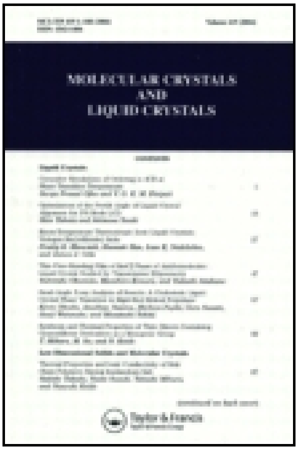


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Conductive Radical Cation Salts with Organic Anions of $\{RO\text{-}C[C(CN)_2]_2\}$

Hideki Yamochi [a], Chiyoko Tada [a], Shuichi Sekizaki [a], Gunzi Saito [a], Masami Kusunoki [b] & Ken-Ichi Sakaguchi [b]
[a] Division of Chemistry, Graduate School of Science, Kyoto University Sakyo-ku, Kyoto, 606-01, Japan
[b] Institute for Protein Research, Osaka University Yamadaoka, Suita, 565, Japan

To cite this article: Hideki Yamochi, Chiyoko Tada, Shuichi Sekizaki, Gunzi Saito, Masami Kusunoki & Ken-Ichi Sakaguchi (1996): Conductive Radical Cation Salts with Organic Anions of $\{RO\text{-}C[C(CN)_2]_2\}$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 284:1, 379-390

To link to this article: http://dx.doi.org/10.1080/10587259608037940

Mol. Cryst. Liq. Cryst., 1996, Vol. 284, pp. 379–390
Reprints available directly from the publisher
Photocopying permitted by license only

CONDUCTIVE RADICAL CATION SALTS WITH ORGANIC ANIONS OF $\{RO\text{–}C[C(CN)_2]_2\}^-$

HIDEKI YAMOCHI, CHIYOKO TADA, SHUICHI SEKIZAKI,
and GUNZI SAITO
Division of Chemistry, Graduate School of Science, Kyoto University
Sakyo-ku, Kyoto 606-01, Japan

MASAMI KUSUNOKI and KEN-ICHI SAKAGUCHI
Institute for Protein Research, Osaka University
Yamadaoka, Suita 565, Japan

Abstract 2-alkyloxy substituted tetracyanoallyl anions (RO–TCA$^-$, R = Me, Et, Pr, Bu) were examined in the formation of the radical cation salts of organic donor molecules systematically. 14 kinds of salts have been obtained so far. Among them, (BEDO–TTF)$_2$(EtO–TCA)(H$_2$O)$_{0.75}$ showed weak metallic temperature dependence of the conductivity down to ca. 180 K (σ_{rt} = 30 S cm^{-1}). The crystal structure analyses of (BEDT–TTF)$_2$(PrO–TCA) (needle form) and (TTT)(MeO–TCA) revealed the layered structure in both cases. The two C(CN)$_2$ groups in an anion are twisted to each other in either salts. The structures of the anion layers showed the existence of various packing patterns for this anion series.

INTRODUCTION

Most of the molecular superconductors consist of organic molecules and inorganic counter ions. Substituting the inorganic ions by stable organic ones, there are advantages that the size, shape, and formal charge of the counter ion can be well tailored by the method of synthetic organic chemistry. Furthermore the introduction of big polarizability into a salt is expected to stabilize the metallic states. Also, the dimensionality of the salts will be increased by use of organic ions having heteroatoms on the periphery.

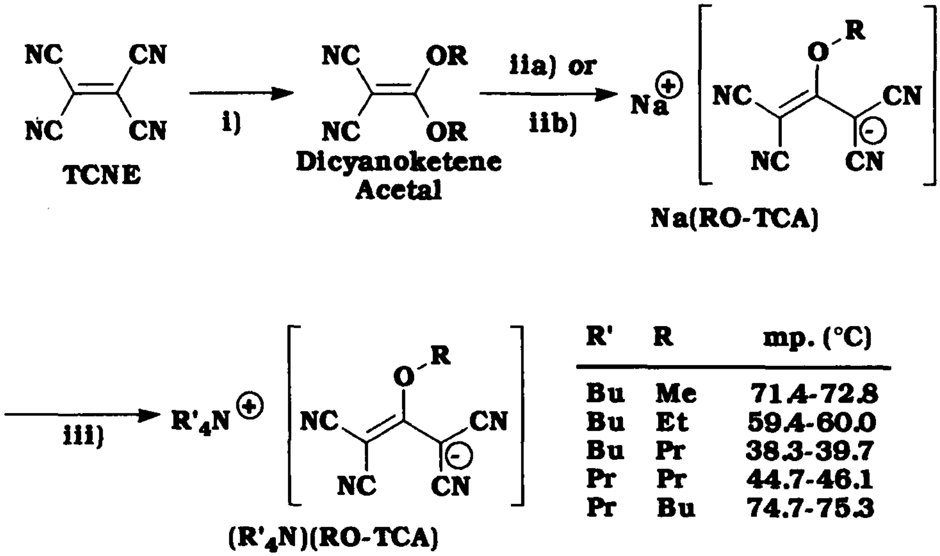
As a series of stable closed-shell organic ions, we had investigated cyanocarbon anions.[1] To obtain a series of anions having the same formal charge and different sizes easier, the title anions of normal alkyloxy substituted tetracyanoallyl anions (RO–TCA$^-$) were examined in the formation of the conductive radical cation salts. In this case, not only the transport properties but also the thermodynamic properties (e.g.

