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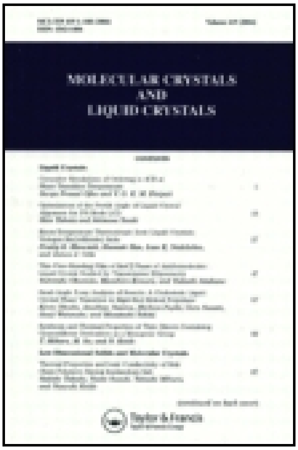

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Crystal Structures and Properties of the Cation Radical and Charge Transfer Salts of 7,10-Dithiafluoroanthene

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CRYSTAL STRUCTURES AND PROPERTIES OF THE CATION RADICAL AND CHARGE TRANSFER SALTS OF 7,10-DITHIAFLUOROANTHENE

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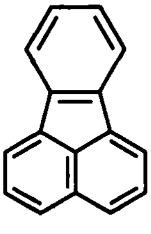
Abstract The cation radical (CR) and charge transfer (CT) salts of 7,10-dithiafluoroanthene with various inorganic and organic acceptors were prepared either by electrocrystallization in the presence of tetraalkylammonium salts or recrystallization of the mixture of donor and acceptors. The structures of these CR and CT salts were determined by X-ray crystallographic analysis and the conductivities of those salts were measured by a four probe method using compaction pellets.

INTRODUCTION

Simple arenes such as naphthalene, fluoroanthene (**1**), perylene, and pyrene give electrically conducting cation radical salts $[\mathrm{Aryl}_2]^{+\cdot}X^-$ by anodic oxidation.[1] Replacement of the sp^2 carbon atoms in these arenes by sulfur atoms brings about remarkable improvement in electrical properties of their cation radical (CR) and charge transfer (CT) salts by the construction of S···S networks with van der Waals interaction in the solid state.[2] Therefore, thiafluoroanthene is also promising as a new effective π-donor. Here we report on the physical properties, structures of the CR and CT salts of 7,10-dithiafluoroanthene (**2**) by X-ray crystallographic analysis, and electrical conductive nature.



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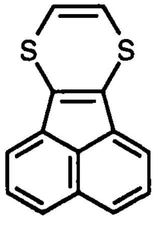

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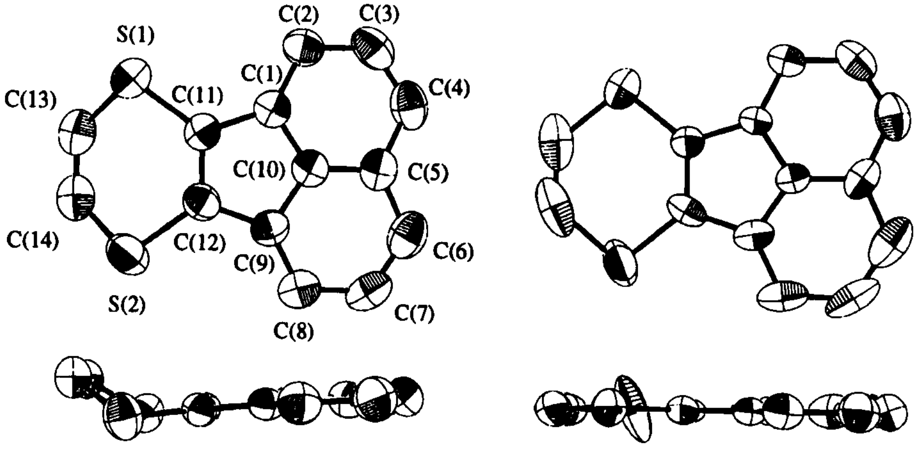
PHYSICAL PROPERTIES AND ELECTROCHEMICAL PREPARATION OF THE CR OF **2**

The synthesis of **2** was previously reported.[3] The cyclic voltammogram of **2** [platinum electrode versus SCE; tetra(*n*-butyl)ammonium perchlorate (0.1 M) in acetonitrile, scan rate 50 mV s^{-1}] showed reversible first oxidation ($E_{1/2}$ = +0.68 V), and irreversible second oxidation potentials (E_p = +1.42 V). The preparation of the CR salts of **2** was carried out by electrocrystallization in the presence of various tetraalkylammonium salts. When the solution of **2** in dichloromethane was electrooxidized by platinum electrodes in the presence of tetra(*n*-butyl)ammonium hexafluorophosphate, tetra(*n*-butyl)ammonium perchlorate, or tetra(*n*-butyl)ammonium tetrafluoroborate as a supporting electrolyte, black crystals of the corresponding CR salts grew on the anode.[4] The compositions of the obtained salts were determined to be $(\mathbf{2})_2PF_6$, $(\mathbf{2})ClO_4$, and $(\mathbf{2})BF_4$ by elemental analyses, respectively. These salts are stable for more than several months at room temperature. The radical cation salts of **2** with PF_6^- (octahedral) and BF_4^- (tetrahedral) were obtained in single crystals suitable for X-ray crystallographic analysis, however, the radical cation salts of **2** with another inorganic anions such as I_3^- (linear), or NO_2^- (planar) were not formed as stable states.



