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A New Type of Two-Dimensional Organic Conductors: Alkylammonium Bis[1,2,5]thiadiazolotetracyanoquinodimethanides

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Anion radical salts of bis[1,2,5]thiadiazolotetracyanoquinodimethan (BTDA) containing forty kinds of alkylammonium ions were prepared whose molar ratios are unique for each cation and changed from 1 : 1 (**2A—2L**) to 2 : 3 (**2M—2Z**), 1 : 2 (**2a—2m**), and 2 : 5 (**2n**) with elongation of the side chains. The electrical conductivities of the salts are largely affected by the molar ratio and the spatial requirement of cations (ρ_{RT} 3.1 Ω cm for **2a** and 4.2×10^6 Ω cm for **2L**), and some of the salts exhibit high electrical conductivities (ρ_{RT} 3.1—8.3 Ω cm for **2a—2e**) with small anisotropy ($\rho_{/\!/}$ 1.7 Ω cm, $\rho_{\perp}$ 21.6 Ω cm for a single crystal of **2g**). Three salts (**2A**, **2M**, and **2g**) showed semiconducting temperature dependence of electrical conductivity with the activation energies of 0.12—0.20 eV. The X-ray study of three kinds of the salts (**2A**, **2g**, and **2m**) revealed that two-dimensional networks are formed by S-N≡C interactions (3.12—3.33 Å) of BTDA anion radicals. The crystals of **2A** and **2g** showing higher conductivities consist of two-dimensionally expanded "ribbon" networks accompanied with equally spaced columnar stackings while molecules are pairing to form dyads in **2m** which exhibits lower conductivity.

Bis[1,2,5]thiadiazolotetracyanoquinodimethan (BTDA, **1**) which forms highly conductive charge-transfer complexes with some donors[1)] is a new type of electron acceptor designed in anticipation of the possible interheteroatom interactions as well as the decreased Coulomb repulsion by the annelation of thiadiazole rings. Recently **1** has been revealed to form a two-dimensional "sheet-like" network by strong transverse interactions of S-N≡C in the crystal.[2)] In connection with the importance of such interactions[3)] in the superconducting $(TMTSF)_2X$ and $(BEDT\text{-}TTF)_2X$ salts,[4)] it is extremely intriguing to examine the anion radical salts of **1** in which two-dimensional networks are also expected to be formed. We report here the electrical properties and crystal structures of BTDA anion radical salts containing simple ammonium ions, from which the two-dimensional character of these salts and the relationship between the properties and crsytal structures are discussed.

Results

Preparation of Anion Radical Salts. Most of the anion radical salts were prepared by reaction of BTDA **1** with corresponding alkylammonium iodides[5)] in acetonitrile and some were prepared by reaction of **1** with free amines followed by the hydrogen abstraction of aminium cation radicals.[5)] These salts were obtained as black powder or microcrystals and the molar ratios were determined on the basis of elemental analyses. They are summarized in Table 1 along with the decomposion points and CN stretching frequencies. Interestingly, the molar ratios of the salts were unique for the kind of ammonium ions as shown in Table 1. Attempts to obtain the 1 : 1 salts which correspond to the complex salts **2M**, **2T**, **2a**, **2i**, and **2m** by metathesis of $Li^+(BTDA)^{\cdot-}$ with corresponding ammonium iodides in acetonitrile were unsuccessful. In addition, treatment of the 1 : 1 salts **2A**, **2G**, and **2K** with another equivalent of BTDA in acetonitrile did not give the 1 : 2 salts but only starting 1 : 1 salts were recovered. This result is in sharp contrast to the case of 7,7,8,8-tetracyanoquinodimethan (TCNQ)[5)] whose 1 : 1 salts give the corresponding 1 : 2 salts by treatment with another equivalent of TCNQ. On the other hand, the molar ratios of $BTDA^{\cdot-}$ salts seem to depend on the size and shape of the cations, and gradually change from 1 : 1 to 2 : 3, 1 : 2, and 2 : 5 with elongation of the side chain of ammonium ions. Thus, ethyltrimethylammonium ion forms 1 : 1 salt **2A**, while diethyldimethyl one forms 2 : 3 salt **2T** and triethylmethyl one forms 1 : 2 salt **2f**.

Electrical Conductivities of Anion Radical Salts. Electrical resistivities measured on the compaction samples with a two-probe method are shown in Table 1. Some of the complex salts (**2a—2e**) exhibit high electrical conductivities because the partial charge-transfer state[6)] is easy to be achieved in these complex salts. It should be noted here that ethyltrimethylammonium 1 : 1 salt **2A** in which the complete charge transfer occurs shows fairy good conductivity (ρ 82 Ω cm). Unfortunately, easy twinning of the crystals prevented the measurements of electrical conductivity on single crystals for many cations. However, we succeeded in preparing three kinds of single crystals (**2A**, triethylammonium 2 : 3 salt **2M**, and methyltributylammonium 1 : 2 salt **2g**) which afford the following electrical resistivities (ρ) and activation energies (E_a): **2A**, ρ 33 Ω cm (E_a 0.198 eV); **2M**, ρ 1.3 Ω cm (E_a 0.124 eV); **2g**, $\rho_{/\!/}$ 1.7 Ω cm (E_a 0.14 eV) along the c axis in the crystal, $\rho_{\perp}$ 21.6 Ω cm along the a axis in the crystal. These single crystal conductivities are rather lower

Table 1. Decomposition Points, CN Stretching Frequencies and Electrical Resistivities[a)] of $R_1R_2R_3R_4N^+ (BTDA)^{\cdot-}_x$ Salts **2A**—**2n**