melting points (mp.'s), solubilities etc.) of the salts are expected to show a systematical dependence on the alkyl chain. This paper describes the synthesis of the anions (R = Me, Et, Pr, and Bu) and the salts of them so far obtained.

RESULTS

Synthesis of RO–TCA$^-$

The synthetic procedure and mp.'s of these anions are summarized in



R'	R	mp. (°C)
Bu	Me	71.4-72.8
Bu	Et	59.4-60.0
Bu	Pr	38.3-39.7
Pr	Pr	44.7-46.1
Pr	Bu	74.7-75.3

SCHEME 1 Synthetic Procedure and melting points of (R'$_4$N)(RO–TCA). *Reagents and Conditions*: i) urea in ROH, 70–90°C for 5 min. iia) $CH_2(CN)_2$ + Na in ROH (for R = Me, Et, Pr). iib) $NaCH(CN)_2$ in THF (for R = Et, Pr, Bu). iii) (R'$_4$N)Br in MeOH (R = Me, Et) or in H_2O (R = Et, Pr, Bu).

TABLE I Yields(%) in Synthetic Procedures of (R'$_4$N)(RO–TCA). Each step correspnds to that in SCHEME 1.

R	TCNE → Dicyano-ketene Acetal i)	Ducyanoketene Acetal → Na(RO-TCA) iia)	iib)	Na(RO-TCA) → (R'$_4$N)(RO-TCA) iii)
Me	52.0 (50)[a]	97.3 (---)[b]		55.9 (R'=Bu)
Et	76.1 (72)[a]	73.6 (64.8)[b]	95.4	85.2 (R'=Bu)
Pr	64.7	43.7	71.5	87.1 (R'=Bu) 55.7 (R'=Pr)
Bu	50.7		quantitative	79.1 (R'=Pr)

a: reference 2. b: reference 3.

SCHEME 1. Yields of each step for each compound are listed in TABLE I. Dicyanoketene acetals were obtained from TCNE by the action of hot alcohols in the presence of urea.[2]

According to the literature[3], the acetal was reacted with sodium malononitrilide to give the sodium salt of $RO{-}TCA^-$ in the alcohol having the same alkyl group to the acetal. The product precipitates from the reaction mixture. This procedure requires 1.5 L of alcohol per a mol of the acetal. It is expected that the $RO{-}TCA^-$ having a long alkyl chain is too soluble in the alcohol to give high yield. We found that this reaction can be carried out in THF using sodium malononitrilide without alcohol. This method improved the yields of the derivatives of R = Et and Pr (see TABLE I), and was also utilized for the butyl derivative to give remarkably good yield.

Preparation of Radical Cation Salts with Organic Donor Molecules

The electrocrystallization of TTF derivatives (FIG. 1), TMTSF, TTT, pyrene, and perylene were carried out in the presence of $(R'_4N)(RO{-}TCA)$. TABLE II summarizes the results for the donor molecules which gave solid salts. As is described below, the structural analyses of the salts demonstrated that these anions are incorporated in the salts without any decompositions at the C–O bonds. These results are in contrast to that for sodium dodecylsulfate ($C_{12}H_{25}{-}OSO_3Na$). During the electrocrystallization of BEDT-TTF, this anion is decomposed to give $(BEDT{-}TTF)_3(HSO_4)_2$.[4]

