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7,10-DITHIAFLUOROANTHENE AND ITS CATION RADICAL SALT

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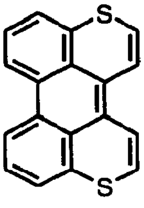
Abstract: The first 7,10-Dithiafluoroanthene has been prepared from acenaphthenone in three steps, via ring expansion reaction of acenaphthenone ethylenedithioacetal. It was shown to be good π-donor and form highly conducting cation radical salts with PF_6^-. X-ray crystallographic analysis of the salt showed columnar stack structure of donors and the salt showed high electrical conductivity at room temperature.

Simple arenes such as naphthalene, fluoroanthene, perylene, and pyrene give electrically conducting cation radical salts $[Aryl_2]^{+\cdot}X^-$ by anodic oxidation.[1] Replacement of the sp^2 carbon atoms in these arenes by sulfur atom brings about remarkable improvement in electrical properties of their charge transfer (CT) complexes and cation radical (CR) salts. For example, the CT complexes of 3,10-dithiaperylene (**1**) and 1,6-dithiapyrene (**2**) show very high conductivity.[2] Therefore, thiafluoroanthene is also a good candidate as a new effective π-donor. Here we report on the synthesis and physical properties of the first example of 7,10-dithiafluoroanthene (**3**) as well as its highly conductive CR salt.



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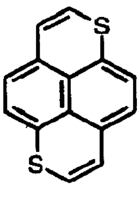

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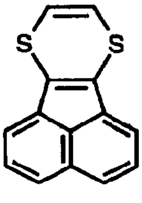
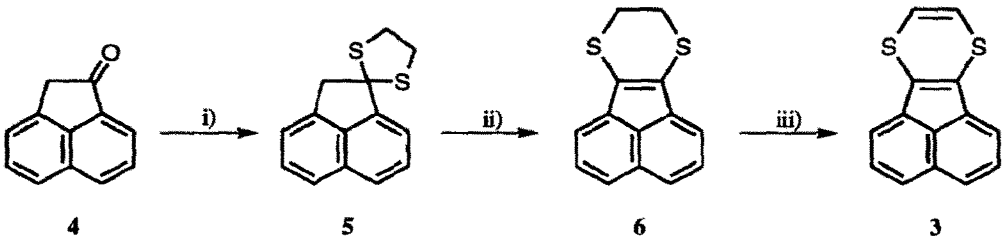


3

The synthetic approach to **3** is summarized in Scheme 1. Compound **3** was synthesized from acenaphthenone (**4**) as a starting material in three steps. 1,2-Ethylenedithioacenaphthylene (**6**) was prepared by the ring expansion reaction of acenaphthenone ethylenedithioacetal (**5**), which was easily available by dithioacetalization of **4**,[3] on treatment with tellurium tetrachloride in dichloromethane.[4] The subsequent dehydrogenation of **6** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave **3** in 56% yield.



Scheme 1. Reagents and conditions: i) $(CH_2SH)_2$, $AlCl_3/CH_2Cl_2$, 82%; ii) $TeCl_4/CH_2Cl_2$, 80%; iii) DDQ/1,4-dioxane, 56%

The cyclic voltammogram of **3** [platinum electrode versus SCE; electrolyte tetra(*n*-butyl)ammonium perchlorate (0.1 M) in acetonitrile, scan rate 50 mV s^{-1}] showed reversible first oxidation potential ($E_{1/2}$ +0.68 V), and irreversible second oxidation potentials ($E_{1/2}$ +1.42 V). The preparation of the CR salt of **3** was carried out by electrocrystallization. When the solution of **3** in dichloromethane was electrooxidized by platinum electrodes in the presence of tetra(*n*-butyl)ammonium hexafluorophosphate as supporting electrolyte, black long needles grew on the anode. The composition of the salt was determined to be $(3)_2PF_6$ by elemental analysis.[5] The salt was stable for more than several weeks at room temperature.

