An Isomeric Series of Thiophene-Fused Tetracyanoquinodimethanes. IV. Crystal Structure of 2:3 Charge-Transfer Salt with Tetraethylammonium

Masanori YASUI, Masamichi HIROTA, Yuji ENDO, Fujiko IWASAKI,* and Keiji KOBAYASHI†
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182
†Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153
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The crystal structure of the charge-transfer salt of one of the isomeric thiophene-fused TCNQs, 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene (**1**), with tetraethylammonium has been determined by the X-ray method. Crystals of $2C_8H_{20}N^+ \cdot (3C_{16}H_4N_4S_2)^{2-}$ belong to monoclinic system, $P2_1/n$, $Z=2$, $a=10.944(2)$, $b=28.765(8)$, $c=9.244(2)$ Å, $\beta=90.00(2)°$, $V=2910(1)$ Å^3, $D_x=1.381$ Mg m^{-3} and $D_m=1.36(2)$ Mg m^{-3}. The final R value is 0.064 for 4224 observed reflections. Two independent molecules, **A** and **B**, of **1** stack to form infinite columns along the a axis as **ABBABB**··· manner. The separations of the molecular planes are 3.47 and 3.39 Å, for **A**···**B** and **B**···**B**, respectively. The columns are linked side-by-side with short S···S contacts of 3.570(3) and 3.529(3) Å. From the comparison of the bond lengths of TCNQ frameworks **A** shows the neutral character, while **B** shows anionic structure.

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**), afforded charge-transfer complexes with tetrathiafulvalene (TTF) as a donor species. Among them, the complex **1-TTF** exhibited high conductivity, but **3-TTF** was a poor organic conductor. Both of these charge-transfer complexes were found to form mixed stacks of the donor and the acceptor species.[1-4] Radical salts, in contrast to charge-transfer complexes composed of π-donors and π-acceptors, usually tend to form segregated stacks in the crystalline state. We obtained the radical anion salt of **1** with tetraethylammonium (Et_4N^+) as a counter cation, which exhibited high conductivity at room temperature (0.46 S cm^{-1}). In this paper we report the crystal structure of this radical salt.

Experimental

Crystals for X-ray analysis were obtained by the method as reported in Part I.[2] Many crystals exhibited to be twinned. After many trials using precession photographs a crystal suitable for intensity measurement was selected. Intensity data were collected using a Rigaku diffractometer with graphite monochromator. No absorption corrections were applied. Crystal data and details of experimental conditions and structure refinements are listed in Table 1. The structure was solved by the direct method with the program MULTAN78.[5] At first the ratio of anions and cations were considered to be 1:1, on the contrary the structure analysis revealed that the ratio was determined to be 2:3. There are two independent molecules of **1**; one (**A**) at the center of inversion and the other at the general position (**B**). During the refinements each molecule of **1** showed an orientational disorder similar to those in the crystals of uncomplexed **1** and **1-TTF**.[3,4] Only the peripheral atoms in the thiophene rings were treated to be disordered and the TCNQ frameworks were treated as

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

	$2(C_8H_{20}N^+)(3C_{16}H_4N_4S_2)^{2-}$
Color	Black
Crystal shape	Plates
Crystal size/mm	0.44×0.32×0.28
M_r	1209.61
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.944(2)
b/Å	28.765(8)
c/Å	9.244(2)
β/°	90.00(2)
V/Å^3	2910(1)
Z	2
D_x/Mg m^{-3}	1.381
D_m/Mg m^{-3}	1.36(1)
Radiation	Mo$K\alpha$
λ/Å	0.71069
μ/mm^{-1}	0.278
For cell parameters	
2θ range/°	23.6—33.8
No. of reflections	24
Scan range 2θ/°	2—55
Scan width $\Delta\omega$/°	1.2+0.45tanθ
Scan speed ω/° min^{-1}	8
Scan mode	ω
Monitored reflections (every 100 reflections)	6 3 1, 0 4 0, 0 0 4
Variation of intensities	0.993—1.005
Range of h,k,l	0—14, 0—37, −12—12
Time for back-ground/s	10
No. of reflections	
Measured	7387
Observed ($\|F_o\|>3\sigma(F)$)	4224
R	0.064
wR	0.110
$\Delta\rho_{max}$—$\Delta\rho_{min}$/eÅ^{-3}	0.380—−0.377

ordered, i.e. with the occupancy factor of 1.0. H atoms were located from the calculation. Full-matrix least-squares were used with anisotropic temperature factors for non-H atoms and isotropic ones for H. The occupancy factors for disordered structures were refined independently to be 0.783(2):0.217(2) for the molecular site **A** and 0.724(2):0.276(2) for **B** by the program SHELX76.[6] $\Sigma w(|F_c|-k^{-1}|F_o|)^2$ was minimized. $w=1.3638/(\sigma^2(F)+0.003537|F_o|^2)$.