a)

b)

FIGURE 1 Molecular structures and atomic numbering scheme of **2** a) in the neutral state and b) in the CR state.
(The hydrogen atoms are omitted.)

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CRYSTAL STRUCTURE OF THE CR SALTS

The crystal structures of the neutral donor **2**,[5] the radical cation salts of **2** with PF_6^- and BF_4^- were determined.[6] The neutral **2** was bent on the peripheral two sulfur atoms, however, the **2** became planar in radical cation salts. The molecular packing of $(\mathbf{2})_2PF_6$ is shown in FIGURE 2. In the $(\mathbf{2})_2PF_6$, the fluorine atoms of anions were disordered. The columnar stack of the donor is found along the *a* axis, where a small degree of alternating intermolecular separation is appeared in the column. The vinylenedithio moieties are partially overlapped in the column with S···S contacts (d_1 = 3.509(2) Å and d_2 = 3.516(2) Å), which are shorter than the sum of van der Waals distances (3.7 Å). The similar S···S contacts (d_3 = 3.528(2) Å) are observed between the columns. Thus S···S networks exist along not only the *a* but also the *c* direction. This structure suggests a possibility of the quasi two dimensional conductive nature parallel to the *ac* plane. And this structure is also responsible for the nature of high electrical conductivity along the *ac* plane. In the $(\mathbf{2})BF_4$, the columnar stack of the donor is found along the *c* axis. Only one short S···S (d_4 = 3.118(7) Å) contact is observed between the vinylenedithio groups along the *c* axis (columnar stacking direction), but there is no S···S networks as shown in FIGURE 3. Thus, the low electrical conductive nature of $(\mathbf{2})BF_4$ can be rationalized on the basis of the molecular packing.

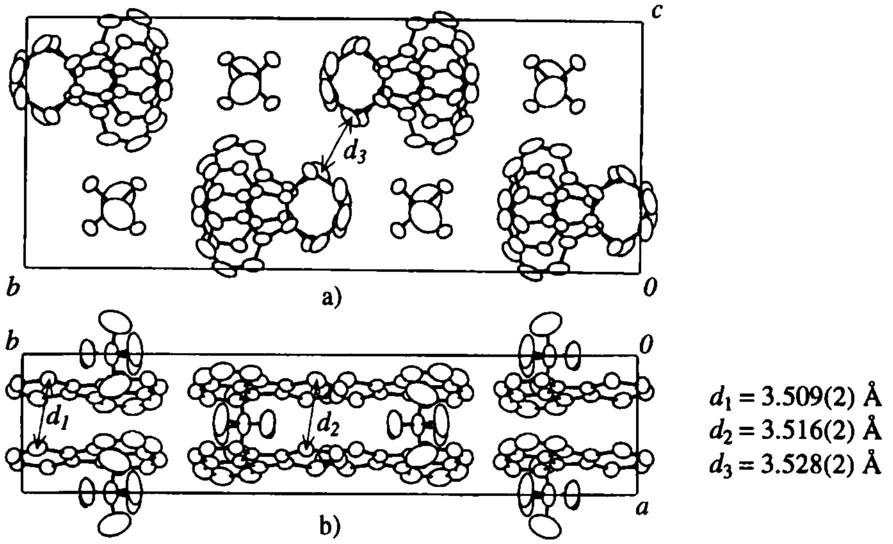

FIGURE 2 Crystal structure of $(\mathbf{2})_2PF_6$ viewed along a) the *a* axis and b) the *c* axis. (The hydrogen atoms are omitted.)