Salt	R_1	R_2	R_3	R_4	Decomp/°C	ν_{CN}/cm^{-1}	ρ_{RT}/Ωcm
1 : 1 salt (x=1)							
2A	Et	Me	Me	Me	269—271	2175	8.2×10
2B	H	H	H	H	290—295	2184	1.2×10^2
2C	$-(CH_2)_4-$		Me	H	243—244	2176	1.7×10^2
2D	$-(CH_2)_5-$		Me	Me	275—276	2173	2.5×10^3
2E	Me	Me	Me	Me	308—309	2171	2.8×10^3
2F	$-(CH_2)_4-$		H	H	245—247	2173	2.9×10^3
2G	*n*-Pr	Me	Me	Me	257—258	2172	3.0×10^3
2H	Me	Me	Me	H	262—270	2165	8.3×10^3
2I	$-(CH_2)_5-$		H	H	254—255	2178	1.6×10^4
2J	$-(CH_2)_5-$		Et	Me	266—267	2172	4.9×10^5
2K	$-(CH_2)_2-O-(CH_2)_2-$		Et	Me	259—260	2173	1.8×10^6
2L	$-(CH_2)_4-$		Me	Me	276—277	2175	4.2×10^6
2 : 3 salt (x=1.5)							
2M	Et	Et	Et	H	236—240	2167	1.2×10
2N	*i*-Pr	Me	Me	H	242—243	2174	1.9×10
2O	*i*-Pr	*i*-Pr	Et	H	225—226	2172	2.1×10
2P	Et	Me	Me	H	244—247	2174	4.1×10
2Q	$-(CH_2)_5-$		Me	H	253—256	2175	7.6×10
2R	*n*-Pr	*n*-Pr	*n*-Pr	Me	238—240	2177	8.2×10
2S	*n*-Bu	Et	Me	Me	253—255	2182	1.1×10^3
2T	Et	Et	Me	Me	262—263	2180	1.3×10^3
2U	*i*-Pr	Me	Me	Me	274—275	2177	3.6×10^3
2V	*n*-Bu	*i*-Pr	Me	Me	227—229	2184	3.7×10^3
2W	*i*-Pr	Et	Me	Me	269—270	2182	6.9×10^3
2X	*n*-Bu	Et	Et	Et	238—242	2183	8.8×10^3
2Y	$-(CH_2)_2-O-(CH_2)_2-$		Et	Et	265—266	2186	1.5×10^4
2Z	$-(CH_2)_4-$		Et	Me	263—265	2180	1.5×10^6
1 : 2 salt (x=2)							
2a	*n*-Bu	*n*-Bu	*n*-Bu	*n*-Bu	234—236	2172	3.1
2b	*n*-Pr	*n*-Pr	*n*-Pr	*n*-Pr	260—262	2166	3.7
2c	*n*-Bu	*n*-Pr	*n*-Pr	*n*-Pr	261—263	2177	4.5
2d	*n*-Pr	*n*-Pr	*n*-Pr	Et	261—263	2172	5.6
2e	*n*-Bu	*n*-Bu	*n*-Bu	*n*-Pr	247—248	2172	8.3
2f	Et	Et	Et	Me	254—260	2178	1.6×10
2g	*n*-Bu	*n*-Bu	*n*-Bu	Me	243—245	2175	1.6×10
2h	*n*-Bu	*n*-Bu	*n*-Bu	Et	229—235	2174	4.1×10
2i	*n*-Pen	*n*-Pen	*n*-Pen	*n*-Pr	218—220	2176	9.6×10
2j	*i*-Pr	Et	Et	Et	243—244	2182	1.3×10^2
2k	*n*-Pen	*n*-Pen	*n*-Pen	Et	194—196	2175	3.3×10^2
2l[b)]	*n*-Hex	*n*-Hex	*n*-Hex	Et	174—180	2176	4.4×10^2
2m	Et	Et	Et	Et	278—280	2182	5.1×10^3
2 : 5 salt (x=2.5)							
2n	*n*-Pen	*n*-Pen	*n*-Pen	*n*-Bu	217—220	2177	4.1×10

a) Measured on compaction pellets by two-probe method at room temperature. b) Containing one molar of H_2O.

than expected from those for the compaction samples because 50- to 1000-fold conductivity is expected in usual pseudo one-dimensional organic solids.[7)] The anisotropy of the conductivity is very small for the salt **2g** (1 : 13 : 140—700[8)] along the c, a, and b axes in the crystal), which clearly shows the two-dimensional electrical character of this salt.

Crystal Structure of Ethyltrimethylammonium 1 : 1 Salt (2A). Three views of the crystal structure of **2A** are shown in Figs. 1—3. The crystal of **2A** consists of segregated layers of anion radicals and cations. The BTDA anion radicals form a two-dimensional "ribbon" network along the c axis (Fig. 1) and stack in a "zigzag" fashion along the b axis (Fig. 2). The cations are packed in the cavity of the alternately stacked anion radicals to separate the planar networks. It should be noted that this stacking motif is quite similar to those found isostructurally in the $(TMTSF)_2X$ salts.[9)] According to the crystallographic requirement that the molecules must lie on the mirror planes, the completely planar BTDA anion radicals are structurally equivalent and equally spaced. The molecular overlapping is a familiar "ring-double bond" type[10)] (Fig. 4) and the stacking distance of 3.24 Å (b/2) is short enough to be compared with those for the conductive TCNQ complexes (3.17—3.26 Å).[11)] The nota-

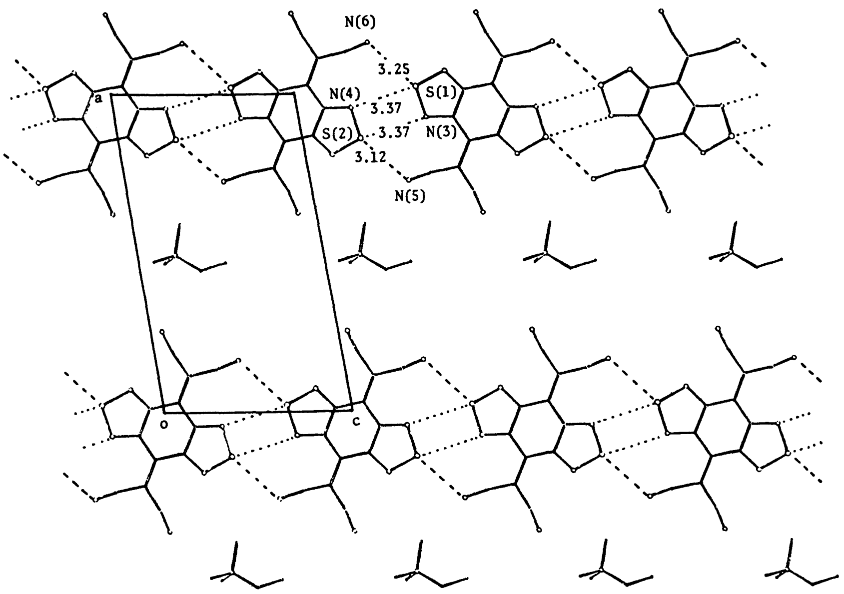


Fig. 1. "Ribbon" network of BTDA$^{\overline{\cdot}}$ in **2A**. S(1)-N(6)≡C(10) [3.25 Å] and S(2)-N(5)≡C(9) [3.12 Å] interactions are indicated by broken lines. Thiadiazole linkages of S(1)-N(4) [3.37 Å] and S(2)-N(3) [3.37 Å] are also indicated by dotted line.

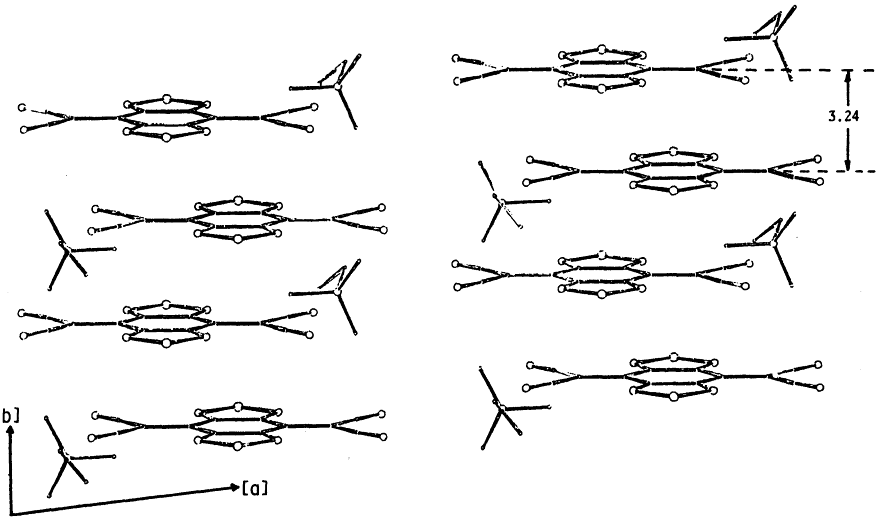


Fig. 2. "Zigzag" stacking in **2A** (tilted 10°). The ammonium N atoms locate on the same plane with the molecular plane of BTDA$^{\overline{\cdot}}$. Only one-sided mirror images are shown for the disordered ammonium ions.

