An Isomeric Series of Thiophene-Fused Tetracyanoquinodimethanes. II.[#] The Crystal and Molecular Structures

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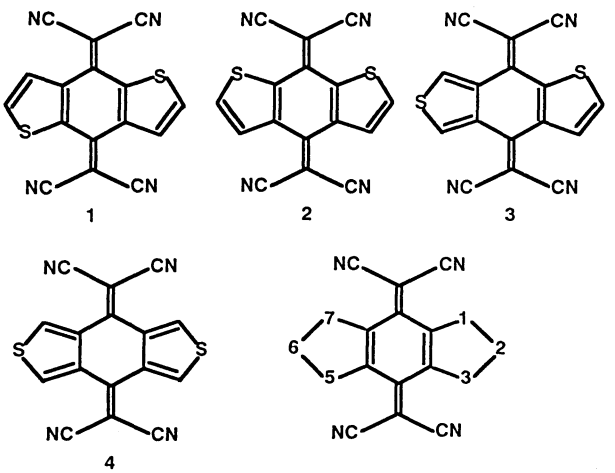
The crystal structures of three isomeric thiophene-fused TCNQs, 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene (**1**), [1,2-*b*:5,4-*b'*] isomer (**2**), and [1,2-*b*:4,5-*c'*] isomer (**3**) have been determined by the X-ray method. The crystals of **1**, **2**, and **3** are an isostructure of the monoclinic system with the space group of $P2_1/n$. For **1**, a=16.588(3), b=7.222(5), c=11.353(3) Å, β=89.88(2)°, V=1360.1(10) Å^3, Z=4, D_x=1.545 Mg m^{-3}. For **2** a=16.594(4), b=7.232(2), c=11.433(2) Å, β=91.05(2)°, V=1371.8(5) Å^3, D_x=1.532 Mg m^{-3}. For **3** a=16.738(2), b=7.342(3), c=10.922(3) Å, β=92.98(2)°, V=1340.4(7) Å^3, D_x=1.568 Mg m^{-3}. These crystals show an orientational disorder with an approximate molecular symmetry of mm. The occupancy factors are 0.834:0.166, 0.709:0.291, and 0.5:0.1:0.15:0.25 for **1**, **2**, and **3**, respectively. The final R values are 0.065, 0.070, and 0.096 for 2308, 2410, and 1566 observed reflections for **1**, **2**, and **3**, respectively. In the crystals molecules form a sheet-like network perpendicular to the b axis, with short intermolecular S···N distances (3.047 and 3.086 Å for **1** and 3.076 Å for **2**). The internetwork distances between S atoms are significantly shorter than the van der Waals contact: 3.451 and 3.461 Å for **1** and **2**, respectively. Each molecule has a butterfly shape. Two dicyanomethylene groups are bent from the quinonoid ring to the same side and two thiophene rings are bent to the opposite side of the dicyanomethylene groups.

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**) exhibited low reduction potentials and formed highly conducting charge-transfer complexes with tetrathiafulvalene (TTF) and conducting salt with tetraethylammonium.[1,2] It is quite of interest to see the molecular planarity of these π-acceptors in relation to an isoelectronic π-acceptor, tetracyanoanthraquinodimethane, which has been suggested to be highly deformed and, consequently, gives no conducting charge-transfer complexes. Also we are interested in the crystal structures of these new acceptors: The mode of fusion of the thiophene rings should affect the crystal structures and provide useful information for the molecular design of synthetic metals. In this paper the structures of a series of thiophene-fused TCNQs **1**, **2**, and **3** will be reported.



Scheme 1.

Experimental

Single crystals of **1**, **2**, and **3** for X-ray analysis were grown from the acetonitrile solution. For **4**, in spite of various attempts, no appropriate crystals for X-ray analysis were obtained. 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** was solved by the direct method with the program MULTAN78.[3] During the refinements the structure showed an orientational disorder with pseudo symmetry of mm. The preliminary occupancy factors of disordered molecules, **A** and **B**, were estimated from the peak heights of D-maps to be 0.8:0.2. Peripheral atoms of the thiophene rings of the molecule **A** were assigned to S(1)-C(2)-C(3) and S(5)-C(6)-C(7), while those of the molecule **B** were to C(1)-C(2)-S(3) and C(5)-C(6)-S(7), after the atomic numbering of the molecules shown in the scheme was fixed about the crystal lattice. The positions of the H atoms were obtained from the calculation. At first the structure was refined by the block-diagonal least-squares. The final refinement with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms was carried out by the full-matrix least-squares using the program SHELX76.[4] In these least-squares the occupancy factors were also refined to be 0.834(1):0.166(1) and the geometry of the molecule **B** with the lower occupancy factor was subjected to be constrained. The final R and wR values are 0.065 and 0.063, respectively for 2308 observed reflections where $w=2.2836/(\sigma^2(F)+0.000239|F_o|^2)$.