Among the combinations examined so far, only the salt between

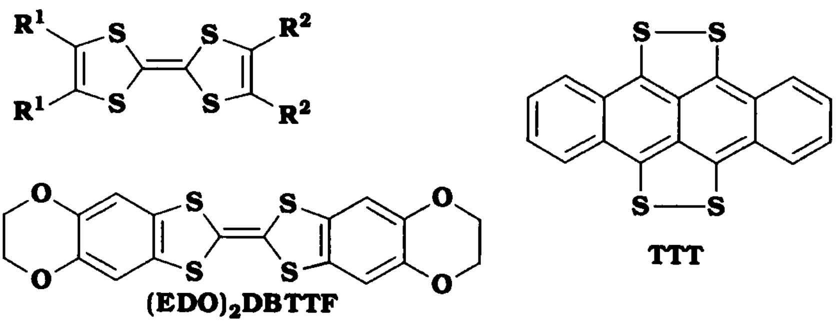


FIGURE 1 Chemical Structure of Donor Molecules Examined.
$R^1= R^2= -CH_3$, $-SCH_3$ ($TTC_1{-}TTF$); $R^1R^1= R^2R^2= -(CH_2)_3-$, $-(CH_2)_4-$, $-SCH_2CH_2S-$ (BEDT-TTF), $-OCH_2CH_2O-$ (BEDO-TTF); $R^1R^1= -OCH_2CH_2O-$, $R^2=-CH_2OH$

BEDO–TTF and EtO–TCA showed a metallic behavior (σ_{rt} = 30 S cm^{-1}, weakly metallic down to ca. 180 K, FIG. 2). However, the quality of the crystals was too poor to analyze the structure. The composition was determined by the elemental analysis as (BEDO–TTF)$_2$(EtO–TCA)(H$_2$O)$_{0.75}$. To obtain more precise conductivity data and the crystal structure, the optimization of the electrocrystallization condition is under way.

TABLE II Summary of Electrocrystallization of TTF derivatives and TTT. In all cases, THF was used as the solvent. The other solvents examined are indicated in the brackets.

Donor	Supporting Electrolyte (R'$_4$N)(RO-TCA)			
	(R'=Bu,R=Me)	(R'=Bu,R=Et)	(R'=Bu,R=Pr)	(R'=Pr,R=Bu)
BEDT-TTF(ET)	///	/// [TCE,Ph-CN]	Needles Plates	Plates [THF+EtOH]
BEDO-TTF(BO)	/// [Ph-CN]	Plates [Ph-CN]	Powder [THF+EtOH]	Powder [THF+EtOH]
(EDO)$_2$DBTTF	Needles [THF+EtOH]	Thin Plates [THF+EtOH]	Thin Plates [THF+EtOH]	Blocks [THF+EtOH]
TTT	Needles	Needles	Needles [THF+EtOH THF+H$_2$O]	Needles [THF+EtOH]

///: No Solid Products were obtained.

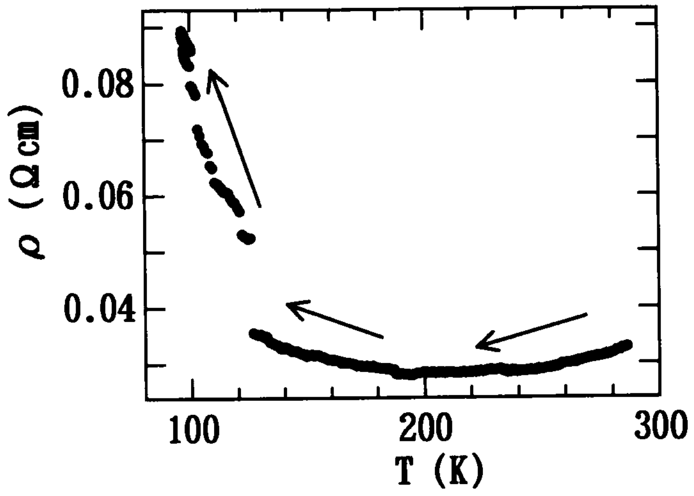


FIGURE 2 Temperature Dependency of the Resistivity of (BEDO–TTF)$_2$(EtO–TCA)(H$_2$O)$_{0.75}$.

At present, the needle form of BEDT–TTF salt with PrO–TCA and the salt of TTT and MeO–TCA have been analyzed the crystal structure.

Crystal and Band Electronic Structure of (BEDT–TTF)$_2$(PrO–TCA)

Applying the constant current (0.2–0.5 μA) to BEDT–TTF (14–18 mg) solution in THF (18 mL) containing (Bu$_4$B)(PrO–TCA) (44–48 mg) gave black needles and plates. Although all of the crystals exhibited the semiconductive behavior, the former modification showed the higher conductivity (σ_{rt} = 3–42 S cm^{-1}, Ea = 0.06 eV) than the latter one (σ_{rt} ≈ 0.01 S cm^{-1}, Ea ≈ 0.12 eV). X-ray diffraction experiments revealed the existence of at least two modifications (needle form: a = 11.184(5) Å, b = 20.73(1), c = 9.584(5), α = 85.90(3)°, β = 65.42(3), γ = 78.23(4), V = 1977(2) Å, plate form: a = 31.4 Å, b = 6.7, c = 7.8, α = 90.1°, β = 34.8, γ = 96.0, V = 923 Å).