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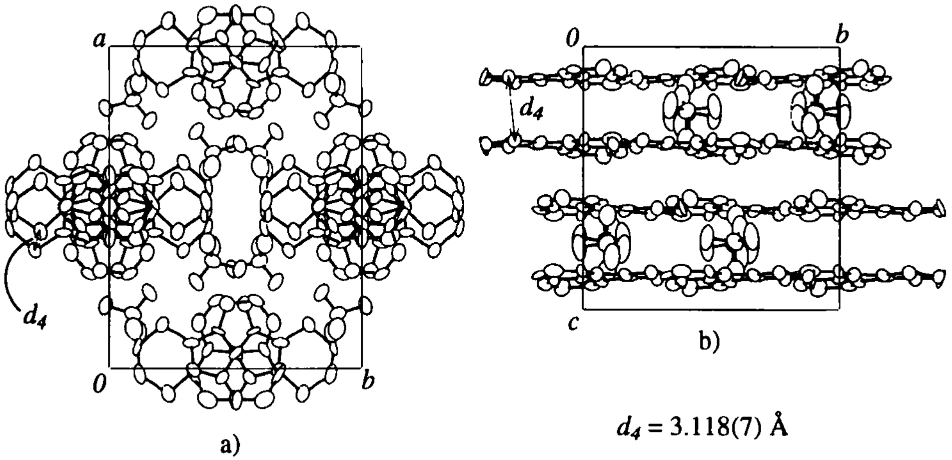

$d_4 = 3.118(7)$ Å

FIGURE 3 Crystal structure of (**2**)BF_4 viewed along a) the *c* axis and b) the *a* axis. (The hydrogen atoms are omitted.)

TABLE I Crystal data of **2**, (**2**)$_2PF_6$, (**2**)BF_4, and (**2**)TCNQ

	Neutral[5]	(**2**)$_2PF_6$[6]	(**2**)BF_4[6]	(**2**)TCNQ[6]
Formula	$C_{14}H_8S_2$	$C_{28}H_{16}S_4PF_6$	$C_{14}H_8S_2BF_4$	$C_{26}H_{12}N_4S_2$
F_w	240.34	625.64	327.14	444.53
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$P\bar{1}$
a / Å	9.408(2)	6.953(3)	16.67(2)	9.036(2)
b / Å	11.129(2)	29.959(7)	12.505(4)	17.504(3)
c / Å	10.822(2)	12.619(3)	13.50(1)	6.8939(6)
α / °	90	90	90	91.64(1)
β / °	98.58(1)	104.99(2)	108.90(8)	98.89(2)
γ / °	90	90	90	76.74(2)
V / Å^3	1120.5(4)	2539(2)	2662(4)	1048.5(6)
Z	4	4	8	2
D_{calc}	1.425	1.636	1.632	1.408
No. of unique reflections	1850	2977	2420	4814
R, R_w	0.038, 0.043	0.047, 0.046	0.056, 0.053	0.045, 0.042

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PREPARATION AND CRYSTAL STRUCTURE OF THE CT SALTS OF 2

Compound **2** formed not only the radical cation salts with inorganic anions but also the charge transfer salts with inorganic and organic acceptors. Compound **2** forms charge transfer salts with iodine and 7,7,8,8-tetracyanoquinodimethane (TCNQ). These CT salts were prepared by mixing the hot solutions of **2** and iodine or TCNQ.[7] The two kinds of iodine salts having distinct compositions were obtained (TABLE III) by using different solvent. The charge transfer salt of **2** with TCNQ having the donor / acceptor ratio of 1 : 1 gave an alternating array of good single crystals suitable for X-ray crystallographic analysis. The X-ray analysis of (**2**)TCNQ was performed[6] and the crystal structure was shown in FIGURE 4. The (**2**)TCNQ have the mixed stacking with donor and acceptor along the *c* axis. There is naturally no short S···S contact within this mixed stacking column. The shortest S···S distance (d_5 = 3.555(2) Å), which is shorter than the normal van der Waals contact, belongs to the head-to-head type intercolumner contact between **2** molecules.