For **2** the structure was also revealed to be disordered. S

[#] For part I; see p. 2168.

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

	1 $C_{16}H_4N_4S_2$	**2** $C_{16}H_4N_4S_2$	**3** $C_{16}H_4N_4S_2$
Color	Purple red	Purple red	Brown
Crystal shape	Plates	Plates	Needles
Crystal size/mm	0.15×0.22×0.45	0.17×0.42×0.37	0.11×0.15×0.65
M_r	316.37	316.37	316.37
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	16.588(3)	16.594(4)	16.738(2)
b/Å	7.222(5)	7.232(2)	7.342(3)
c/Å	11.353(3)	11.433(2)	10.922(3)
β/°	89.88(2)	91.05(2)	92.98(2)
V/Å^3	1360.1(10)	1371.8(5)	1340.4(7)
Z	4	4	4
D_x/Mg m^{-3}	1.545	1.532	1.568
Radiation	Mo$K\alpha$	Mo$K\alpha$	Cu$K\alpha_1$
λ/Å	0.71069	0.71069	1.54048
μ/mm^{-1}	0.374	0.371	3.542
For cell parameters			
2θ range/°	27.2—33.5	29.4—34.9	93.5—117.5
No. of reflections	24	24	24
Scan range 2θ/°	2—55	2—55	2—130
Scan width $\Delta\omega$/°	1.4+0.5tanθ	1.3+0.5tanθ	1.2+0.5tanθ
Scan speed 2θ/° min^{-1}	4	4	4
Scan mode	2θ–ω	2θ–ω	2θ–ω
Monitored reflections	4 0 −4, 6 0 4,	4 0 −4, 6 0 4	2 2 3, −2 2 4
(every 50/150 reflections)	0 2 2	0 2 2	0 2 5
Variation of intensities	0.989—1.002	0.986—1.002	0.978—1.004
Range of h,k,l	−21—21, 0—9, 0—14	−21—21, 0—9, 0—14	−20—20, 0—9, 0—13
Time for back-ground/s	10	10	10
No. of reflections			
Measured	3321	3326	2026
Observed ($\|F_o\|>3\sigma(F)$)	2308	2410	1566
R	0.065	0.070	0.096
wR	0.063	0.065	0.096
$\Delta\rho_{max}$—$\Delta\rho_{min}$/eÅ^{-3}	0.325—−0.511	0.315—−0.423	0.414—−0.689

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

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

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
(**1**) (×10^5 for S of molecule **A**, ×10^4 for others)									
S(1A)	52362(6)	23082(16)	1857(10)	3.61(3)	S(3B)	5036(4)	1340(9)	2671(6)	5.34(7)
S(5A)	17585(6)	18926(16)	21326(10)	3.60(3)	S(7B)	1919(4)	2674(9)	−270(6)	5.63(7)
N(1A)	4967(3)	3938(6)	−2354(4)	5.42(6)	N(1B)	4924(4)	3881(9)	−2400(6)	4.93(7)
N(2A)	2510(3)	4829(7)	−2473(4)	5.90(6)	N(2B)	2464(4)	4775(9)	−2460(6)	5.72(7)
N(3A)	4490(3)	1924(8)	5177(4)	7.88(6)	N(3B)	4545(4)	2056(9)	5163(6)	7.65(7)
N(4A)	2057(3)	2646(7)	4834(4)	5.72(6)	N(4B)	2110(4)	2773(9)	4875(6)	5.67(7)
C(2A)	5545(2)	1475(6)	1493(4)	3.89(6)	C(1B)	5087(4)	1674(9)	571(6)	5.41(7)
C(3A)	4967(3)	1299(6)	2333(4)	3.08(6)	C(2B)	5622(4)	1795(9)	1496(6)	4.44(7)
C(4A)	3418(2)	2017(5)	2463(4)	3.04(6)	C(4B)	3439(4)	2082(9)	2474(6)	3.98(7)
C(6A)	1427(2)	2164(6)	756(4)	4.06(6)	C(5B)	1914(4)	1402(9)	1687(6)	5.39(7)
C(7A)	2001(3)	2470(7)	−83(4)	3.00(6)	C(6B)	1351(4)	1741(9)	804(6)	4.30(7)
C(8A)	3575(2)	2844(5)	−74(3)	3.15(6)	C(8B)	3564(4)	2842(9)	−65(6)	4.00(7)
C(9A)	3648(3)	3535(6)	−1194(4)	3.60(6)	C(9B)	3619(4)	3507(9)	−1201(6)	3.97(7)
C(10A)	3356(2)	2070(6)	3665(4)	3.45(6)	C(10B)	3395(4)	2173(9)	3682(6)	4.06(7)
C(11A)	4258(2)	2346(5)	665(4)	3.14(6)	C(11B)	4249(4)	2365(9)	653(6)	3.96(7)
C(12A)	4187(2)	1867(5)	1847(4)	3.31(6)	C(12B)	4202(4)	1917(9)	1847(6)	4.02(7)
C(13A)	2733(2)	2188(5)	1685(4)	3.07(6)	C(13B)	2744(4)	2237(9)	1717(6)	3.96(7)
C(14A)	2796(2)	2539(5)	489(4)	3.14(6)	C(14B)	2788(4)	2556(9)	517(6)	4.05(7)
C(15A)	4399(3)	3740(6)	−1810(4)	4.17(6)	C(15B)	4367(4)	3696(9)	−1839(6)	4.01(7)
C(16A)	2995(3)	4224(7)	−1889(4)	4.19(6)	C(16B)	2958(4)	4178(9)	−1882(6)	3.98(7)
C(17A)	4008(3)	1977(7)	4477(4)	5.11(6)	C(17B)	4055(4)	2099(9)	4476(6)	4.19(7)
C(18A)	2615(3)	2372(6)	4291(4)	4.04(6)	C(18B)	2659(4)	2489(9)	4327(6)	4.03(7)