Despite the poor quality of crystals, the crystal structure of the highly conducting needle form was determined. The triclinic unit cell contains two of the formula unit of (BEDT–TTF)$_2$(PrO–TCA) (the space group is P$\bar{1}$, Z = 2, D$_{obs.}$ = 1.61 g cm^{-3}, D$_{calc.}$ = 1.63 g cm^{-3}). The final R-value was 11.5% (2434 unique reflections of which F ≥ 3σ(F) were used to refine 460 parameters).

The crystal structure consists of the alternating stack of donor and anion layers (FIG. 3). The packing motif in the donor layer resembles

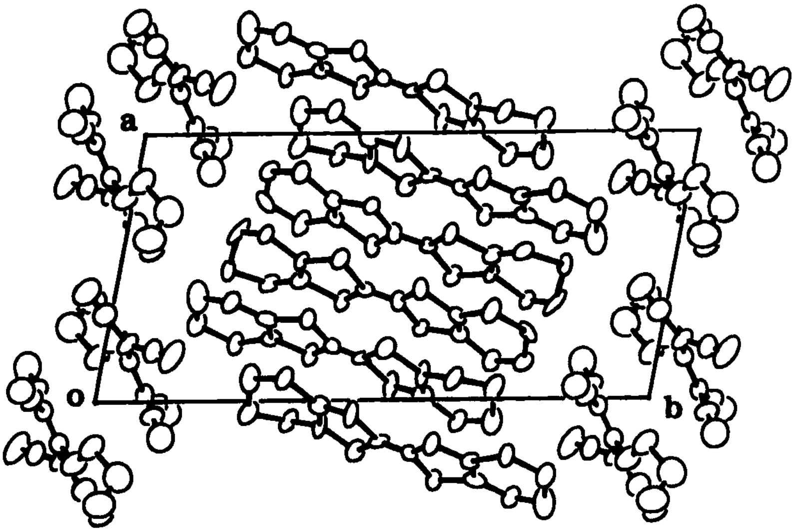


FIGURE 3 Crystal Structure of needle form (BEDT–TTF)$_2$(PrO–TCA). Projected along the c–axis.

that in $(ET)_2ClO_4(CH_2Cl\text{-}CHCl_2)_{0.5}$[5] (FIG. 4). Along the c–axis, side–by–side intermolecular S··S atomic contacts shorter than the sum of van der Waals radii (vdW) were observed. Within the face–to–face stacking column along the a+c direction, an extended Hückel based calculation gave the three kinds of unique overlap integrals ($S = 4.63$, -0.98, and -5.19×10^{-3}). The column consists of a tetramer of the donor molecules. Because of this tetramerization, the band electronic structure[6] showed a semiconducting gap between the highest occupied and lowest unoccupied states (FIG. 5), which corresponds to the observed conducting properties.

The PrO–TCA forms face–to–face type columnar stack along the a–axis (FIG. 3). The neighboring anions are related by a center of inversion, and hence all the anion planes are parallel to each other. Two $C(CN)_2$ groups in an anion molecule are twisted with the dihedral angle of 36.6°.

Although the molecular planes of the donor and anion are near to parallel, an anion shows only one weak heteroatomic contact (3.25 Å) shorter than vdW of N··S (3.35 Å) with a donor molecule (II in FIG. 4). Defining the best planes of donor molecule and anion by the central C_6S_8