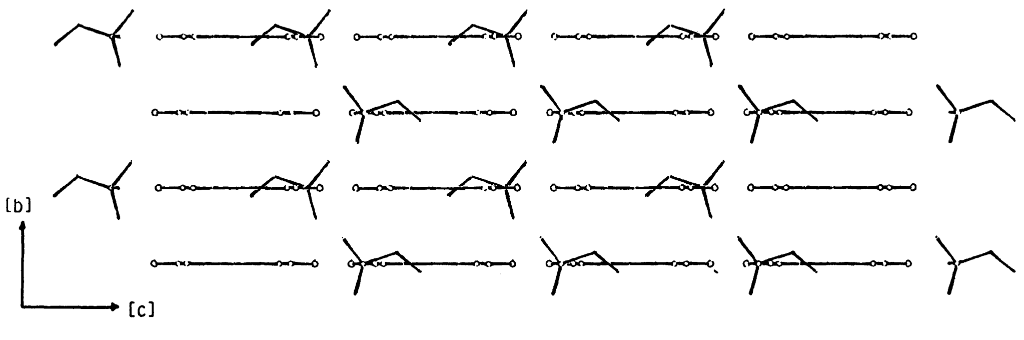


Fig. 3. Coplanar "ribbon" network in **2A** (side view). The interplanar distance is 3.24 Å. Only one-sided mirror images are shown for the disordered ammonium ions.

ble feature of this crystal is the two-dimensional "ribbon" network formed by two short S-N≡C interactions (3.12 and 3.25 Å) together with the thiadiazole linkages (3.37 Å) (Fig. 1). This network is also formed restrictedly in coplanar (Fig. 3), indicating the charge delocalization through the side-by-side network. The appearance of S-N linkage of fused rings, which does not exist in the crystal of neutral **1**,[2] is one of indications that the thiadiazole N atoms possess enhanced negative charge by delocalization since the S-N interaction between thiadiazole rings is caused by the polarized sulfur nitrogen bond.[12] The more definite indications appear in the molecular structure of BTDA$^{\cdot-}$ shown in Table 2 in which those of **1** and TCNQ$^{\cdot-}$[13] are also shown for comparisons. It should be pointed out that the dicyanomethylene C=C bond becomes shorter than that of TCNQ$^{\cdot-}$ (1.390 Å vs. 1.420 Å) and the thiadiazole C=N bond length is longer than that of **1** (1.346 Å vs. 1.330 Å).

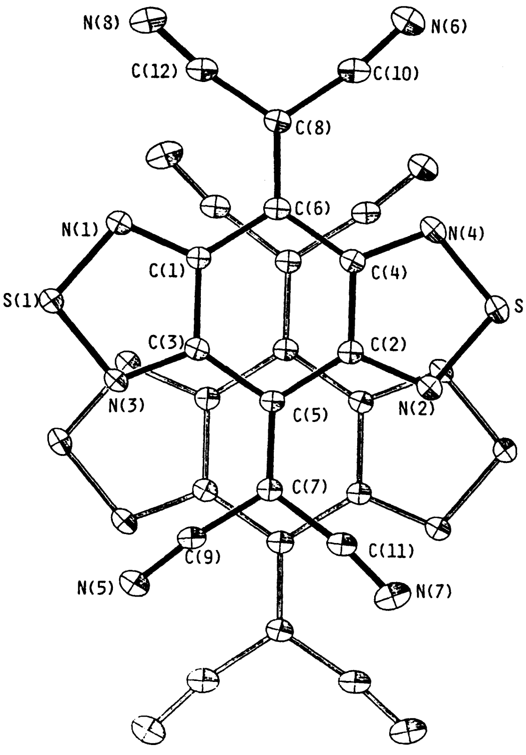


Fig. 4. "Ring-double bond" type overlapping in **2A**. Selected bond lengths: S(1)-N(1) 1.615(4), S(1)-N(3) 1.610(4), S(2)-N(2) 1.624(4), S(2)-N(4) 1.605(4), N(1)-C(1) 1.348(6), N(2)-C(2) 1.347(5), N(3)-C(3) 1.345(5), N(4)-C(4) 1.345(6), N(5)-C(9) 1.142(6), N(6)-C(10) 1.146(7), N(7)-C(11) 1.138(7), N(8)-C(12) 1.137(7), C(1)-C(3) 1.442(6), C(1)-C(6) 1.444(6), C(2)-C(4) 1.443(6), C(2)-C(5) 1.439(6), C(3)-C(5) 1.431(6), C(4)-C(6) 1.433(6), C(5)-C(7) 1.394(6), C(6)-C(8) 1.385(6), C(7)-C(9) 1.427(6), C(7)-C(11) 1.423(6), C(8)-C(10) 1.434(7), C(8)-C(12) 1.432(7) Å.

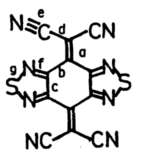
Crystal Structure of Methyltributylammonium 1:2 Salt (2g). Because of the positional disorder of the ammonium ions, the unit cell contains Z=0.5 for the formula of $\mathrm{MeBu_3N^+(BTDA)^{\cdot-}_2}$. BTDA anion radicals are related by a center of symmetry at the origin of the unit cell. Similarly to the case of **2A**, the strong transverse interactions of S-N≡C (3.27 and 3.30 Å) connect the anion radicals to form a linear "ribbon" network along the a axis. The positionally disordered cations are packed between the "ribbon" networks along the b axis. An important difference from **2A** is that the networks are not coplanar but corrugated resulting in the formation of a three-dimensional "honeycomb" structure as shown in Fig. 5. Furthermore, the mode of stacking is a uniform type (not a zigzag type) in which BTDA anion radicals are structurally equivalent and equally spaced with the short interplanar distance of 3.24 Å (Fig. 6) and the "ring-double bond" type overlapping (Fig. 7). BTDA molecule possesses an almost planar conformation although the deviations of cyano groups from the molecular plane cause a slight twisting of the exo methylene double bond (1.6°). The bond lengths of dicyanomethylene C=C bond (1.379 Å) and thiadiazole C=N bond (1.340 Å) are intermediate between those in neutral **1** and those in 1 : 1 salt **2A** (Table 2), which reflect the fact that only a half of the negative charge is located on a BTDA molecule in 1 : 2 salt **2g**.