Atomic scattering factors were used from International Tables for X-Ray Crystallography.[7] 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,[8] ORTEP II.[9] The final atomic parameters are given in Table 2.[10]

Discussions

The molecular structures with the atomic numbering are shown in Fig. 1. Bond distances and angles are

Table 2. Positional Parameters ($\times 10^5$ for S of Higher Occupancy Factors, $\times 10^4$ for Others) 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
S(1A)	−6940(14)	−269(5)	32543(13)	2.76(3)	C(16B)	2324(4)	−1022(2)	388(4)	2.87(7)
C(2A)	−325(5)	546(2)	3371(5)	2.79(7)	C(17B)	4871(4)	1488(2)	−274(5)	3.29(7)
C(3A)	74(7)	727(3)	2089(7)	2.42(7)	C(18B)	4632(5)	1207(2)	−2618(5)	4.27(7)
C(8A)	−423(3)	−459(1)	536(4)	2.28(6)	N(1B)	2186(5)	−816(2)	3867(4)	5.34(7)
C(9A)	−822(4)	−888(1)	1046(4)	2.92(6)	N(2B)	2004(4)	−1353(1)	−192(4)	4.22(7)
C(11A)	−322(3)	−53(1)	1452(4)	2.24(6)	N(3B)	5217(4)	1811(1)	323(5)	4.71(7)
C(12A)	78(3)	382(1)	961(4)	2.27(6)	N(4B)	4775(5)	1324(2)	−3788(5)	6.71(8)
C(15A)	−1087(4)	−991(2)	2531(5)	4.06(7)	C(1A′)	−717(17)	−106(8)	3054(14)	4.98(9)
C(16A)	−989(4)	−1299(2)	197(5)	3.81(7)	C(2A′)	−566(13)	392(6)	3522(14)	2.87(8)
N(1A)	−1310(5)	−1113(2)	3666(5)	6.79(7)	S(3A′)	28(10)	781(4)	2314(9)	4.59(8)
N(2A)	−1172(5)	−1643(2)	−370(5)	5.87(7)	C(1B′)	2834(17)	290(8)	2989(15)	5.30(9)
S(1B)	28119(16)	2573(6)	32829(14)	2.71(3)	C(2B′)	3028(14)	727(6)	3470(13)	3.03(9)
C(2B)	3172(6)	835(2)	3303(7)	3.16(8)	S(3B′)	3676(7)	1077(2)	2177(7)	3.89(8)
C(3B)	3540(8)	1007(3)	1986(9)	3.01(8)	C(5B′)	4151(17)	231(8)	−2956(15)	5.35(9)
C(4B)	3983(3)	688(1)	−570(4)	2.40(6)	C(6B′)	3922(14)	−212(5)	−3397(13)	2.95(9)
S(5B)	41553(17)	2388(7)	−32466(15)	2.97(3)	S(7B′)	3358(7)	−582(2)	−2123(7)	3.11(7)
C(6B)	3822(6)	−344(2)	−3280(7)	3.11(8)	N(1E)	2874(3)	2836(1)	−1016(4)	3.42(6)
C(7B)	3431(10)	−505(3)	−1950(9)	2.72(8)	C(1E)	1688(5)	3095(2)	−1308(5)	4.26(7)
C(8B)	3079(3)	−199(1)	623(4)	2.27(6)	C(2E)	2926(5)	2649(2)	534(5)	4.04(7)
C(9B)	2653(3)	−625(1)	1217(4)	2.46(6)	C(3E)	3904(5)	3177(2)	−1279(6)	4.69(7)
C(10B)	4482(4)	1104(1)	−1132(4)	2.94(7)	C(4E)	2993(4)	2415(2)	−1985(5)	3.78(7)
C(11B)	3196(3)	213(1)	1477(4)	2.31(6)	C(5E)	563(5)	2814(2)	−1145(7)	6.09(8)
C(12B)	3618(3)	638(1)	920(4)	2.47(6)	C(6E)	2819(6)	3008(2)	1717(6)	6.07(8)
C(13B)	3822(3)	278(1)	−1432(4)	2.35(6)	C(7E)	5159(5)	2993(2)	−1057(7)	6.49(8)
C(14B)	3411(3)	−147(1)	−865(4)	2.22(6)	C(8E)	2948(5)	2514(2)	−3584(6)	5.02(7)
C(15B)	2407(4)	−710(2)	2700(5)	3.44(7)					