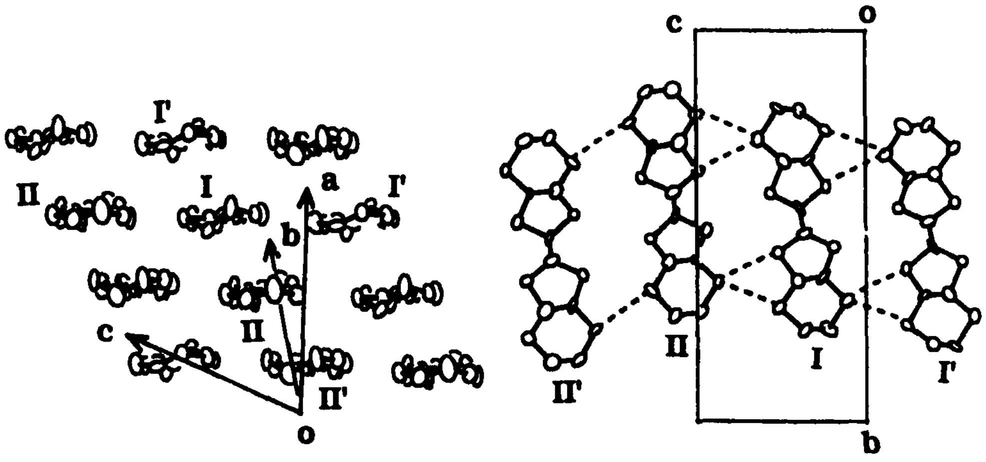


FIGURE 4 The donor layer in the needle form $(BEDT\text{-}TTF)_2(PrO\text{-}TCA)$. Projected along the donor longitudinal axis (left) and c–axis (right). I and II indicate the crystallographically unique molecules. I' and II' are correlated to I and II by center of inversion, respectively. Intermolecular S··S contacts shorter than vdW are shown by dashed lines (right).

and the central oxyallyl C_3O skeletons, respectively, the dihedral angles between them are 38.7–40.5°.

Crystal Structure of (TTT)(MeO–TCA)

Galvanostatic electrolysis (0.50 μA) of the THF (18 mL) solution of TTT (10.7 mg) in the presence of (Bu_4N)(MeO–TCA) (50.6 mg) gave black needles. The composition was determined as 1:1 by the structural analysis described below. As expected from this stoichiometry, this salt exhibited semiconductive resistivity of 1.8 X 10^3 Ω cm at room temperature. Similar electrolytic procedures using (Bu_4N)(EtO–TCA), (Bu_4N)(PrO–TCA), and (Pr_4N)(BuO–TCA) gave only the poor quality of crystals. The optimization of the electrocrystallization condition for these anion species is now under way.

(TTT)(MeO–TCA) belongs to a monoclinic crystal system ($P2_1/n$, a = 12.351(2) Å, b = 23.632(4), c = 7.603(1), β = 101.48(1)°, V = 2174.9(6) Å, Z = 4, $D_{obs.}$ = 1.58 g cm^{-3}, $D_{calc.}$ = 1.60 g cm^{-3}). The positional parameters of hydrogen atoms were calculated from those of the bonding carbon atoms and were not refined. Also, their thermal parameters were not refined. The final R-value was 4.2 % in the refinements of 316 parameters using the 2992 reflections of which $F \geq 3\sigma(F)$.

FIGURE 6 shows the c–axis projection of the crystal structure in which one donor molecule and one anion are crystallographically unique.

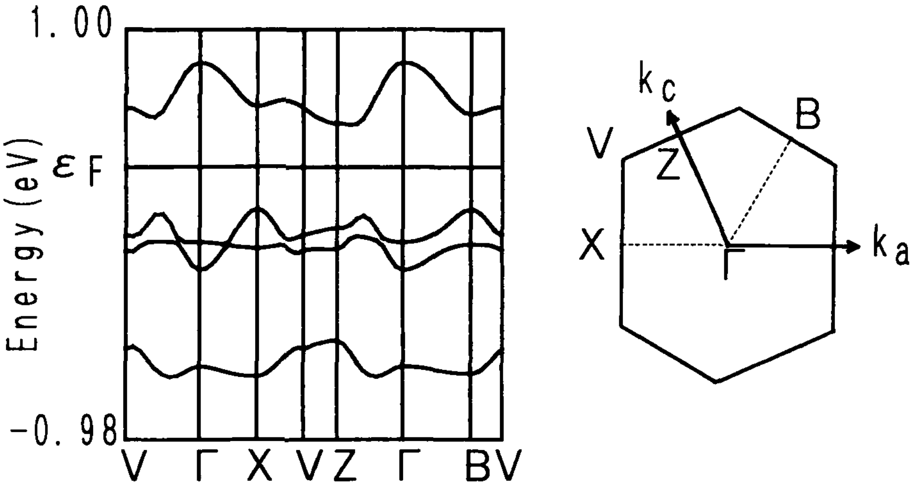


FIGURE 5 Dispersion Relation of Needle Form $(BEDT\text{–}TTF)_2$(PrO–TCA).