Crystal Structure of Tetraethylammonium 1:2 Salt (2m). Three views of crystal structure are shown in

Table 2. Comparison of Bond Lengths[a)] (Å) in BTDA Molecule

Bond	BTDA$^{\cdot-}$ in **2A**	BTDA$^{1/2\cdot-}$ in **2g**	BTDA-1 in **2m**	BTDA-2 in **2m**	BTDA°[b)]	TCNQ$^{\cdot-}$[c)]
a	1.390(6)	1.379(8)	1.372(12)	1.381(12)	1.356(7)	1.420(4)
b	1.437(6)	1.449(8)	1.454(12)	1.452(12)	1.457(6)	1.423(4)
c	1.433(5)	1.422(8)	1.428(12)	1.434(12)	1.422(6)	1.373(4)
d	1.429(7)	1.422(10)	1.443(13)	1.430(14)	1.438(6)	1.416(4)
e	1.140(6)	1.127(10)	1.128(14)	1.135(14)	1.143(5)	1.153(7)
f	1.346(6)	1.340(8)	1.336(12)	1.338(12)	1.330(4)	
g	1.614(4)	1.612(6)	1.615(8)	1.615(9)	1.617(6)	

a) Bond lengths are averaged over assumed mmm symmetry.
b) Ref. 2. c) These values are for $\mathrm{Rb^+TCNQ^{\cdot-}}$, Ref. 13.



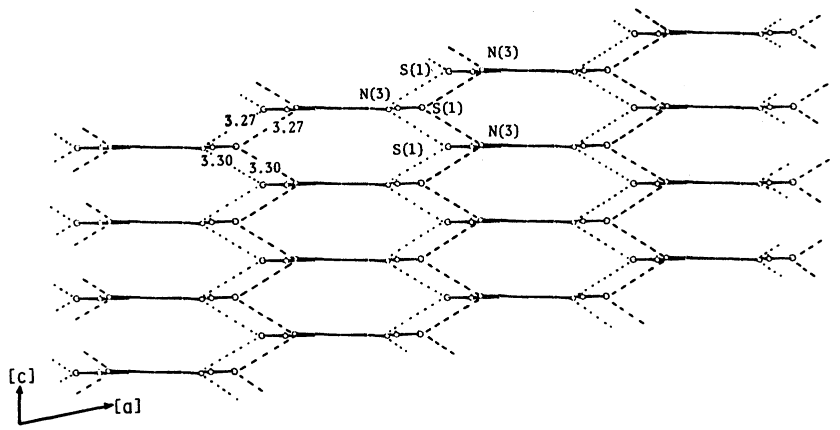


Fig. 5. "Honeycomb" network in **2g** (side view perpendicular to the molecular plane of BTDA). S(1)-N(3)≡C(5) [3.27 and 3.30 Å] interactions are indicated by broken lines. The interplanar distance is 3.24 Å. Disordered ammonium ions are not included for ease.

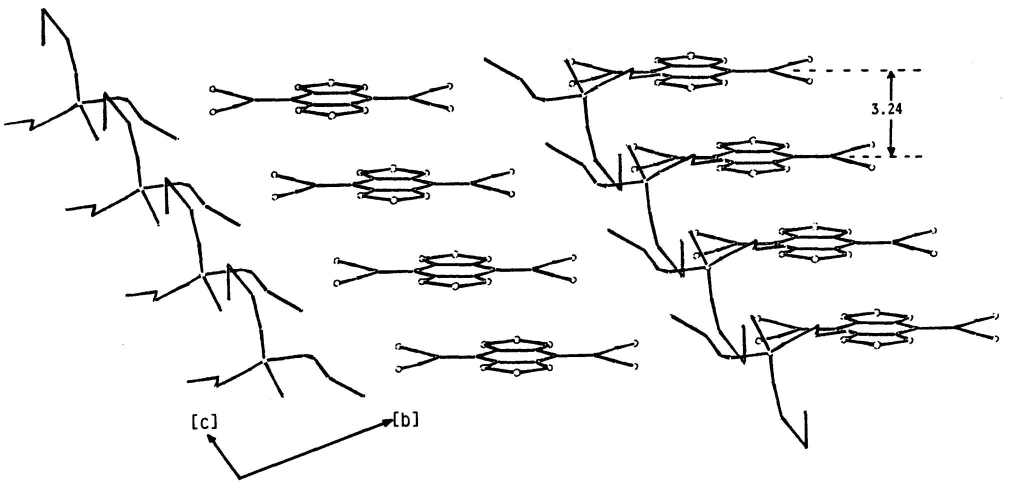


Fig. 6. Uniform segregated stacking in **2g** (tilted 10°). Ammonium ions are disordered along the stacking c axis (multiplicity 0.5), and also related by a center of symmetry which are not shown for ease.

Figs. 8—10. Because of $Z=2$ for the space group $P\bar{1}$, two different kinds of BTDA molecules exsist in the crystal (abbreviated as BTDA-1 and BTDA-2). Each molecule forms columnar stacks along the c axis in which molecules are not equally spaced but pairing to form dyads (Fig. 8). The interplanar distances are 3.17 and 3.39 Å for BTDA-1, and 3.26 and 3.41 Å for BTDA-2, respectively. Although each molecule forms corrugated "ribbon" networks along the a axis like **2g** (Figs. 9 and 10), these networks can not form the "honeycomb" because of the dyad formation as well as the ununiform overlapping patterns. That is, the molecular overlappings are "ring-double bond" type in the dyads for both BTDA-1 and BTDA-2, but molecules are slipped in parallel in the overlapping between the dyads (Figs. 11 and 12). Although both molecules are almost planar, slight twisting of dicyanomethylene C=C bond (2.8° and 1.4°) are observed for BTDA-2. Comparisons of molecular structure of BTDA-1 and BTDA-2 with those of neutral **1** and 1 : 1 salt **2A** indicate that BTDA-2 possesses the larger amount of negative charge than BTDA-1 (Table 2). For example, bond f for BTDA-2 is elongated [C(205)=C(207), 1.392 Å] which is nearly the same value with that for 1 : 1 salt **2A** [C(5)=C(7), 1.394 Å]. This charge distribution also affects the molecular packing. The cationic center of ammonium N atom is located on the same plane with the molecular plane of BTDA-2 (Fig. 10), while the molecular plane of BTDA-1 is shifted vertically (Fig. 9).

Discussion

The annelation of 1,2,5-thiadiazole rings to the TCNQ skeleton results in two significant differences from TCNQ itself. One of them is the two-dimensional electrical property and crystal structure formed by the strong interheteroatom interactions of