Occupancy factor: A=0.834(1), B=0.166(1).

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
(2) ($\times10^5$ for S of molecule **A**, $\times10^4$ for others)									
S(1A)	52381(7)	23087(24)	2056(13)	3.10(3)	S(3B)	5069(3)	1364(7)	2654(4)	5.05(7)
S(7A)	18709(8)	26637(27)	−2714(13)	3.55(4)	S(5B)	1779(3)	1815(7)	2144(4)	4.69(7)
N(1A)	4962(4)	3937(10)	−2298(6)	5.34(8)	N(1B)	5001(3)	3948(7)	−2267(4)	5.12(9)
N(2A)	2473(4)	4854(10)	−2470(6)	5.48(8)	N(2B)	2513(3)	4826(7)	−2476(4)	5.90(9)
N(3A)	4512(4)	2062(11)	5143(6)	7.43(8)	N(3B)	4513(3)	2033(7)	5149(4)	7.93(9)
N(4A)	2060(3)	2763(10)	4764(5)	5.09(8)	N(4B)	2063(3)	2700(7)	4758(4)	4.97(8)
C(2A)	5548(3)	1439(9)	1534(5)	3.55(7)	C(1B)	5171(3)	2144(7)	413(4)	4.86(9)
C(3A)	4963(5)	1238(11)	2327(7)	4.53(8)	C(2B)	5602(3)	1625(7)	1398(4)	3.12(8)
C(4A)	3412(3)	2034(8)	2445(5)	2.78(7)	C(4B)	3431(3)	2001(7)	2436(4)	2.91(8)
C(5A)	1839(5)	2013(11)	1985(7)	3.46(8)	C(6B)	1429(3)	2208(7)	749(4)	3.94(9)
C(6A)	1384(3)	2038(9)	962(5)	3.19(7)	C(7B)	1976(3)	2556(7)	−111(4)	4.78(9)
C(8A)	3571(3)	2887(8)	−62(5)	2.92(7)	C(8B)	3596(3)	2872(7)	−60(4)	3.37(8)
C(9A)	3636(4)	3567(8)	−1191(5)	3.15(7)	C(9B)	3667(3)	3562(7)	−1183(4)	3.15(8)
C(10A)	3352(3)	2120(8)	3641(5)	3.41(7)	C(10B)	3362(3)	2086(7)	3624(4)	3.01(8)
C(11A)	4256(3)	2360(8)	670(5)	2.98(7)	C(11B)	4279(3)	2345(7)	689(4)	3.37(8)
C(12A)	4182(3)	1859(8)	1843(5)	2.91(7)	C(12B)	4202(3)	1846(7)	1855(4)	3.18(8)
C(13A)	2710(3)	2177(8)	1649(5)	2.80(7)	C(13B)	2730(3)	2147(7)	1640(4)	2.91(8)
C(14A)	2786(3)	2598(8)	472(5)	2.70(7)	C(14B)	2812(3)	2569(7)	471(4)	2.78(8)
C(15A)	4385(4)	3769(9)	−1778(5)	3.58(7)	C(15B)	4424(3)	3773(7)	−1764(4)	4.03(9)
C(16A)	2970(4)	4266(10)	−1884(5)	3.86(8)	C(16B)	3009(3)	4239(7)	−1888(4)	4.00(9)
C(17A)	4017(4)	2083(10)	4437(6)	4.54(8)	C(17B)	4032(3)	2040(7)	4440(4)	4.54(9)
C(18A)	2614(4)	2468(9)	4224(5)	3.67(7)	C(18B)	2623(3)	2415(7)	4210(4)	3.26(8)

Occupancy factor: A=0.709(1), B=0.291(1).