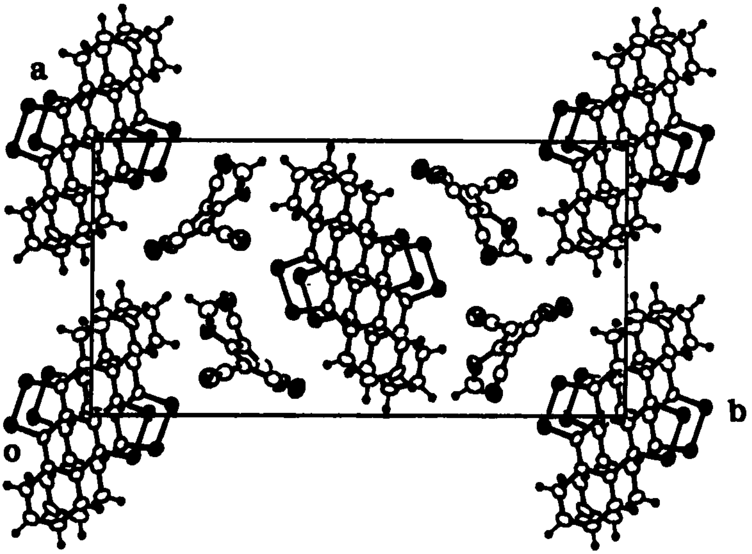


FIGURE 6 c–axis Projection of Crystal Structure of (TTT)(MeO–TCA).

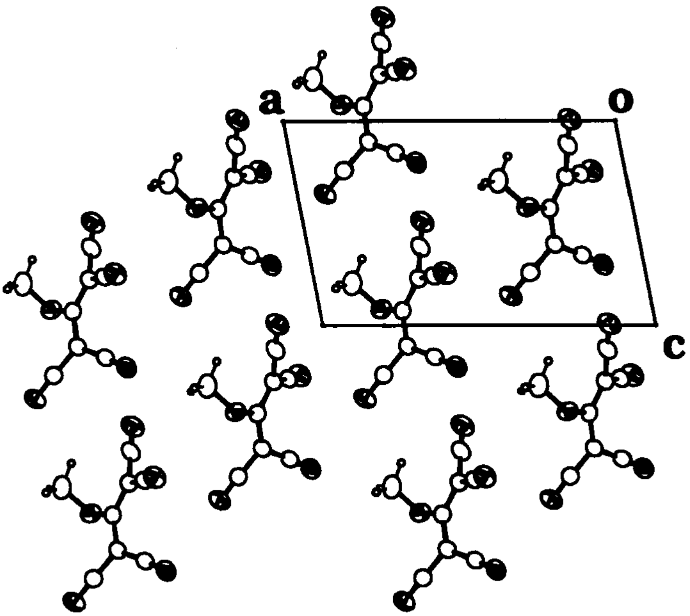


FIGURE 7 Anion Layer of (TTT)(MeO–TCA). The layer at y = 1/4 is projected along the b–axis. Nitrogen, oxygen, and sulfur atoms were shaded.

Similar to $(BEDT\text{-}TTF)_2(PrO\text{-}TCA)$, this salt consists of a layered structure alternating along the b-axis. TTT molecules form the columnar stacks along the c-axis in which the donor molecules form dimers (the intra- and inter-dimer interplanar distances are 3.32 and 3.46 Å, respectively). Within and between the dimers, the donor molecules are related by center of inversion, and hence all of TTT molecules are parallel in a column. 13 numbers of intermolecular S··C or C··C contacts shorter than the sum of vdW were observed within the dimer (3.27–3.43 Å). Also between the dimer, two C··C contacts of 3.35 Å were found, though S··S contacts shorter than vdW were not observed in both cases.

Similar to the $PrO\text{-}TCA^-$ in the BEDT-TTF salt, two $C(CN)_2$ groups of $MeO\text{-}TCA^-$ in this salt are twisted with the dihedral angle of 30.1°. The anion forms a layer parallel to the ac-plane of which electric dipole is finite (FIG. 7). However, the adjacent anion layers are related by center of inversion and they cancel out the permanent dipole moments of the