S-N≡C and the other is the decreased on-site Coulomb repulsion in the reduction form of **1**. The former is the most important characteristic of **1** since none of the organic electron acceptor have shown such a two-dimensional network so far.[14] The crystal structures described here are different from each other, indicating that the patterns of interactions are variable according to the spatial requirements of counter cations. This fact shows that the molecular interaction of BTDA is not only strong but also flexible. However, some common features are observed, which are the "ribbon" network and face-to-face columnar stacking. The "ribbon" is coplanar in **2A** and corrugated in **2g** and **2m**. The stacking pattern of **2A** is equally spaced "zig-zag" type like $(TMTSF)_2X$ salts and that of **2g** is equally spaced uniform type like TTF·TCNQ complex,[15] while molecules are dimerized in **2m** which is often observed in anion radical salts with low electrical conductivities. The fact that molar ratios of the salts are unique for each cation seems to be related with these networks since the ratios are gradually changed from 1 : 1 to 2 : 5 as the cations get larger. Cyclic ammonium ions tend to give 1 : 1 salts compared with corresponding acyclic cations as seen in a comparison of **2L** and **2J** with **2T** and **2S**. This fact also indicates that the spatial conditions play an important role in determining the molar ratios. This behavior is explained by considering that the cations locate between BTDA molecules which are connected in two directions of "ribbon" and stacking. Therefore, the larger the cation is, the more repeated units of "ribbon" and stacking are needed since the distances of the transverse S-N≡C interaction and the face-to-face overlapping are in some definite range of 3.12—3.33 and 3.17—3.41 Å, respectively. Once the molar ratio is determined with keeping this range of distances for a certain cation, the shape of the cation affects the mode of stacking and the "ribbon" network which reflect its electrical conductivity. These common features of the crystal structures make some difficulty in obtaining single crystals since disorder or twinning is very easy to occur in the direction where BTDA and cations are aligned alternately (the a axis for **2A**, the b axis for **2g** and **2m**). Whether the semiconducting properties of three salts (**2A**, **2M**, and **2g**) described here are attributed to this easy twinning or not is still ambiguous.

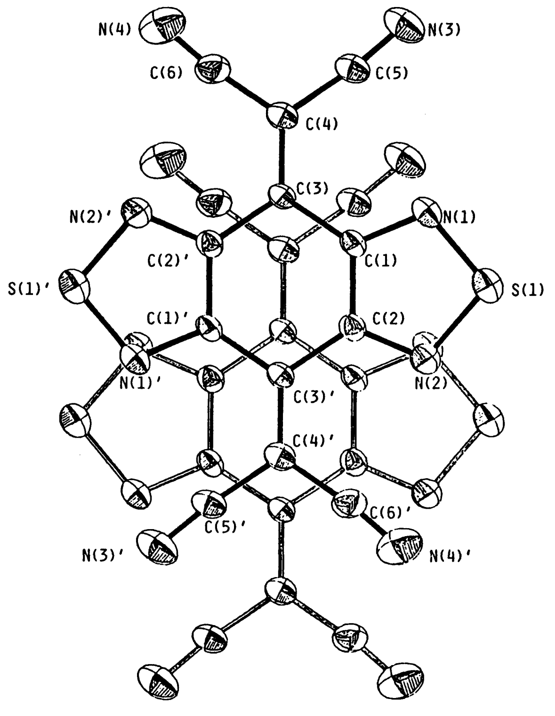


Fig. 7. "Ring-double bond" type overlapping in **2g**. Selected bond lengths: S(1)-N(1) 1.611(6), S(1)-N(2) 1.613(6), N(1)-C(1) 1.339(8), N(2)-C(2) 1.340(8), N(3)-C(5) 1.128(10), N(4)-C(6) 1.125(11), C(1)-C(2) 1.422(8), C(1)-C(3) 1.447(8), C(2)-C(3) 1.450(8), C(3)-C(4) 1.379(8), C(4)-C(5) 1.424(9), C(4)-C(6) 1.420(10) Å.

The second point is the decreased Coulomb repulsion in the reduction form of BTDA. This is first suggested by measuring the reduction potentials of **1**. The cyclic voltammogram of **1** shows four reversible reduction waves with the half wave potentials of −0.02, −0.49, −1.21, and −1.76 V vs. SCE.[1a,16] The

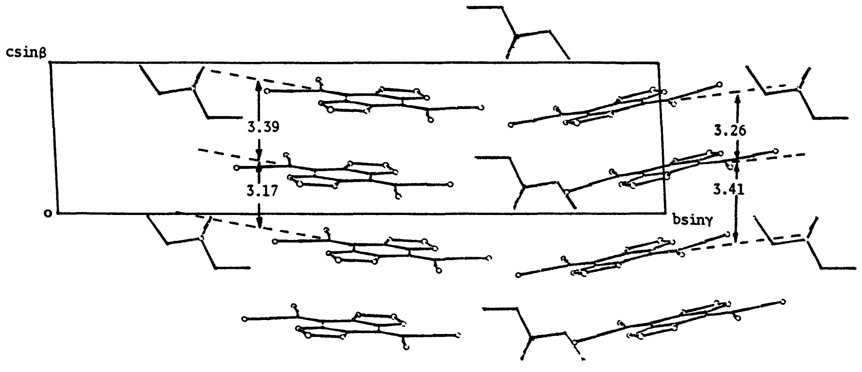


Fig. 8. Dimeric segregated columns in **2m** viewed along the a axis. The interplanar distances are 3.17 and 3.39 Å for BTDA-1 (left) and 3.26 and 3.41 Å for BTDA-2 (right), respectively.

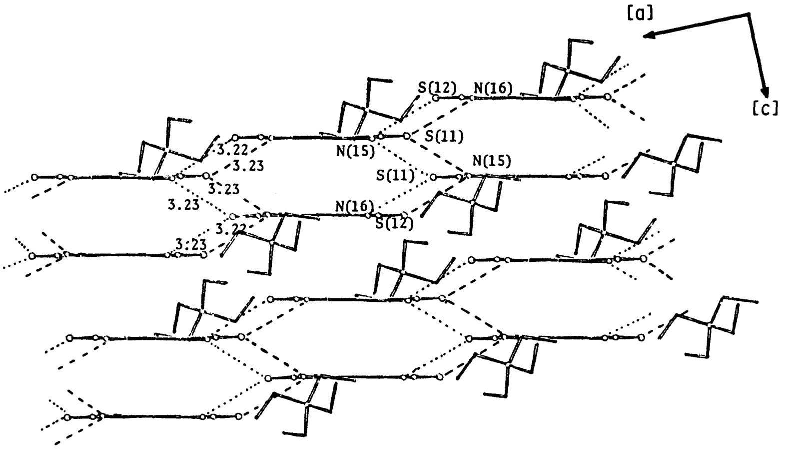


Fig. 9. Dimerized "ribbon" network of BTDA-1 in **2m** (side view). S(11)-N(15)≡C(109) [3.23 Å], S(11)-N(16)≡C(110) [3.23 Å], and S(12)-N(15)≡C(109) [3.22 Å] are indicated by broken lines.