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^2	Occupancy factor	Atom	x	y	z	B_{eq}/Å^2	Occupancy factor
(3) ($\times10^4$)											
N(1)	4937(5)	4024(13)	−1766(8)	5.98(15)	1.00	C(2A)	5300(15)	1118(34)	1951(21)	3.59(18)	0.50
N(2)	2487(5)	4746(13)	−2430(8)	5.56(14)	1.00	S(3A)	4725(3)	1147(10)	3194(4)	4.26(11)	0.50
N(3)	4070(4)	1966(14)	5774(7)	6.12(15)	1.00	C(1B)	4882(16)	1851(33)	786(19)	2.83(18)	0.40
N(4)	1640(4)	2880(12)	4926(7)	5.10(14)	1.00	S(2B)	5417(4)	1165(14)	2070(7)	3.95(13)	0.40
C(4)	3127(4)	2002(12)	2811(7)	2.98(14)	1.00	C(3B)	4593(14)	1064(33)	2911(19)	3.84(18)	0.40
C(8)	3421(4)	2640(12)	177(7)	2.97(14)	1.00	S(1C)	4982(12)	1774(32)	539(20)	4.42(18)	0.10
C(9)	3561(4)	3384(13)	−923(7)	3.40(14)	1.00	C(2C)	5295(24)	1139(39)	1958(27)	3.12(18)	0.10
C(10)	2987(4)	2157(12)	4022(7)	2.94(14)	1.00	C(3C)	4698(22)	1172(39)	2755(27)	3.23(18)	0.10
C(11)	4050(4)	2078(12)	1065(7)	3.14(14)	1.00	C(5A)	1649(11)	1803(27)	2035(15)	2.79(17)	0.60
C(12)	3895(4)	1769(12)	2314(7)	3.26(14)	1.00	S(6A)	1111(3)	1749(8)	672(4)	4.81(10)	0.60
C(13)	2483(4)	2065(12)	1848(7)	3.21(14)	1.00	C(7A)	1905(10)	2173(26)	−167(15)	3.11(17)	0.60
C(14)	2614(4)	2315(12)	597(7)	3.14(14)	1.00	S(5B)	1523(6)	1674(21)	2146(12)	4.03(16)	0.25
C(15)	4344(5)	3724(14)	−1356(8)	4.17(15)	1.00	C(6B)	1270(20)	1885(38)	621(23)	3.83(18)	0.25
C(16)	2950(5)	4112(14)	−1759(8)	4.29(15)	1.00	C(7B)	1865(21)	2194(38)	−125(25)	3.06(18)	0.25
C(17)	3617(5)	2033(15)	4989(7)	4.53(15)	1.00	C(5C)	1624(21)	1753(39)	1934(28)	2.89(18)	0.15
C(18)	2212(4)	2543(13)	4495(7)	3.46(14)	1.00	C(6C)	1153(22)	1857(39)	888(27)	3.29(18)	0.15
C(1A)	4892(13)	1734(27)	933(16)	2.79(17)	0.50	S(7C)	1745(10)	2289(29)	−285(18)	4.27(17)	0.15

atoms of thiophene rings of the molecule **A** with higher occupancy factors are assigned to S(1) and S(7), while those of the molecule **B** with lower occupancy factors are S(3) and S(5). H atoms were located from the calculation. The structure was refined by full-matrix least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. The occupancy factors of the disordered molecules were also refined with the constrained molecule **B** using the program SHELX76. The final R is 0.070 for 2410 observed reflections where w=1 for all reflections. Occupancy factors were 0.709(2) : 0.291(2) for molecules **A** : **B**.

Very complicated disorder was observed in the crystal **3**. The occupancy factors of the four orientations of the molecules, [S(3), S(6)], [S(1), S(6)], [S(2), S(7)], and [S(2), S(5)], were 0.50 : 0.1 : 0.15 : 0.25, which were estimated from the peak heights of the D-maps. The same atomic parameters were used for TCNQ moieties of these four molecules, i.e. the occupancy factors of 1.0. The thiophene rings with the same sulfur positions were treated to have the same geometry, that is, the peripheral positions of atoms 1-2-3 were classified to three models, C(1A)-C(2A)-S(3A), C(1B)-S(2B)-C(3B), and S(1C)-C(2C)-(3C) and those of 5-6-7 were classified to C(5A)-S(6A)-C(7A), S(5B)-C(6B)-C(7B), and C(5C)-C(6C)-S(7C). Therefore the occupancy factor of C(1B)-S(2B)-C(3B), for example, was 0.40 (=0.15+0.25) from the molecules of [S(2), S(7)] and [S(2), S(5)]. The structure was refined by

the full-matrix least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. $w=1$ for all reflections. The final R value is 0.096 for 1566 observed reflections.