Occupancy factors; A : A′=0.783(2) : 0.217(2), B : B′=0.724(2) : 0.276(2).

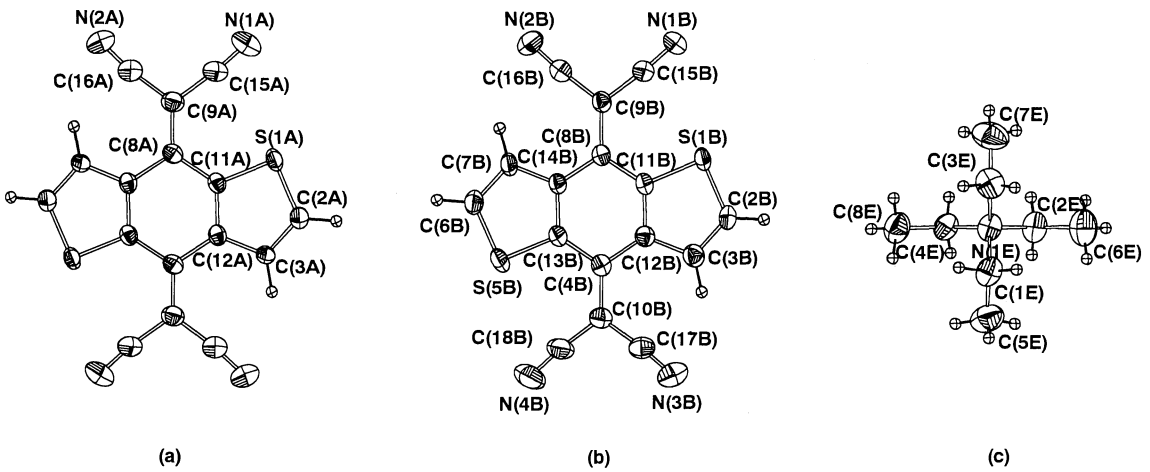


Fig. 1. ORTEPII drawings of the molecules with atom numbering. Non-H atoms are drawn with thermal ellipsoids of 50% probability. (a) **1A**, (b) **1B**, (c) Et_4N^+.