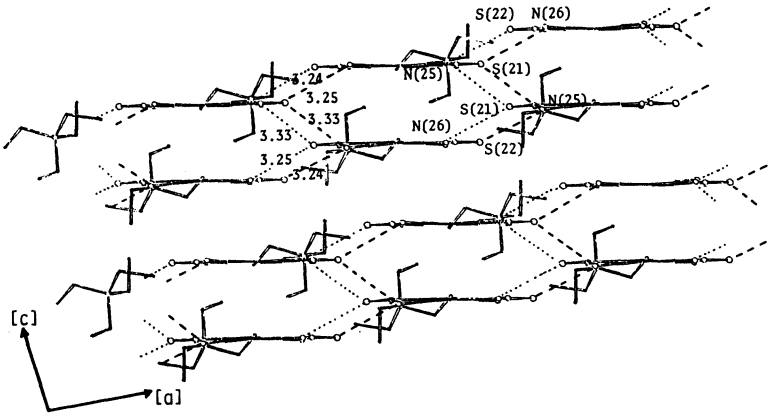
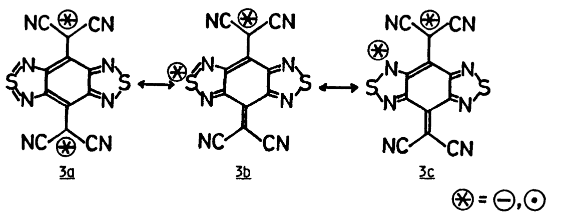


Fig. 10. Dimerized "ribbon" network of BTDA-2 in **2m** (side view). S(21)-N(25)≡C(209) [3.33 Å], S(21)-N(26)≡C(210) [3.25 Å], and S(22)-N(25)≡C(209) [3.24 Å] are indicated by broken lines.

semiquinone formation constant (K_{sem}) calculated using these values is 8.10 while that of TCNQ is 9.31. This contraction is attributed to the decreased Coulomb repulsion of $\mathbf{1}^{\cdot-}$ compared with TCNQ$^{\cdot-}$. This is also suggested by the fact that the dianion of BTDA is easily isolated as stable sodium salts[17] while the dianion of TCNQ is unstable and isolated only when special metal complex ions were used.[18] In this study, the comparisons of the molecular geometry in BTDA molecule show that the negative charge is delocalized to the fused thiadiazole rings. That is, the C=N double bond of thiadiazole (bond f in Table 2) is elongated by adding the negative charge on a BTDA molecule (1.330 Å in BTDA^{0}, 1.340 Å in BTDA$^{1/2\cdot-}$ and 1.346 Å in BTDA$^{\cdot-}$), which is rationalized by considering the contribution of the structures **3b** and **3c** (Scheme 1) for the anion radical of BTDA **1**. The fact that 1 : 1 salt **2A** which is completely charge transferred exhibits higher electrical conductivity than usual Mott insulators[19] may be attributed to this decreased Coulomb repulsion of $\mathbf{1}^{\cdot-}$.



Scheme 1.

Conclusion

This study has revealed the novel properties of BTDA$^{\cdot-}$ which can construct the segregated columnar stacks with the face-to-face overlapping (uniform type or zigzag type) as well as the "ribbon" networks (coplanar or corrugated) by strong transverse interactions.[20] The modes of overlapping and transverse interactions in BTDA$^{\cdot-}$ are strongly affected by the spatial requirements of the cations, while these interactions also define the molar ratios of the salts since the ratios were unique for the cations. Although all of

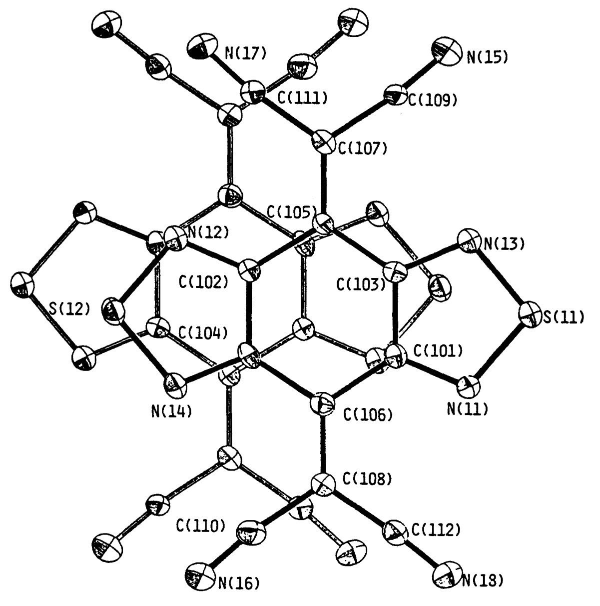


Fig. 11. Molecular overlapping of BTDA-1 in **2m** between the dyads. Selected bond lengths: S(11)-N(11) 1.609(8), S(11)-N(13) 1.608(9), S(12)-N(12) 1.612(8), S(12)-N(14) 1.630(8), N(11)-C(101) 1.322(12), N(12)-C(102) 1.339(11), N(13)-C(103) 1.351(12), N(14)-C(104) 1.332(12), N(15)-C(109) 1.122(13), N(16)-C(110) 1.128(15), N(17)-C(111) 1.133(14), N(18)-C(112) 1.128(15), C(101)-C(103) 1.419(12), C(101)-C(106) 1.462(13), C(102)-C(104) 1.437(12), C(102)-C(105) 1.455(12), C(103)-C(105) 1.443(12), C(104)-C(106) 1.454(13), C(105)-C(107) 1.382(12), C(106)-C(108) 1.362(13), C(107)-C(109) 1.445(13), C(107)-C(111) 1.438(13), C(108)-C(110) 1.442(13), C(108)-C(112) 1.445(14) Å.

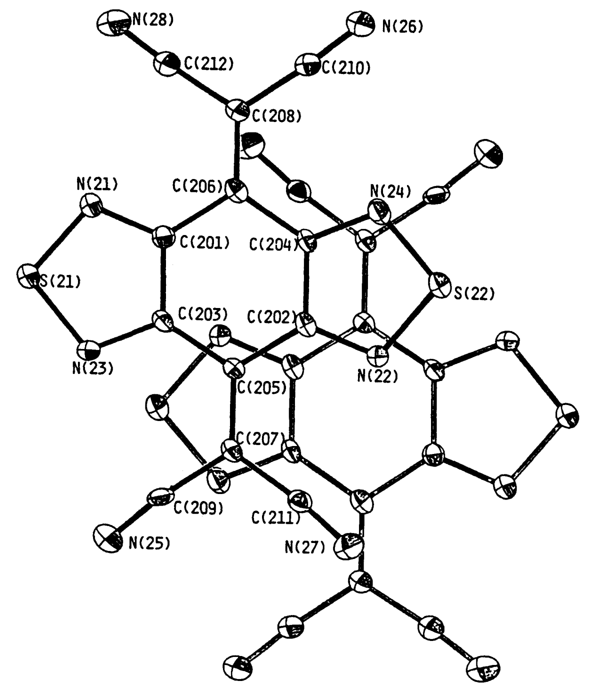


Fig. 12. Molecular overlapping of BTDA-2 in **2m** between the dyads. Selected bond lengths: S(21)-N(21) 1.613(9), S(21)-N(23) 1.624(9), S(22)-N(22) 1.612(8), S(22)-N(24) 1.611(9), N(21)-C(201) 1.330(12), N(22)-C(202) 1.343(12), N(23)-C(203) 1.346(12), N(24)-C(204) 1.333(12), N(25)-C(209) 1.134(14), N(26)-C(210) 1.140(15), N(27)-C(211) 1.140(13), N(28)-C(212) 1.126(16), C(201)-C(203) 1.437(12), C(201)-C(206) 1.457(12), C(202)-C(204) 1.430(12), C(202)-C(205) 1.439(12), C(203)-C(205) 1.434(12), C(204)-C(206) 1.477(12), C(205)-C(207) 1.392(12), C(206)-C(208) 1.370(13), C(207)-C(209) 1.433(13), C(207)-C(211) 1.433(13), C(208)-C(210) 1.423(14), C(208)-C(212) 1.432(15) Å.

three anion radical salts examined here were semiconductors with the activation energies of 0.12—0.20 eV, BTDA and analogous compounds[21] containing higher chalcogen atoms instead of sulfur atoms are promising electron acceptors to afford organic metals whose metallic states are stabilized by the novel two-dimensional structures as described here.