Atomic scattering factors were used from International Tables for X-Ray Crystallography.[5] 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,[6] ORTEP II.[7] The final atomic parameters are given in Table 2.[8]

Discussion

Crystals of **1**, **2**, and **3** are isostructural. Each crystal structure shows an orientational disorder with an approximate molecular symmetry of mm, though occupancy factors are not equal. The following discussions are made for the molecules with higher occupancy factor (molecule **A**). Not only these uncomplexed molecules but also molecules of thiophene-fused TCNQs in the crystals of charge transfer complexes with TTF and the salt with tetraethylammonium show the similar orientational disorder.[9] These disordered structures could be ascribed to the similarity of the dimensions related with C–S–C and C=CH–C groups of the thiophene moieties.

Molecular Structures. Molecular structures with the atomic numbering are shown in Fig. 1. Bond distances and angles are listed in Table 3. Molecular structures are a butterfly shape as shown in Fig. 2. Dihedral angles between some selected planes are listed in Table 4. For three isomers, the plane (**I**) defined by the four

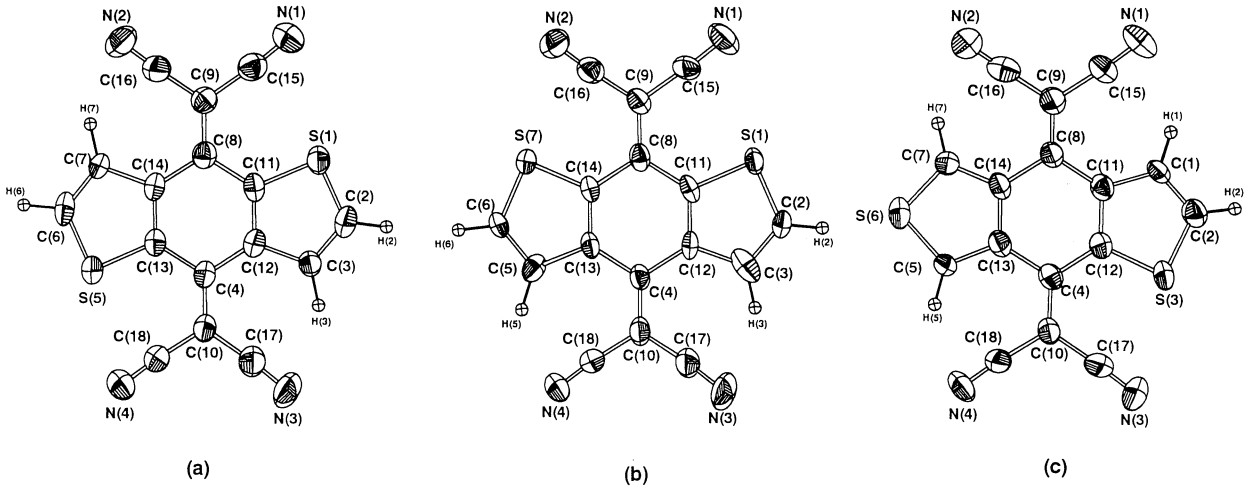


Fig. 1. ORTEPII drawings of the molecules with atom numbering. (a) **1A**, (b) **2A**, (c) **3A**.

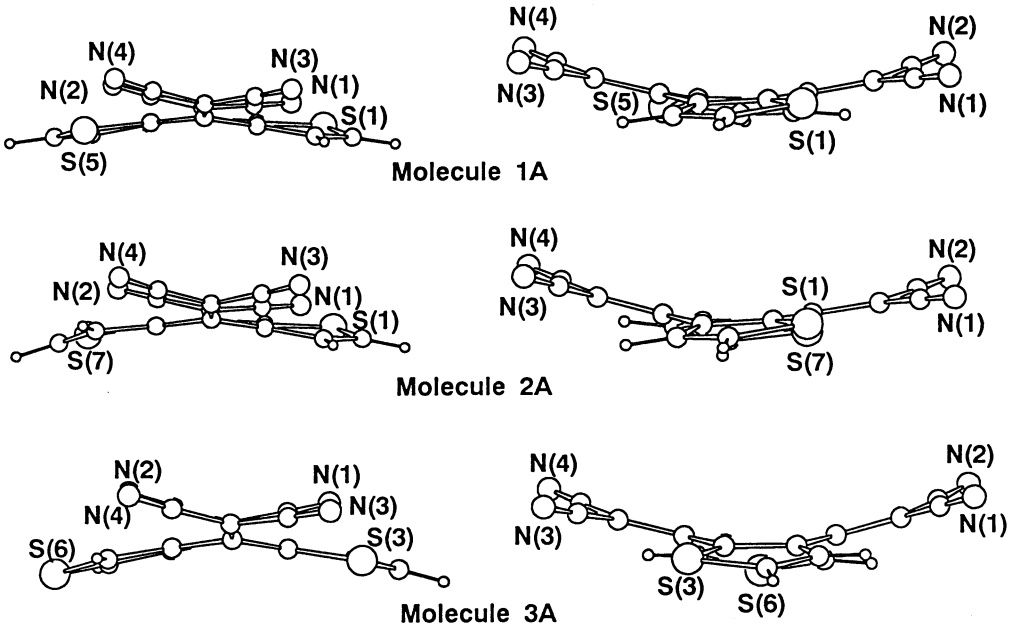


Fig. 2. Sideview of the molecules **1A**, **2A**, and **3A**.