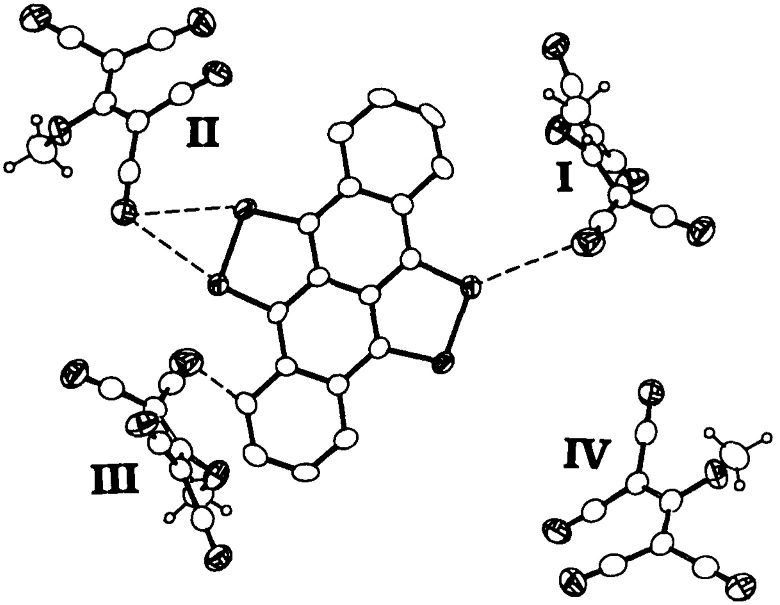


FIGURE 8 Relative Orientation of Components in (TTT)(MeO–TCA).
The molecules were projected onto the donor best plane. Hydrogen atoms of the donor molecules were omitted for simplicity. Nitrogen, oxygen, and sulfur atoms were shaded. The dashed lines exhibit the intermolecular S··N and C··N contacts shorter than the sum of vdW. The symmetry operations to derive the drawn molecules are as following.: I(x,y,z), II(−x+0.5,y−0.5,−z+1.5), III(−x,−y,−z), IV(x−0.5,−y+0.5,−z−2.0)

anions. No atomic contacts between the anion atoms having p–orbital were observed.

FIGURE 8 shows the relative orientation of TTT and the surrounding MeO–TCA⁻. The intermolecular atomic contacts shorter than the sum of vdW were observed at S··N (3.10–3.30 Å (vdW = 3.35 Å)) and C··N (3.24 Å (vdW = 3.25 Å)). The best planes were defined from the positional parameters of the non-hydrogen atoms and the central C_3O unit for TTT and the anion, respectively. The dihedral angles were 74.5° and 48.4° between TTT ~ anion I(III) and between TTT ~ anion II(IV), respectively.

DISCUSSION

Melting Points of (R'_4N)(RO–TCA)

Normal alkanes show the almost monotonic increase of mp.'s with the increment of the chain length. On the other hand, alkyl substituted TTF derivatives of TXC_n–TTF are known to exhibit a minimum in the plot of mp. vs. alkyl chain length. This phenomena is interpreted as the result of the competition between the central TTF moiety and the alkyl chain to give the convenient packing motif for each part.[7]

As is summarized in SCHEME 1, the mp. of Bu_4N salt of RO–TCA decreases from R = Me, Et, to Pr. The Pr_4N salt of BuO–TCA shows the higher mp. than that of PrO–TCA salt. These observations suggest that the series of RO–TCA salt in which the counter (radical) cation is unique will show the similar kind of alkyl chain dependency of mp. to the TXC_n–TTF series. Although they show only the decomposition points, the $(EDO)_2$DBTTF and TTT salts of RO–TCA show such behavior (TABLE III).

Comparison of the RO–TCA⁻ in $(BEDT\text{-}TTF)_2$(PrO–TCA) and (TTT)(MeO–TCA)

Despite the compositions and the alkoxy groups are different in these two salts, the anions show the similar molecular geometry (TABLE IV). In both cases, the central C_3O skeleton is planer (the deviation of the oxygen atom from the best plane defined by the allylic carbon atoms

TABLE III Decomposition Points(°C) of RO–TCA Salts.

	R in RO-TCA			
Donor	Me	Et	Pr	Bu
$(EDO)_2$DBTTF	351-355	348-353	341-349	348-351
TTT	249-252	215-218	194-197	216-219

(Plane 1 in TABLE IV) is less than 0.07 Å in either salts). The two $C(CN)_2$ groups in an anion are twisted to each other to form a propella shaped configuration of the substituents around the central carbon atom.

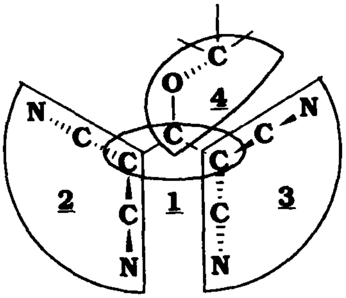
From the viewpoint of the electronic structure, however, this torsion does not affect so much. To consider the overlap integrals between a couple of p–orbitals, the concept of the simple Hückel molecular orbital theory is adequate. When each of the nodal plane of the two p–orbitals contains the axis of σ–bond and the planes are twisted with the dihedral angle of θ, the overlap integral between them is estimated as the product of $(\cos\theta)\times$(the overlap integral between the non–twisted p–orbitals). As shown in TABLE IV, the overlap integrals between the allyl and dicyanomethylene groups retain more than 90 % of the non–twisted case. These anions are regarded to have the delocalized allylic π–electrons.