Experimental

General. IR spectra were measured in KBr disks on a Shimadzu IR-435 spectrometer with a DR-1 data recorder. The ν_{CN} values were determined as the minima of the transmittances measured by every 0.5 $\mathrm{cm^{-1}}$ using the $\nu_{\max}$ of 1944 and 1871 $\mathrm{cm^{-1}}$ of the polystyrene film as standard. All the melting points are uncorrected. Electrical resistivities were measured by a conventional two-probe method for compaction samples at room temperature, and by a four-probe method for single crystals using the gold wire and gold paste for the connection.

Materials. Anion radical salts **2A**—**2n** were prepared by reaction of BTDA (0.4 mmol) with the corresponding ammonium iodides (3—5 equivalents) in boiling acetonitrile (30 ml) except for the case of **2C**, **2N**, **2O**, **2P**, and **2Q** in which free amines (1 equivalent) were used instead of the iodides. The salts showed correct elemental analyses for C, H, and N (±0.4%) without purification. Single crystals of **2A** and **2M** were prepared by electrochemical reduction (5—10 μA) of BTDA (10^{-3} mol $\mathrm{dm^{-3}}$) containing $\mathrm{Me_3NEt^+MeSO_4^-}$ or $\mathrm{Et_3NH^+BF_4^-}$ as supporting electrolyte (10^{-1} mol $\mathrm{dm^{-3}}$) in acetonitrile. Single crystals of **2g** were obtained when a hot acetonitrile solution of **1** and the iodide was cooled slowly, and those for **2m** were prepared by recrystallization from acetonitrile.

Structural Analysis of Ethyltrimethylammonium 1 : 1 Salt (2A). A needle-like crystal with dimensions of 0.08×0.30×0.15 $\mathrm{mm^3}$ along the a, b, and c axes was used for the X-ray study. Crystal data are as follows: a=15.854(1), b=6.482(1), c=9.141(1) Å, β=100.07(1)°, V=924.9(2) $\mathrm{Å^3}$, $P2_1/m$, Z=2, D_{calcd}=1.47 g $\mathrm{cm^{-3}}$. A total of 1979 independent reflections was collected with graphite monochromated Cu $K\alpha$ radiation (λ=1.5418 Å) up to 2θ=128° using a Rigaku automated four circle diffractometer (AFC-6). The structure was solved by the direct method and refined by the block-diagonal least-squares method. Refinement was converged successfully for the space group $P2_1/m$ rather than the noncentrosymmetric $P2_1$. Therefore, the molecules are restricted in the way that all the atoms of BTDA molecule are located on the mirror planes of y=1/4 and y=3/4. The cations are disordered in the way that methylene C atoms are separated largely in two mirror images while others are slightly shifted. Most of hydrogen atoms are located by the difference

Table 3. Fractional Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) of Ethyltrimethylammonium (1 : 1) Salt **2A**

Atom	X	Y	Z	BEQV$^{a)}$
S1	1505(1)	2500(0)	7298(1)	3.1
S2	−142(1)	2500(0)	13837(1)	3.0
N1	2003(2)	2500(0)	8997(4)	3.1
N2	−643(2)	2500(0)	12129(4)	2.6
N3	524(2)	2500(0)	7542(4)	2.9
N4	836(2)	2500(0)	13591(4)	2.8
N5	−1463(3)	2500(0)	6003(5)	4.8
N6	2901(3)	2500(0)	15089(5)	4.1
N7	−2489(3)	2500(0)	9721(5)	4.5
N8	3821(3)	2500(0)	11244(5)	5.5
C1	1395(3)	2500(0)	9858(5)	2.5
C2	−34(3)	2500(0)	11270(4)	2.2
C3	536(3)	2500(0)	9017(5)	2.4
C4	824(3)	2500(0)	12116(4)	2.3
C5	−221(2)	2500(0)	9672(4)	2.2
C6	1583(3)	2500(0)	11462(5)	2.5
C7	−1047(3)	2500(0)	8843(5)	2.6
C8	2411(3)	2500(0)	12254(5)	2.7
C9	−1231(3)	2500(0)	7258(5)	3.1
C10	2624(3)	2500(0)	13845(5)	3.2
C11	−1818(3)	2500(0)	9438(5)	2.9
C12	3169(3)	2500(0)	11601(5)	3.6
N0	−3785(2)	2500(0)	12686(5)	3.8
C01	−2837(3)	2500(0)	13233(6)	4.5
C02	−4048(5)	561(15)	12036(9)	5.0
C03	−3981(5)	4202(15)	11480(9)	4.9
C04	−4267(5)	3259(0)	13915(8)	4.7
C06	−4021(6)	2003(0)	15325(9)	7.0

a) BEQV=(4/3) $\sum_{ij} \beta_{ij} (a_i \cdot a_j)$.

Table 4. Fractional Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) of Methyltributylammonium (1 : 2) Salt **2g**

Atom	X	Y	Z	BEQV$^{a)}$
S1	−2935(2)	1037(1)	−347(5)	4.2
N1	−2915(5)	71(4)	1364(13)	3.6
N2	−1207(6)	1391(4)	−1841(13)	3.5
N3	−4771(7)	−1751(5)	5500(17)	5.9
N4	−1396(9)	−3020(5)	5605(20)	6.9
C1	−1511(6)	−19(4)	804(13)	2.8
C2	−530(6)	741(4)	−1021(14)	2.8
C3	−1054(6)	−816(4)	1903(13)	2.8
C4	−2012(7)	−1561(4)	3631(15)	3.4
C5	−3556(7)	−1630(5)	4567(17)	4.1
C6	−1597(8)	−2361(5)	4642(18)	4.3
N100	8447(35)	4627(24)	−832(84)	7.7
C111	7349(47)	3763(22)	663(114)	7.6
C112	5757(39)	3949(21)	617(84)	5.5
C113	4717(54)	4190(35)	2345(130)	10.4
C114	3974(62)	3833(39)	5529(138)	10.5
C121	10176(42)	4722(29)	−131(125)	7.3
C122	11598(39)	5609(28)	−228(84)	6.5
C123	12812(36)	5084(29)	−151(112)	7.6
C124	14556(52)	5505(25)	−765(113)	8.4
C131	8497(50)	4815(37)	2910(102)	8.7
C141	7316(43)	4416(25)	−3840(100)	7.0
C142	6728(47)	4130(32)	−7162(105)	7.9
C143	6144(49)	4351(28)	−11177(89)	7.1
C144	5539(61)	5161(32)	−8859(149)	10.2

a) BEQV=(4/3) $\sum_{ij} \beta_{ij} (a_i \cdot a_j)$.