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

Bond length	**1A** l/Å	**2A**[a] l/Å	**3A**[b] l/Å	Bond angle	**1A** θ/°	**2A**[a] θ/°	**3A**[b] θ/°
S(1)–C(2)	1.682(4)	1.714(7)	1.387(37)	C(2)–S(1)–C(11)	90.9(2)	90.3(3)	114.9(20)
S(1)–C(11)	1.711(4)	1.724(6)	1.454(25)	S(1)–C(2)–C(3)	116.0(3)	115.3(6)	110.7(20)
C(2)–C(3)	1.356(6)	1.349(11)	1.724(29)	C(2)–C(3)–C(12)	109.4(4)	110.7(7)	92.4(11)
C(3)–C(12)	1.466(6)	1.471(11)	1.719(12)	C(6)–S(5)–C(13)	91.2(2)	107.2(6)	110.4(13)
S(5)–C(6)	1.670(5)	1.381(10)	1.689(22)	S(5)–C(6)–C(7)	116.2(4)	116.5(5)	95.2(10)
S(5)–C(13)	1.707(4)	1.507(10)	1.456(22)	C(6)–C(7)–C(14)	108.9(4)	90.6(3)	110.4(13)
C(6)–C(7)	1.364(7)	1.699(7)	1.683(20)	C(10)–C(4)–C(12)	123.0(4)	123.4(5)	125.7(8)
C(7)–C(14)	1.472(6)	1.727(6)	1.427(21)	C(10)–C(4)–C(13)	123.3(4)	122.8(5)	122.1(8)
N(1)–C(15)	1.135(7)	1.142(10)	1.131(14)	C(12)–C(4)–C(13)	113.7(3)	113.8(5)	112.1(8)
N(2)–C(16)	1.132(7)	1.135(10)	1.142(14)	C(9)–C(8)–C(11)	123.8(4)	123.8(5)	123.8(8)
N(3)–C(17)	1.129(8)	1.141(11)	1.119(15)	C(9)–C(8)–C(14)	122.6(4)	121.6(5)	123.0(8)
N(4)–C(18)	1.129(7)	1.135(10)	1.120(13)	C(11)–C(8)–C(14)	113.6(3)	114.6(5)	113.1(8)
C(4)–C(10)	1.369(6)	1.374(8)	1.363(13)	C(8)–C(9)–C(15)	124.4(4)	123.8(6)	124.3(9)
C(4)–C(12)	1.458(6)	1.468(8)	1.424(13)	C(8)–C(9)–C(16)	125.0(4)	124.3(6)	124.3(9)
C(4)–C(13)	1.446(6)	1.469(8)	1.467(12)	C(15)–C(9)–C(16)	110.6(4)	111.8(6)	111.0(8)
C(8)–C(9)	1.371(6)	1.388(8)	1.351(13)	C(4)–C(10)–C(17)	126.0(4)	124.7(6)	122.9(9)
C(8)–C(11)	1.456(6)	1.450(8)	1.455(13)	C(4)–C(10)–C(18)	124.1(4)	123.4(6)	124.7(8)
C(8)–C(14)	1.455(6)	1.464(8)	1.471(13)	C(17)–C(10)–C(18)	109.7(4)	111.5(6)	112.3(8)
C(9)–C(15)	1.436(6)	1.431(9)	1.435(14)	S(1)–C(11)–C(8)	124.1(3)	124.3(4)	130.3(12)
C(9)–C(16)	1.430(6)	1.440(9)	1.435(14)	S(1)–C(11)–C(12)	112.4(3)	112.9(4)	108.3(11)
C(10)–C(17)	1.425(7)	1.417(10)	1.453(14)	C(8)–C(11)–C(12)	123.5(4)	122.7(5)	121.5(8)
C(10)–C(18)	1.434(6)	1.428(9)	1.446(13)	C(3)–C(12)–C(4)	127.8(4)	128.2(6)	122.4(7)
C(11)–C(12)	1.391(6)	1.397(8)	1.419(13)	C(3)–C(12)–C(11)	111.1(4)	110.4(6)	113.4(7)
C(13)–C(14)	1.385(6)	1.387(8)	1.410(13)	C(4)–C(12)–C(11)	121.1(4)	121.3(5)	124.2(8)
				S(5)–C(13)–C(4)	123.5(3)	126.2(5)	125.6(11)
				C(4)–C(13)–C(14)	123.8(4)	122.1(5)	123.6(8)
				S(5)–C(13)–C(14)	112.6(3)	111.6(5)	110.7(11)
				C(7)–C(14)–C(8)	127.3(4)	124.9(4)	125.8(11)
				C(7)–C(14)–C(13)	111.1(4)	112.9(4)	113.3(10)
				C(8)–C(14)–C(13)	121.6(4)	122.2(5)	120.9(8)
				N(1)–C(15)–C(9)	175.9(5)	176.6(7)	175.5(11)
				N(2)–C(16)–C(9)	176.1(5)	176.4(8)	177.1(11)
				N(3)–C(17)–C(10)	175.6(6)	175.0(8)	176.2(12)
				N(4)–C(18)–C(10)	176.1(5)	174.8(8)	175.8(10)