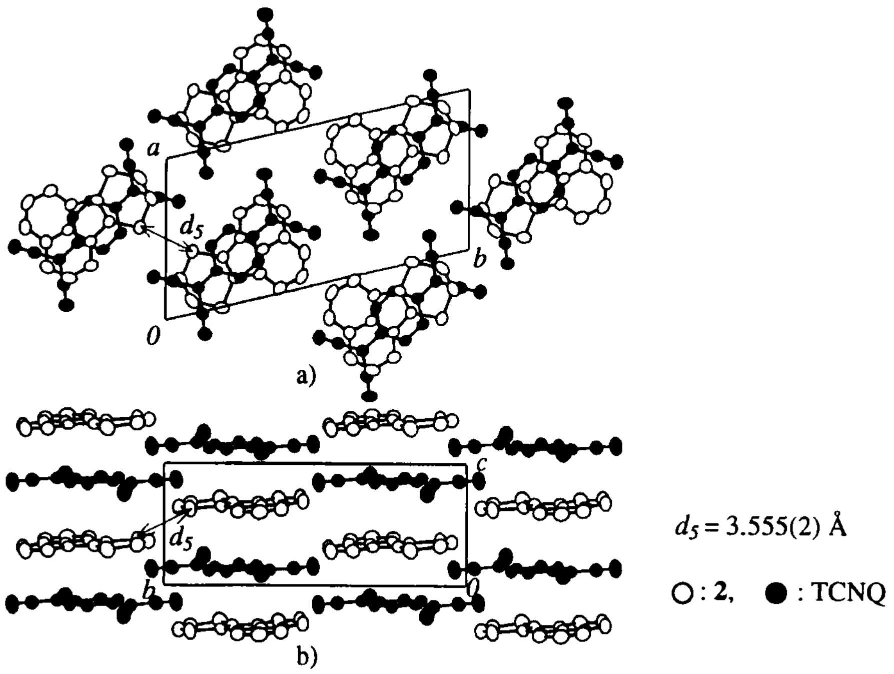

FIGURE 4 Crystal structure of (**2**)TCNQ viewed along a) the *c* axis and b) the *a* axis. (The hydrogen atoms are omitted.)

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The selected bond lengths of 7,10-dithiafluoroanthene skeletons for neutral **2**, (**2**)$_2$PF$_6$, (**2**)BF$_4$, and (**2**)TCNQ are summarized in TABLE IV. On going from the neutral to the oxidized state, it is expected that the bond lengths *b*, *b'* and *c*, *c'* shorten and the bond lengths*a* and *d* lengthen, simply considering the node in HOMO of **2** shown in FIGURE 5. In the (**2**)TCNQ salt, the averaged bond lengths of *b* and *b'* of **2** are shorter, and *a* and *d* are longer than the neutral **2**, but *c* and *c'* are almost the same lengths. (**2**)TCNQ could have some degree of charge transfer, judging from the change of bond lengths between neutral and cation radical state. Furthermore, the degree of CT for (**2**)TCNQ was estimated to be ca. 0.2 by using the nitrile stretching frequency (ν = 2216 cm^{-1}) according to the IR method.[8]

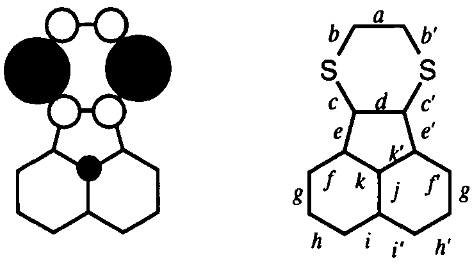

FIGURE 5 Numbering scheme for bond lengths and highest occupied molecular orbital (HOMO) of **2**

TABLE II Bond lengths and of **2**, (**2**)$_2$PF$_6$, (**2**)BF$_4$, and (**2**)TCNQ

Bond length / Å		Neutral	(**2**)$_2$PF$_6$	(**2**)BF$_4$	(**2**)TCNQ
c	S(1)-C(11)	1.753(3)	1.725(3)	1.69(2)	1.748(3)
b	S(1)-C(13)	1.754(4)	1.733(4)	1.70(2)	1.736(4)
c'	S(2)-C(12)	1.741(3)	1.720(3)	1.72(2)	1.748(3)
b'	S(2)-C(14)	1.759(4)	1.733(5)	1.70(2)	1.733(4)
f	C(1)-C(2)	1.357(4)	1.374(4)	1.38(2)	1.368(5)
k	C(1)-C(10)	1.409(4)	1.404(4)	1.40(2)	1.411(5)
e	C(1)-C(11)	1.465(4)	1.459(4)	1.46(2)	1.468(2)
g	C(2)-C(3)	1.416(5)	1.407(4)	1.46(2)	1.416(5)
h	C(3)-C(4)	1.364(5)	1.358(5)	1.37(2)	1.374(6)
i	C(4)-C(5)	1.416(5)	1.404(5)	1.42(2)	1.421(5)
i'	C(5)-C(6)	1.420(5)	1.406(5)	1.42(2)	1.413(5)
j	C(5)-C(10)	1.391(4)	1.397(4)	1.42(2)	1.385(5)
h'	C(6)-C(7)	1.352(5)	1.367(6)	1.38(3)	1.363(5)
g'	C(7)-C(8)	1.414(5)	1.414(6)	1.37(2)	1.411(5)
f'	C(8)-C(9)	1.370(4)	1.383(4)	1.34(2)	1.362(5)
k'	C(9)-C(10)	1.402(4)	1.392(4)	1.39(2)	1.409(4)
e'	C(9)-C(12)	1.476(4)	1.452(4)	1.47(2)	1.468(5)
d	C(11)-C(12)	1.357(4)	1.385(4)	1.35(2)	1.358(5)
a	C(13)-C(14)	1.309(5)	1.318(6)	1.36(2)	1.317(5)