Table 5. Fractional Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) of Tetraethylammonium (1:2) Salt **2m**

Atom	X	Y	Z	BEQV$^{a)}$
S11	−3121(3)	814(1)	−1911(4)	2.8
S12	3209(3)	−237(1)	−3131(4)	2.7
S21	−8026(3)	5904(1)	4015(4)	2.9
S22	−1649(3)	4997(1)	1818(4)	2.8
N11	−1443(8)	1070(3)	−2352(11)	2.4
N12	1531(8)	−493(3)	−2675(11)	2.5
N13	−2910(8)	247(3)	−1789(12)	2.6
N14	2995(8)	339(3)	−3248(11)	2.4
N15	−4437(10)	−878(3)	−1109(14)	3.9
N16	4537(10)	1481(3)	−3813(15)	4.4
N17	−794(10)	−1514(3)	−1905(15)	4.0
N18	785(10)	2085(3)	−2992(15)	4.3
N21	−6294(8)	6194(3)	3962(12)	2.6
N22	−3369(8)	4702(3)	1916(11)	2.4
N23	−7854(8)	5337(3)	3461(12)	2.6
N24	−1838(8)	5556(3)	2384(12)	2.7
N25	−9500(10)	4186(3)	2752(15)	4.2
N26	−201(10)	6711(3)	3035(15)	4.1
N27	−5807(10)	3639(3)	1420(14)	3.8
N28	−4111(11)	7238(3)	4131(17)	5.2
N51	2536(8)	7472(3)	−1716(11)	2.5
C101	−628(10)	716(3)	−2415(13)	2.1
C102	729(9)	−129(3)	−2554(12)	1.7
C103	−1462(9)	239(3)	−2126(12)	1.9
C104	1577(9)	351(3)	−2888(12)	2.0
C105	−848(9)	−211(3)	−2147(12)	1.7
C106	957(10)	804(3)	−2826(13)	2.3
C107	−1665(10)	−674(3)	−1843(13)	2.3
C108	1758(10)	1262(3)	−3102(13)	2.1
C109	−3243(10)	−764(3)	−1476(13)	2.2
C110	3325(11)	1357(4)	−3496(15)	3.0
C111	−1103(10)	−1132(3)	−1894(14)	2.4
C112	1151(10)	1714(4)	−3013(15)	3.0
C201	−5496(10)	5854(3)	3483(13)	2.0
C202	−4172(9)	5040(3)	2459(13)	2.2
C203	−6379(9)	5356(3)	3211(13)	2.0
C204	−3283(9)	5535(3)	2710(13)	2.0
C205	−5765(9)	4927(3)	2716(12)	1.7
C206	−3876(9)	5981(3)	3269(13)	2.1
C207	−6640(9)	4447(3)	2465(13)	2.0
C208	−3035(10)	6456(3)	3451(14)	2.5
C209	−8242(10)	4322(3)	2634(14)	2.4
C210	−1459(11)	6581(3)	3206(16)	3.0
C211	−6103(10)	4009(3)	1892(13)	2.4
C212	−3686(11)	6884(3)	3837(16)	3.1
C501	2577(11)	6920(3)	−2076(15)	3.1
C502	2599(13)	6630(4)	−266(18)	4.2
C503	2477(12)	7688(4)	−3686(15)	3.4
C504	2452(14)	8234(5)	−3650(20)	5.2
C505	1145(11)	7525(4)	−723(16)	3.3
C506	−374(12)	7284(4)	−1807(19)	4.3
C507	3927(12)	7737(4)	−339(16)	3.4
C508	5457(12)	7725(5)	−1043(19)	4.7

a) BEQV=(4/3) $\sum_{ij} \beta_{ij} (a_i \cdot a_j)$.

Fourier map, which are included in the refinement together with the others calculated. The final R value is 0.049 for 1596 reflections with $|F_o|>1.5\sigma|F_o|$. The final atomic coordinates are given in Table 3.

Structural Analysis of Methyltributylammonium 1 : 2 Salt (2g). An almost twinning plate-like crystal with the dimensions of 0.10×0.30×0.30 mm^3 was used for the data collection on a Rigaku automated four circle diffractometer (AFC-5R) with rotating anode using graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). A total of 2850 reflections within $2\theta=60°$ was collected. Although the Weissenberg photograph shows the disorder or twinning along the b and c axis, the most primitive cell was chosen for the structual determination. Thus obtained crystal data are as follows: a=8.943(2), b=14.756(3), c=3.991(1) Å, α=92.31(2), β=93.64(2), γ=110.27(2)°, V=492.0(2) Å^3, $P\bar{1}$, Z=0.5, D_{calcd}=1.42 g cm^{-3}. The structure was solved by the direct method and the parameters of BTDA molecule were obtained. After the block-diagonal least-squares refinement for these atoms with anisotropic temperature factors, the remaining atoms of ammonium ion were searched by the difference Fourier syntheses. By supposing the doubled unit cell along the stacking c axis, the positions of ammonium ions were proved to be disordered along this axis.[22] Furthermore, the N atom of the ammonium ion does not locate the center of symmetry, indicating that the cation is also orientationally disordered. Although these disordering made some difficulty, the atoms of the cation were successively picked up from the difference Fourier map. The final R value including these atoms is 0.097 for 1972 reflections with $|F_o|>3\sigma|F_o|$, and hydrogen atoms are not included in the refinement. The final atomic coordinates are given in Table 4.

Structural Analysis of Tetraethylammonium 1 : 2 Salt (2m). A needle-like crystal with dimensions of 0.15×0.15×0.25 mm^3 was used for the data collection. Crystal data are as follows: a=8.959(1), b=27.442(3), c=6.924(1) Å, α=92.78(1), β=97.24(1), γ=100.74(1)°, V=1654.6(4) Å^3, $P\bar{1}$, Z=2, D_{calcd}=1.55 g cm^{-3}. A total of 7199 reflections within $2\theta=52°$ was collected on a Rigaku automated four circle diffractometer (AFC-5) using graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). The structure was solved by the direct method by supposing the space group to be noncentrosymmetric $P1$, and four kinds of BTDA molecules appear in the Fourier map. These atoms were refined by the block-diagonal least-squares method followed by the difference Fourier syntheses from which the positions of two ammonium ions were determined. After refinement with isotropic temperature factors, two pairs of BTDA molecules and two ammonium ions were related by a center of symmetry indicating the space group to be centrosymmetric $P\bar{1}$ rather than $P1$. After transformation to the space group $P\bar{1}$ and successive refinement with anisotropic temperature factors, all the hydrogen atoms were located on the difference Fourier map. These are included in the refinement to give the final R value of 0.071 for the 3577 reflections with $|F_o|>3\sigma|F_o|$. The final atomic coordinates are given in Table 5.

For these three crystals, RANTAN 81 program[23] with some modification was used in the direct method. The atomic scattering factors from the International Tables for X-Ray Crystallography[24] were used. All the computation were carried out by an ACOS 1000 computer at Tohoku University using the applied library program of UNICS III system.[25]

Table of analytical values of anion radical salts **2A—2n**; listings of positional and thermal parameters, bond lengths and angles, and structural factors for **2A**, **2g**, and **2m** are kept at the Chemical Society of Japan (Document No. 8777).

The authors are grateful to Dr. Kokichi Oshima at Cryogenetic Center, The University of Tokyo for the temperature dependent resistivity measurement of **2g**.

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