a)For **2**, S(5) and C(7) mean C(5) and S(7), respectively. b) For **3**, S(1), C(3), S(5), C(6) mean C(1), S(3), C(5), S(6), respectively.

Table 4. Dihedral Angles (ϕ) between Some Selected Planes

Planes		**1A** ϕ/°	**2A** ϕ/°	**3A** ϕ/°
I	II	7.5(2)	7.2(3)	9.2(4)
I	III	9.3(2)	9.2(2)	12.4(3)
I	IV	168.6(2)	170.4(3)	161.3(4)
I	V	16.4(2)	19.4(3)	15.2(4)
II	III	16.4(2)	15.9(2)	21.5(4)
IV	V	153.6(1)	152.4(2)	147.1(3)

Plane I C(11), C(12), C(13), and C(14),
Plane II X(1), X(2), X(3), C(11), and C(12), (X=S/C),
Plane III X(5), X(6), X(7), C(13), and C(14),
Plane IV N(1), N(2), C(8), C(9), C(15), and C(16),
Plane V N(3), N(4), C(4), C(10), C(17), and C(18).

atoms C(11), C(12), C(13), and C(14) of the quinonoid ring is almost planar with the maximum deviations of 0.024(2), 0.015(3), and 0.011(5) Å for molecules **1A**, **2A**, and **3A**, respectively. The quinonoid rings are of a boat type with the bow and stern for C(4) and C(8), respectively. The deviations of these atoms from the plane **I** are −0.162(6) and −0.125(6) Å for the molecule **1A**, −0.203(9) and −0.113(9) Å for **2A** and −0.18(1) and −0.22(1) Å for **3A**. These values indicate that the deformation from a planar structure is severe at the dicyanomethylene moiety located among two peri-hydrogen atoms of the thiophene rings. Two dicyanomethylene groups are bent to the same side from the plane **I**. Two thiophene rings are bent from the plane **I** to the opposite side of the dicyanomethylene groups to avoid a steric interaction between cyano groups and thiophene rings. The mean values of nonbonding intramolecular S···C, S···N, and C···C distances between the peri-atoms of the thiophene rings and the cyano groups of **1A** and **2A** are 2.857, 3.144, and 2.924 Å, respectively. Such a butterfly shape of the molecule with a boat type quinonoid group was reported in 9,9,10,10-tetracyano-1,4-naphthoquinodimethane,[10] 11,11,12,12-tetracyano-9,10-anthraquinodimethane,[11] and 10-(dicyanomethylene)-9(10*H*)-anthracenone.[12] The dihedral angles of 9,9,10,10-tetracyano-1,4-naphthoquinodimethane are close to those of the present compounds, while the distortions from the planar struc-

ture are much larger in anthraquinodimethanes. On the other hand in the case of bis(1,2,5-thiadiazole)-fused tetracyanoquinodimethane the molecule takes planar conformation.[13]

For the molecule **1A**, the lengths of S(1)–C(2) and S(5)–C(6) bonds, S–C(thiophene ring), are shorter than those of S(1)–C(11) and S(5)–C(13) bonds, S–C(fused). This tendency is also observed in the molecule **2A**. In the thiophene rings of **1A** and **2A** molecules endocyclic C=C bonds are shorter than that of the thiophene molecule (1.370 Å) and C–C bonds are longer than the corresponding bond of thiophene (1.423 Å). The angles of C–S–C is slightly smaller than that of thiophene (92.2°). The lengths of C=C bonds in the quinonoid rings (C(11)–C(12) and C(13)–C(14)) are significantly longer than the corresponding bonds of TCNQ (1.346 Å)[14] and shorter than those of fused C=C bonds of naphtho- and anthraquinodimethanes.[10–12] On the other hand the lengths of other endocyclic C–C bonds (C(4)–C(12), C(4)–C(13), C(8)–C(11), C(8)–C(14)), and exocyclic C=C bonds (C(4)–C(10), C(8)–C(9)) are similar to those of the corresponding bonds of TCNQ (1.446 and 1.374 Å, respectively) and other fused TCNQs. The angles of endocyclic angles, C(12)–C(4)–C(13) and C(11)–C(8)–C(14), and those of NC–C–CN, C(15)–C(9)–C(16), and C(17)–C(10)–C(18), are significantly smaller than those of TCNQ (118.3 and 116.1°, respectively).