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

Length	l/Å	Length	l/Å	Angle	θ/°	Angle	θ/°
S(1A)–C(2A)	1.699(6)	C(8A)–C(12A^i)	1.452(5)	C(2A)–S(1A)–C(11A)	92.7(2)	S(1A)–C(11A)–C(8A)	125.8(3)
S(1A)–C(11A)	1.716(4)	C(9A)–C(15A)	1.434(6)	S(1A)–C(2A)–C(3A)	113.0(5)	S(1A)–C(11A)–C(12A)	110.5(3)
C(2A)–C(3A)	1.366(10)	C(9A)–C(16A)	1.430(6)	C(2A)–C(3A)–C(12A)	111.5(6)	C(8A)–C(11A)–C(12A)	123.7(3)
C(3A)–C(12A)	1.440(9)	C(11A)–C(12A)	1.400(5)	C(9A)–C(8A)–C(11A)	122.8(3)	C(3A)–C(12A)–C(11A)	112.3(4)
C(8A)–C(9A)	1.389(5)	N(1A)–C(15A)	1.133(8)	C(9A)–C(8A)–C(12A^i)	122.8(4)	C(3A)–C(12A)–C(8A^i)	125.8(5)
C(8A)–C(11A)	1.449(5)	N(2A)–C(16A)	1.139(7)	C(11A)–C(8A)–C(12A^i)	114.4(3)	C(11A)–C(12A)–C(8A^i)	121.9(3)
				C(8A)–C(9A)–C(15A)	124.8(4)	N(1A)–C(15A)–C(9A)	173.7(6)
S(1B)–C(2B)	1.707(7)	C(8B)–C(11B)	1.430(5)	C(8A)–C(9A)–C(16A)	125.9(4)	N(2A)–C(16A)–C(9A)	173.7(5)
S(1B)–C(11B)	1.726(4)	C(8B)–C(14B)	1.431(5)	C(15A)–C(9A)–C(16A)	109.2(4)		
C(2B)–C(3B)	1.375(12)	C(9B)–C(15B)	1.418(6)				
C(3B)–C(12B)	1.450(10)	C(9B)–C(16B)	1.422(6)	C(2B)–S(1B)–C(11B)	91.5(3)	C(17B)–C(10B)–C(18B)	110.1(4)
S(5B)–C(6B)	1.716(7)	C(10B)–C(17B)	1.424(6)	S(1B)–C(2B)–C(3B)	114.1(6)	S(1B)–C(11B)–C(8B)	124.9(3)
S(5B)–C(13B)	1.720(4)	C(10B)–C(18B)	1.415(7)	C(2B)–C(3B)–C(12B)	110.8(7)	S(1B)–C(11B)–C(12B)	111.8(3)
C(6B)–C(7B)	1.381(13)	C(11B)–C(12B)	1.404(5)	C(6B)–S(5B)–C(13B)	92.1(3)	C(8B)–C(11B)–C(12B)	123.3(4)
C(7B)–C(14B)	1.437(11)	C(13B)–C(14B)	1.404(5)	S(5B)–C(6B)–C(7B)	112.2(6)	C(3B)–C(12B)–C(4B)	126.4(5)
C(4B)–C(10B)	1.416(6)	N(1B)–C(15B)	1.147(7)	C(6B)–C(7B)–C(14B)	112.7(8)	C(3B)–C(12B)–C(11B)	111.6(5)
C(4B)–C(12B)	1.441(5)	N(2B)–C(16B)	1.148(6)	C(10B)–C(4B)–C(12B)	122.7(4)	C(4B)–C(12B)–C(11B)	121.8(3)
C(4B)–C(13B)	1.434(5)	N(3B)–C(17B)	1.145(6)	C(10B)–C(4B)–C(13B)	122.7(4)	S(5B)–C(13B)–C(4B)	124.7(3)
C(8B)–C(9B)	1.422(5)	N(4B)–C(18B)	1.144(8)	C(12B)–C(4B)–C(13B)	114.6(3)	S(5B)–C(13B)–C(14B)	112.0(3)
				C(9B)–C(8B)–C(11B)	122.1(3)	C(4B)–C(13B)–C(14B)	123.2(3)
N(1E)–C(1E)	1.521(6)	C(1E)–C(5E)	1.480(9)	C(9B)–C(8B)–C(14B)	122.9(3)	C(7B)–C(14B)–C(8B)	126.9(5)
N(1E)–C(2E)	1.531(7)	C(2E)–C(6E)	1.507(9)	C(11B)–C(8B)–C(14B)	115.0(3)	C(7B)–C(14B)–C(13B)	111.0(5)
N(1E)–C(3E)	1.516(7)	C(3E)–C(7E)	1.486(9)	C(8B)–C(9B)–C(15B)	125.7(4)	C(8B)–C(14B)–C(13B)	122.0(3)
N(1E)–C(4E)	1.511(6)	C(4E)–C(8E)	1.506(8)	C(8B)–C(9B)–C(16B)	124.6(4)	N(1B)–C(15B)–C(9B)	174.3(5)
				C(15B)–C(9B)–C(16B)	109.6(4)	N(2B)–C(16B)–C(9B)	174.7(5)
				C(4B)–C(10B)–C(17B)	124.6(4)	N(3B)–C(17B)–C(10B)	174.9(5)
				C(4B)–C(10B)–C(18B)	125.3(4)	N(4B)–C(18B)–C(10B)	174.8(6)
				C(1E)–N(1E)–C(2E)	111.7(4)	C(3E)–N(1E)–C(4E)	111.1(4)
				C(1E)–N(1E)–C(3E)	106.8(4)	N(1E)–C(1E)–C(5E)	115.1(4)
				C(1E)–N(1E)–C(4E)	111.1(4)	N(1E)–C(2E)–C(6E)	115.9(5)
				C(2E)–N(1E)–C(3E)	110.5(4)	N(1E)–C(3E)–C(7E)	115.7(5)
				C(2E)–N(1E)–C(4E)	105.8(4)	N(1E)–C(4E)–C(8E)	115.3(4)

Symmetry code: i=$-x$, $-y$, $-z$.