Electrochemical measurements show that $RO\text{–}TCA^-$ is a stable anion. In the cyclic voltammograms at a platinum electrode in acetonitrile containing 0.1 M $(Bu_4N)(BF_4)$, these anions show the oxidation peaks at around 1.3 V vs. S.C.E. This value means that usual TTF derivatives and TTT cation radicals can not oxidize the anions and hence RO–TCA's exist as completely ionized mono–anions in the salts.[8]

The relative orientation between the donor molecule and the anions differs between these two salts. As mentioned before, the molecular planes of donor and anion are aligned near to parallel in $(BEDT\text{–}TTF)_2(PrO\text{–}TCA)$. This type of the arrangement is often observed in organic donor–acceptor type charge transfer complexes. It is noteworthy that the dihedral angle of 38.7–40.5° in this salt is smaller than that (58.5°) in the (TTF)(TCNQ) which is a representative complex having

TABLE IV Intramolecular Dihedral Angles in RO–TCA.
Each least–squares plane was calculated based on the atomic parameters displayed in the right figure. In parenthesis, the cosine is indicated.

	PrO-TCA in needle form 2:1 BEDT-TTF Salt		MeO-TCA in 1:1 TTT Salt	
Plane 2 - 3	36.6°		30.1°	
1 2	22.8	(0.92)	13.5	(0.97)
1 3	18.8	(0.95)	20.8	(0.93)
1 4	21.8		50.7	



segregated columnar structure.[9] In the (TTT)(MeO–TCA) salt, there observed two kinds of relative orientations between the donor molecule and the anion, though only one anion is crsytallographically unique. The dihedral angle between them is bigger in one case (74.5°) and is smaller in another (48.4°) than that in (TTF)(TCNQ). In the metallic radical cation salts of the planar organic donor molecules and rod-shaped or polymeric inorganic anions, the nearly perpendicular orientation between the components is common (eg. BEDT–TTF salts with I_3, IBr_2, AuI_2, $Cu(NCS)_2$, etc.). These observations anticipate the various packing motives of RO–TCA⁻'s in the salts.

CONCLUDING REMARKS

The examination of RO–TCA⁻ has proved that this series of organic anions is enough stable to utilize as a counter anion of organic radical cation salts. In the BEDT–TTF and TTT salts, this type of anion showed twisted configuration of two $C(CN)_2$ moieties. This geometry will affect the packing motif of the component molecules in their salts, however, the electronic structure of RO–TCA⁻ is expected to have the well delocalized allylic character. Our investigation to control the crystal and electronic structures and thermodynamic properties has just started and even only some of basic data have been obtained, this series of anions proved to be a preferable candidate for our purpose because of their stability and the variety of the packing patterns.

REFERENCES

1. H.Yamochi, T.Tsuji, G.Saito, T.Suzuki, T.Miyashi, and C.Kabuto, Synthetic Metals, 27, A479(1988).
2. W.J.Middleton and V.A.Engelhardt, J.Am.Chem.Soc., 80, 2778(1958).
3. W.J.Middleton, E.L.Little, D.D.Coffman and V.A.Engelhardt, J.Am.Chem.Soc., 80, 2795(1958).
4. A.Otsuka, G.Saito, T.Nakamura, M.Matsumoto and Y.Kawabata, unpublished data.
5. H.Kobayashi, A.Kobayashi, Y.Sasaki, G.Saito, T.Enoki, and H.Inokuchi, J.Am.Chem.Soc., 105, 297(1983).
6. T.Mori, A.Kobayashi, Y.Sasaki, H.Kobayashi, G.Saito and H.Inokuchi, Bull.Chem.Soc.Jpn., 57, 627(1984).
7. J.K.Jeszuka, T.Enoki, Z.Shi, K.Imaeda, H.Inokuchi, N.Iwasawa, H.Yamochi and G.Saito, Mol.Cryst.Liq.Cryst., 196, 167(1991).
8. G.Saito and J.P.Ferraris, Bull.Soc.Chem.Jpn., 53, 2141(1980).
9. T.E.Phillips, T.J.Kistenmacher, J.P.Ferraris and D.O.Cowan, J.C.S.Chem.Commun., 471(1973).