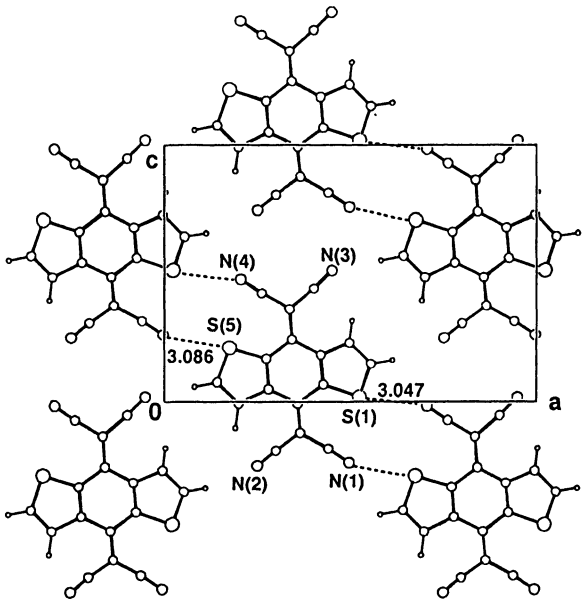


Fig. 3. Projection of the crystal structure of **1** viewed along the *b* axis within the range y=0.0 to 0.5.

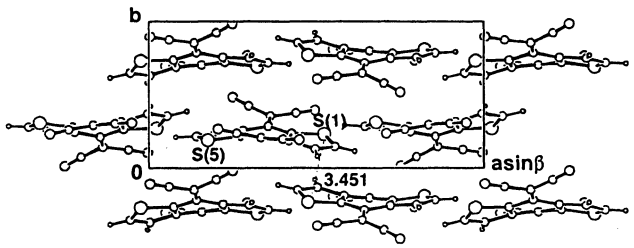


Fig. 4. Projection of the crystal structure of **1** viewed along the *c* axis.

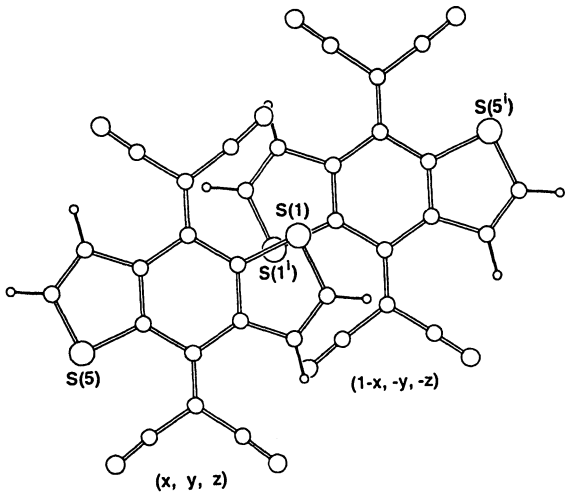


Fig. 5. Molecular overlapping of **1A**.

Crystal Structures. The crystal structures of **1** viewed along the *b* and *c* axes are shown in Figs. 3 and 4, respectively. The molecules form a sheet-like network perpendicular to the *b* axis, although each molecule inclines from the *ac* plane by about 13°. In the network there are short intermolecular interactions between S atoms of the thiophene rings and N atoms of TCNQ moieties. The S···N distances are 3.047(5) [S(1)···N(4^{i}), i=(x+1/2, 1/2−y, z−1/2)] and 3.086(5) Å [S(5)···N(1^{ii}), ii=(x−1/2, 1/2−y, z+1/2)] for **1** and 3.076(7) Å [S(1)···N(4^{i})] for **2**, which are significantly shorter than the sum of the van der Waals radii (3.35 Å). A planar network formed by the S···N contacts is also observed in bis(1,2,5-thiadiazole)-fused tetracyanoquinodimethane.[13] The internetwork distances between S atoms are significantly shorter than the sum of the van der Waals radii (3.70 Å): 3.451(2) Å [S(1)···S(1^{iii}), iii=(1−x, −y, −z)] for **1** and 3.461(3) Å [S(1)···S(1^{iii})] for **2**. Figure 5 shows the molecular overlapping viewed perpendicular to the TCNQ plane. The detailed discussions about the intermolecular interactions of **3** may be meaningless because of the complicated disordered structure.

It is interesting that the packing scheme is not dependent on the mode of fusion of the thiophene units in these molecules. Thus the similarity of the molecular shape, rather than the location of the sulfur atoms in the molecular periphery, is important factor to determine the crystal structures in these acceptor series.

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