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ELECTRICAL CONDUCTIVITY OF CR AND CT SALTS

Electrical conductivities of the CR and CT salts were measured using compressed pellets by a four probe method (TABLE III). $(\mathbf{2})_2PF_6$ showed relatively high electrical conductivity of $\sigma = 5$ S cm^{-1} at room temperature. The temperature dependence of the single crystal conductivity of $(\mathbf{2})_2PF_6$ was measured along the needle (*a* direction) by a two probe method and exhibited metallic behavior down to 240 K. In contrast, $(\mathbf{2})ClO_4$ and $(\mathbf{2})BF_4$ were almost insulator, which is consistent with the donor / acceptor ratio of 1 : 1 revealed by X-ray structure analysis. The iodine salts showed 10^{-3} to 10^{-4} Scm^{-1}. On the other hand, the TCNQ salt of **2** showed very low conductivity due to the alternative mixed stacking of donor and acceptor in the crystal.

TABLE III Physical properties, elemental analyses, and conductivity of CR and CT salts of **2**

CR or CT salt	D.p. / °C	Found (Calcd.) / %			σ / Scm^{-1}
Appearance		C	H	N	
$(\mathbf{2})_2PF_6$ Black needle	210	53.96 (53.75)	12.5 (2.58)		5.0
$(\mathbf{2})ClO_4$ Black Plate	163	49.67 (49.49)	2.37 (2.37)		$<10^{-8}$
$(\mathbf{2})BF_4$ Black plate	230	51.38 (51.40)	2.49 (2.46)		$<10^{-8}$
$(\mathbf{2})I_{4.6}$ (from CH_2Cl_2) Black powder	115	20.61	0.93		4.1×10^{-3}
$(\mathbf{2})I_{3.5}$ (from CH_3CN) Black powder	120	24.63	1.12		3.1×10^{-4}
$(\mathbf{2})TCNQ$ Dark brown plate	223	70.0 (70.25)	22.72 (2.72)	12.66 (12.60)	$<10^{-8}$

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4. General procedure for preparation of the cation radical salts is as follows: A solution of **2** (0.2 mmol) in dichloromethane (30 ml) containing tetra(*n*-butyl)ammonium hexafluorophosphate (1.2 mmol), tetra(*n*-butyl)ammonium perchlorate (1.2 mmol), or tetra(*n*-butyl)ammonium tetrafluoroborate (1.2 mmol) was cooled to –30 °C and electrolyzed using a divided electrolytic cell between platinum electrodes by constant low current density (2 μA cm^{-2}). Black long needles grew on the anode.
5. The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with Cu Kα radiation monochromatized by graphite (λ(Cu Kα) = 1.54178 Å, 2θ-ω scans, $2\theta_{max}$ = 123°). The crystal structure was solved by direct method and refined by full-matrix least-squares method. The atomic deviations of 8- and 9-carbon atom of **3** in neutral state are 0.7950 and 0.7978 Å from the molecular plane, respectively. The dihedral angle between acenaphthylene and vinylenedithio plane is 36.51°.
6. The X-ray diffraction data were collected with Mo Kα radiation monochromatized by graphite (λ(Mo Kα) = 0.71069 Å, 2θ-ω scans, $2\theta_{max}$ = 55°), and the solution and refinement of the crystal structure were achieved by the same procedure as above.[4]
7. (**2**)I_x: These salts described in this report were prepared by mixing the two hot saturated solutions of **2** (12mg, 0.05mmol) and I_2 (25.4mg, 0.2mmol) in acetonitrile or dichloromethane. The black salts precipitated out on cooling, which were collected by filtration and washed with the same solvent, respectively.
   (**2**)TCNQ: To a solution of **2** (48mg, 0.2mmol) in hot acetonitrile (10 ml) was added a solution of 7,7,8,8-tetracyanoquinodimethane (TCNQ) (41mg, 0.2mmol) in hot acetonitrile. The resulting precipitates were collected by filtration and washed with acetonitrile to give dark brown plates.
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