not so changed in spite of the large change of the molecular planarity.



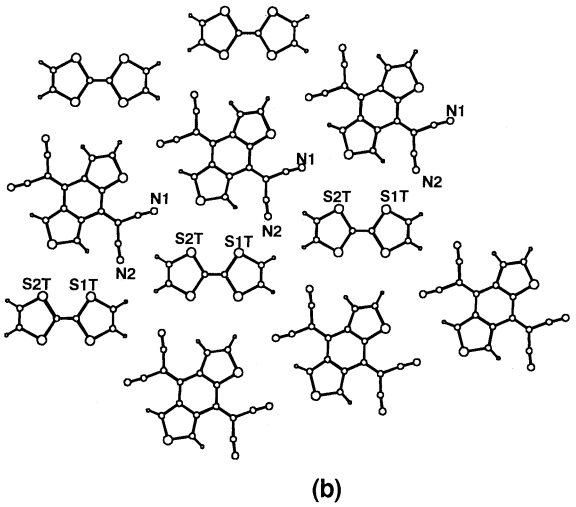


Fig. 4. Molecular network of (a) **1**–**TTF** and (b) **3**–**TTF**.

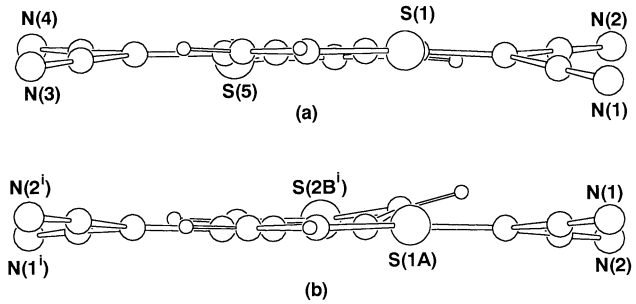


Fig. 5. Side view of the molecules of (a) **1** and (b) **3** in the TTF complexes.

As disclosed above, **1**–**TTF** crystallizes in a mixed stacked –D–D–A–A–D–D–A–A– structure. Nevertheless, the compressed solid sample exhibits high conductivity. We suspect that **1**–**TTF** crystallizes in polymorph and the specimen employed for the measurement of conductivity may be a mixture of polymorphic crystals. Single crystals of charge-transfer complexes of **1** and TTF were obtained, when warm acetonitrile solution of TTF and thiophene-fused TCNQ were mixed and the solvent was allowed to evaporate. Several prisms among most of fine needles could be picked up for X-ray analysis. Fine needles were not appropriate for X-ray analysis.

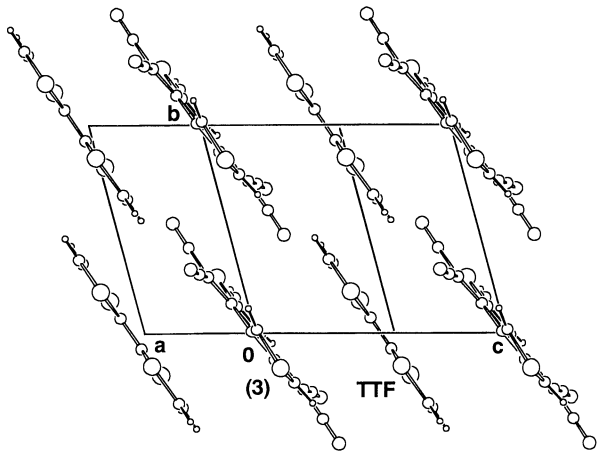


Fig. 6. Projection of the crystal structure of **3**–**TTF** viewed along the a^* axis.

Structure of 3–TTF. The crystal structure of **3**–**TTF** viewed along the a^* axis is shown in Fig. 6. In the crystals of **3**–**TTF** the molecules form mixed stacks along the c axis with the separation of 3.59 Å. Although the mode of the molecular overlapping shown in Fig. 3d is close to that of **1**–**TTF**, an overlapping area of the molecules is smaller than that of **1**–**TTF**. These structural features show the low conductivity observed in **3**–**TTF**.

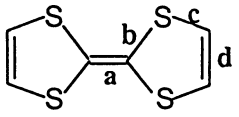
The donor and acceptor molecules are arranged side-by-side to form a sheet-like network. It is very interesting that the molecular arrangements in the network are similar to those of **1**–**TTF** as shown in Figs. 4 and 6, in spite of the difference of stacking modes of **1**–**TTF** and **3**–**TTF**. A sheet-like network formed with TTF and fused-TCNQ is also reported in TTF complex with bis(1,2,5-thiadiazole)-fused tetracyanoquinodimethane,[10] although relative arrangement of donor and acceptor molecules and planarity of the sheet are significantly different.

The quinonoid plane of the complexed molecule **3** is planar with the maximum deviation of 0.004(2) Å. The dihedral angles between quinonoid plane and other parts of the molecules shown in Table 4 are much smaller than those of the uncomplexed molecule **3**. Molecules of **1** and **3** in the complexes show similar orientational disorders with those in crystals of **1** and **3**, respectively. In the case of **3** both complexed and uncomplexed crystals show so complicated disorder as to discuss the detailed molecular structures.

Structure of TTF. Table 5 shows a comparison of the structures of **TTF** in various electronic states.[11–13]

Table 5. A Comparison of the Structure of TTF

Bonds	TTF^0 l/Å	$TTF^{\delta+}$ l/Å	TTF^+ l/Å	**1**–TTF l/Å	**3**–TTF l/Å
a	1.349(3)	1.369(4)	1.404(14)	1.418(11)	1.338(7)
b	1.757(2)	1.743(3)	1.713(9)	1.725(8)	1.758(5)
c	1.730(2)	1.737(3)	1.725(11)	1.734(9)	1.731(5)
d	1.314(3)	1.323(4)	1.306(16)	1.307(13)	1.309(6)
Ref.	11	12	13	Present study	



The molecular geometry of **TTF** in the **1**–**TTF** complex shows a TTF^+ character, while that in **3**–**TTF** shows a neutral type. On the other hand the difference of the TCNQ moieties of **1** and **3** in the complexed state and in the neutral molecules is not clear because of the disordered structures.

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