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

Plane		**1A** ϕ/°	**1B** ϕ/°
I	II	1.1(4)	3.0(2)
I	III		2.1(2)
I	IV	4.3(4)	8.9(1)
I	V		166.5(1)

Plane I C(4), C(8), C(11), C(12), C(13), and C(14),
Plane II S(1), C(2), C(3), C(11), and C(12),
Plane III S(5), C(6), C(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).

listed in Table 3. The dihedral angles between selected planes are listed in Table 4.

Figures 2 and 3 show the crystal structures of **1**-Et_4N^+ viewed along the a and c axes, respectively. Crystals of the anion radical salt are composed of Et_4N^+ and **1** with the ratio of 2:3. Two independent anion radicals **A** and **B** stack to form infinite columns along the a axis as **ABBABB**···manner. The angles of the quinonoid planes **A** and **B** to the a axis are 70.6 and 69.8°, respectively, and those to the c axis are 12.6 and 13.0°, respectively. The separations of the molecular planes are 3.47 and 3.39 Å for **A**···**B** and **B**···**B**, respectively. These lengths, especially for **B**···**B** planes, are quite shorter than that of the normal van der Waals contacts and suggest the intracolumner interaction, although the intracolumner distance of S(1B)···S(5B^{ii}) (ii=1$-x$, $-y$, $-z$, 3.613(2) Å) is only slightly shorter than that of the van der Waals contact. The mode of molecular overlapping is different between **A**···**B** and **B**···**B** as shown in Fig. 4. For **A**···**B** the molecular centers deviate along the direction of the dicyanomethylene groups, while for **B**···**B** the centers are shifted to the thiophene rings. The examples such as **B**···**B** overlapping mode are quite few in TCNQ complexes. These columns are linked side-by-side along the c axis. Some short intercolumner **S**···**S** contacts, such as S(1A)···S(1A^{iii}) (iii=$-x$, $-y$, 1$-z$; 3.570(3) Å) and S(1B)···S(5B^{iv}) (iv=x, y, 1+z; 3.529(3) Å), show the two dimensional interactions in this crystal. Figure 5 shows intermolecular interactions in the two dimensional molecular sheet. Along the b axis anions and cations are arranged alternately. There are no special interactions between cations and anions.

A molecular planarity of **1** in the salt is better than

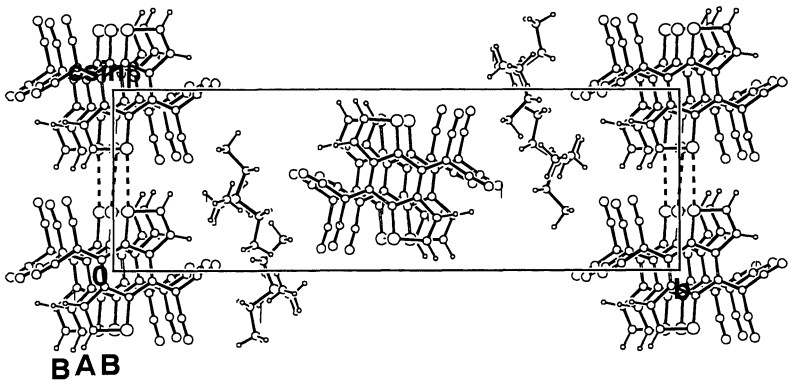


Fig. 2. Projection of the crystal structure viewed along the *a* axis.

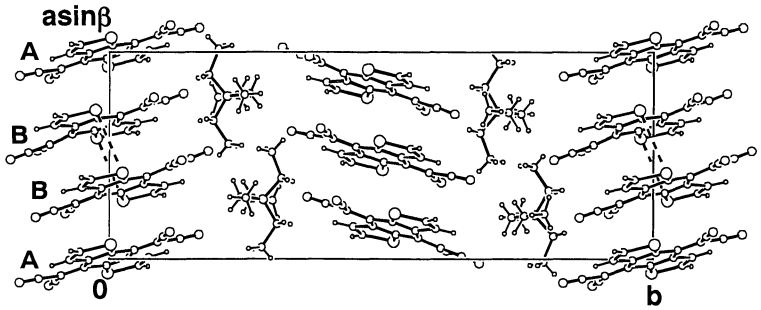


Fig. 3. Projection of the crystal structure viewed along the *c* axis.