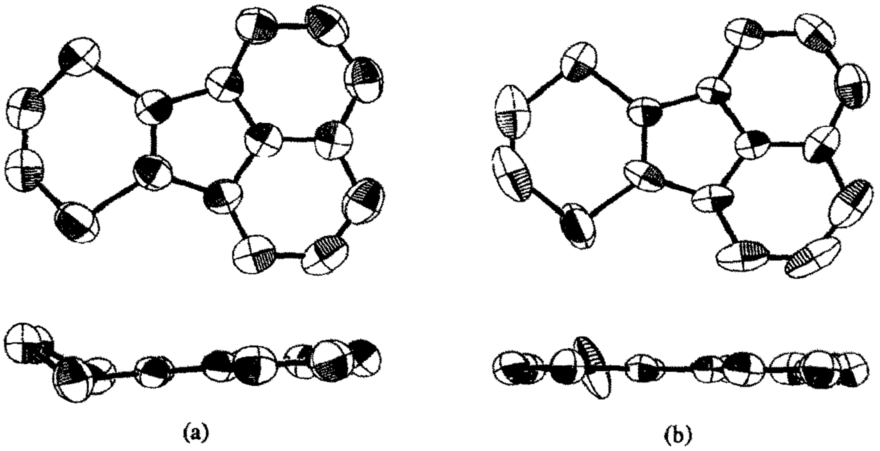


Fig. 1. Molecular structures of **3** (a) in neutral state and (b) in the PF_6 salt. (The hydrogen atoms are omitted.)

The crystal structure of $(3)_2PF_6$ was determined by means of X-ray diffraction at room temperature; $C_{28}H_{16}S_4PF_6$ = 625.64, monoclinic, *C2/c*, $a = 6.953(3)$, $b = 29.959(7)$, $c = 12.619(3)$ Å, $\beta = 104.99(2)°$, $V = 2539(2)$ Å^3, $D_{calc} = 1.636$ g cm^{-3}, $Z = 4$, reflection/variable = 7.22, and $R = 0.047$.[6] The only one **3** is crystallographically independent and the PF_6^- anion is on twofold rotation axis. The donor skeleton in the salt is planar and is different from the neutral one (Fig. 1).[7] The fluorine atoms of anions are disordered. The molecular packing is shown in Fig. 2. 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 radii (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 would show quasi two dimensional conductive nature parallel to the *ac* plane.

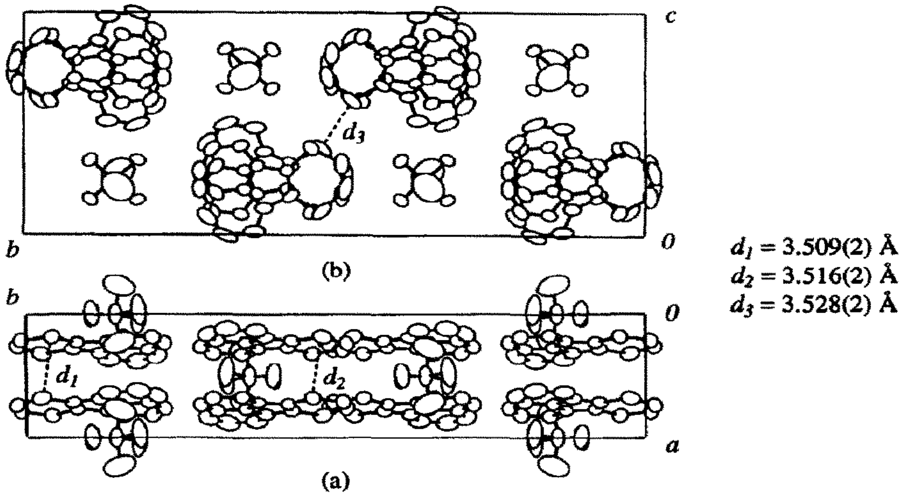


Fig. 2. Crystal structure of $(3)_2PF_6$ viewed along (a) the *a* axis and (b) the *c* axis. (The hydrogen atoms are omitted.)

Electrical conductivity of the salt was measured by compressed pellets by a four probe method. $(3)_2PF_6$ showed relatively high electrical conductivity of σ = 5 S cm^{-1} at room temperature. The temperature dependence of the single crystal conductivity of $(3)_2PF_6$ was measured along the needle (*a* direction) by a two probe method and exhibited metallic behavior down to 240 K (Fig. 3).

Additional chemical modifications of this new donor and formation of charge transfer complex with another acceptors are now in progress.

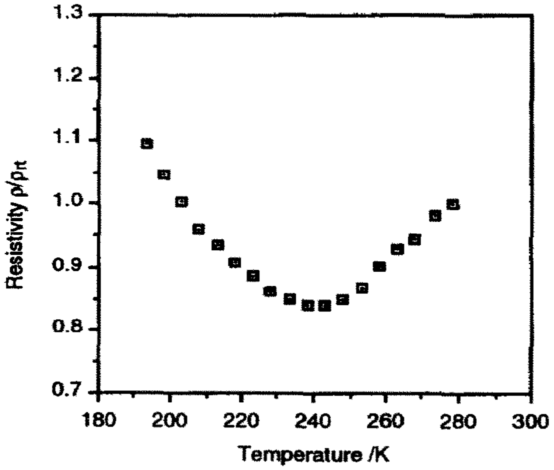


Fig. 3. Temperature dependence of the resistivity of $(3)_2PF_6$ (Measured on a single crystal by a two-probe method.)