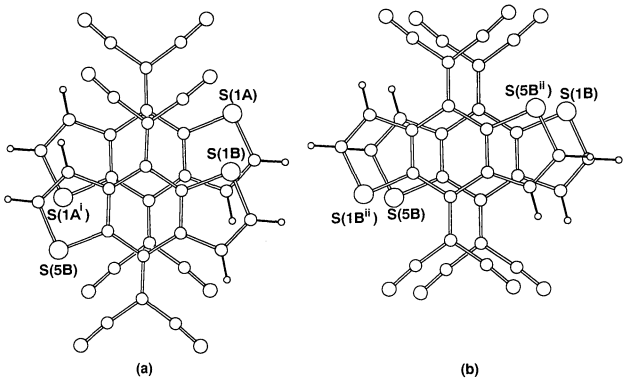


Fig. 4. Molecular overlapping of (a) **1A**–**1B** and (b) **1B**–**1B**.

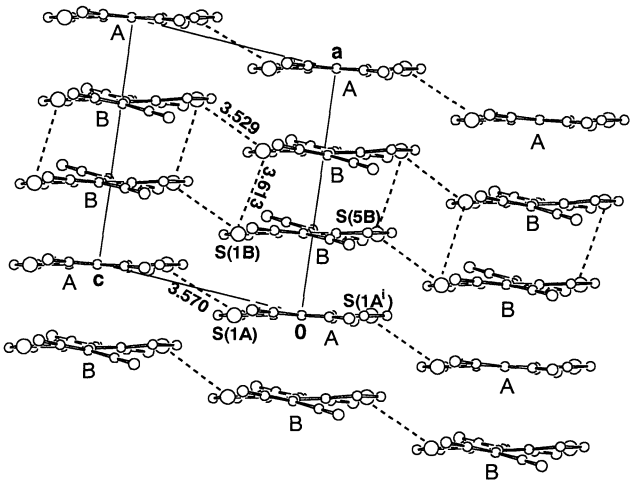
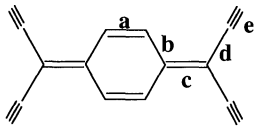


Fig. 5. Two-dimensional molecular network of **1**.

that of the uncomplexed **1**, which is shown from the comparison between the dihedral angles listed in Table 4 and Table 4 of Part II.[3] Bond lengths of the thiophene rings of both **A** and **B** molecules, especially **A**, are close to those of the uncomplexed molecule **1**[3] rather than to those of the complexed molecule of **1-TTF**.[4] However, the bond lengths of TCNQ frameworks are different between **A** and **B**. Table 5 shows a comparison of the structures of TCNQ moieties in various electronic states with **1**, **2**, **1-TTF**, and **1-Et$_4$N$^+$**. The bond lengths of C=C bonds (denoted **a** in the scheme) in these thiophene-fused TCNQs are longer than the normal values of TCNQs, because of the effect of a fused ring. The differences of lengths of the other bonds between **A** and **B** are clearly observed; **A** shows the neutral character, while **B** shows anionic structure. In the unit cell of 2 : 3 salt of **1-Et$_4$N$^+$** crystals there are two **A**, four **B**, and four cations. Whole charges of the crystals are compensated by considering the fact that only **B** molecules show the anionic character.

Table 5. A Comparison of the Structure of TCNQ-Moieties

Bonds	$TCNQ^0$ l/Å	$TCNQ^-$ l/Å	**1** l/Å	**2** l/Å	**1**–TTF l/Å	**1**–Et_4N^+	
						1A l/Å	**1B** l/Å
a	1.346(3)	1.373(1)	1.388(6)	1.392(8)	1.384(10)	1.400(5)	1.404(5)
b	1.448(4)	1.423(3)	1.454(6)	1.463(8)	1.461(10)	1.451(5)	1.434(5)
c	1.374(3)	1.420(1)	1.370(6)	1.381(8)	1.384(10)	1.389(5)	1.419(6)
d	1.441(4)	1.416(8)	1.431(7)	1.429(9)	1.438(12)	1.432(6)	1.420(7)
e	1.140(3)	1.153(7)	1.131(7)	1.138(10)	1.137(12)	1.136(8)	1.146(8)
Ref.	11	12	3	3	4	Present study	



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