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References and Notes

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5. A solution of **3** (0.2 mmol) in dichloromethane (30 ml) containing tetra(*n*-butyl)ammonium hexafluorophosphate (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. Elemental analysis of $(\mathbf{3})_2PF_6$. Found: C, 53.96; H, 2.52%. Calcd for $C_{28}H_{16}S_4PF_6$: C, 53.75; H, 2.58%.
6. The X-ray diffraction data were collected by using a Rigaku automated four-circle diffractometer with Mo Kα radiation monochromatized by graphite (λ(Mo Kα) = 0.71069 Å, 2θ-ω scans, $2\theta_{max}$ = 55°). The crystal structure was solved by direct method and refined by full-matrix least-squares method. The final atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre.
7. The X-ray diffraction data were collected with Cu Kα radiation monochromatized by graphite (λ(Cu Kα) = 1.54178 Å, 2θ-ω scans, $2\theta_{max}$ = 123°), and the solution and refinement of the crystal structure were achieved by the same procedure as above.[6] 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°. Crystal data of **3**: $C_{14}H_8S_2$ = 240.34, monoclinic, $P2_1/c$, a = 9.408(2), b = 11.129(2), c = 10.822(2) Å, β = 98.58(1)°, V = 1120.5(4) Å^3, D_{calc} = 1.425 g cm^{-3}, Z = 4, reflection/variable = 8.78, and R = 0.038.
8. Physical properties of new compounds are as follows:
   3: 56%; mp 92-94 °C (from hexane-dichloromethane); ^{1}H NMR (CDCl$_3$) δ = 6.26 (2H, s), 7.44 (2H, dd, J = 2.7 and 6.1 Hz), 7.47 (2H, dd, J = 2.7 and 6.1 Hz), 7.71 (2H, dd, J = 2.1 and 6.1 Hz); ^{13}C NMR (CDCl$_3$) δ = 119.61, 120.50, 127.44, 127.56, 127.65, 129.46, 136.21; IR (KBr) 3032, 1476, 1428, 1134, 818, 768, 650, 566 cm^{-1}. MS (20 eV) m/z (rel intensity) 240 (M$^+$, 100), 208 (20), 164 (23); HRMS (70 eV) Found: 240.0063. Calcd for $C_{14}H_8S_2$: 240.0067. Found: C, 69.43; H, 3.41%. Calcd for $C_{14}H_8S_2$: C, 69.97; H, 3.35%.
   5: 82%; mp 57-58 °C (from hexane-dichloromethane); ^{1}H NMR (CDCl$_3$) δ = 3.55 (4H, d, J = 1.2 Hz), 4.13 (2H, s), 7.1-7.8 (6H, m); ^{13}C NMR (CDCl$_3$) δ = 41.50, 55.43, 69.64, 119.25, 120.25, 122.78, 124.53, 128.03, 128.30, 130.68, 136.12, 140.27,146.76; IR (KBr) 3040, 2904, 1364, 1278, 1210, 1102, 970, 958, 884, 850, 824, 752, 564 cm^{-1}; MS (20 eV) m/z (rel intensity) 244 (M$^+$, 65), 216 (100), 184 (99), 152 (65); HRMS (70 eV) Found: 244.0343. Calcd for $C_{14}H_{12}S_2$: 244.0380. Found: C, 68.84; H, 5.01%. Calcd for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95%.
   6: 80%; mp 135-137 °C (from hexane-dichloromethane); ^{1}H NMR (CDCl$_3$) δ = 3.41 (4H, s), 7.41 (2H, dd, J = 1.5 and 7.0 Hz), 7.45 (2H, t, J = 7.0 Hz), 7.65 (2H, dd, J = 1.5 and 7.0 Hz); ^{13}C NMR (CDCl$_3$) δ = 26.71, 118.80, 123.75, 126.15, 127.35, 127.49, 138.89; IR (KBr) 1470, 1460, 1430, 1410, 1285, 1245, 1185, 1140, 817, 736 cm^{-1}; MS (20 eV) m/z (rel intensity) 242 (M$^+$, 97), 214 (100), 170 (42), 126 (11); HRMS (70 eV) Found: 242.0233. Calcd for $C_{14}H_{10}S_2$: 242.0224. Found: C, 69.03; H, 4.21%. Calcd for $C_{14}H_{10}S_2$: C, 69.38; H, 4.16%.

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