Unusual cation radical salts of non-planar bis(1,3-dithiole) donors incorporating solvent molecules

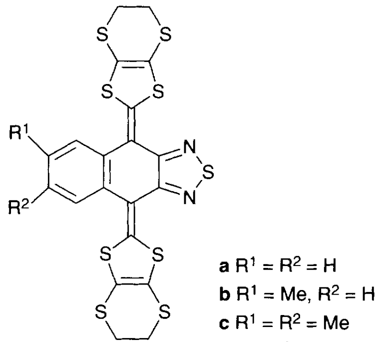
Yoshiro Yamashita,* Masaaki Tomura and Kenichi Imaeda

Institute for Molecular Science, Okazaki 444, Japan

Novel non-planar bis(1,3-dithiole) donors showing one-stage two-electron oxidation afford unusual cation radical salts as single crystals, whose properties are strikingly affected by the incorporated solvent molecules.

Organic conductors are usually obtained from planar molecules showing multi-stage redox properties.[1] Planar structures are considered to be necessary for good π-overlapping for stacking. Although non-planar molecules are unfavourable on this point, it seems possible to use them to increase dimensionality *via* multi-dimensional interactions in the crystals. In addition, they may be able to include small molecules in their crystal lattice.[2] For the non-planar molecules, ion radical states are in general unstable due to the limited conjugation, and two-electron oxidation or reduction is often observed.[3] In that case, on-site Coulomb repulsion is considered to be small in the dication or dianion state. Therefore, non-planar molecules are attractive potential sources of unusual organic conductors. We recently prepared the non-planar bis(1,3-dithiole) donor **1d** which gave metallic cation radical salts.[4] In an extension of that work, we have now found that donors **1a–c** showing two- electron oxidation at one stage afforded cation radical salts incorporating solvent molecules. We report here their unusual properties involving the striking effects of the incorporated molecules.

Similarly to **1a**,[5] new donors **1b,c** were prepared by a Wittig–Horner reaction of carbanion **2**[6] with diones **3**, which were obtained using the Diels–Alder reaction of dione **4**[7] with the corresponding buta-1,3-dienes. The oxidation potentials, measured by cyclic voltammetry, are shown in Table 1. The values are higher than that of tetrathiafulvalene (TTF), indicating that **1** are weaker donors than TTF. This is attributed to the electron-withdrawing nature of the fused thiadiazole ring. Another characteristic point is that donors **1a–c** showed one reversible redox peak, in contrast to **1d**.[4a] The peak widths are larger than that for ideal two-electron transfer (28.25 mV), indicating that two one-electron transfer processes overlap. The differences between the first and second oxidation potentials ($E_1 - E_2$) were estimated from the peak widths according to the Myers and Shain's method.[8] The semiquinone formation constants K_{sem} calculated using these values are much smaller than that of TTF as shown in Table 1. This fact indicates that the cation radical states in **1a–c** are thermodynamically unstable. However, their cation radical salts were isolated as single crystals when they were electrochemically oxidized in the presence of Bu_4NPF_6 in tetrahydrofuran (THF). The composition of the salts of **1b** and **1c** determined by elemental analysis, was 2 : 1 : 1 (donor : PF_6 : THF), while **1a** gave a salt with a ratio of 1 : 1 : 1 (donor : PF_6 : THF). These salts were stable on standing in air at room temperature for several months and no loss of THF molecules was observed. Their conductivity data are shown in Table 2. The 2 : 1 : 1 salts showed high conductivities. In particular, the salt of the dimethyl derivative **1c** showed a metallic temperature dependence for its conductivity down to 180 K. The crystal structure of $(\mathbf{1c})_2(PF_6)(THF)$ is shown in Fig. 1.† The donor molecule is butterfly-shaped due to the steric interaction between the perihydrogens of the aromatic ring and the sulfur atoms as found in **1d**. The deformed molecules are uniformly stacked along the *b*-axis. It should be noted here that an intercolumnar S···S contact (3.69 Å), which may increase the dimensionality, was observed in addition to an intracolumnar one (3.70 Å). The calculated overlap integral along the intercolumnar direction is about half that of the stacking direction, suggesting that the salt is two-dimensional in nature. Another characteristic feature is that THF molecules are located in a disordered manner in the cavities produced by donor molecules. The solvent molecules seem to play an important role in constructing the crystal structure. Therefore, we



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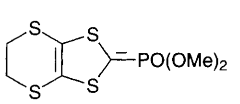

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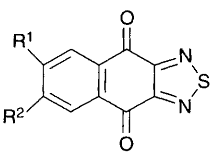

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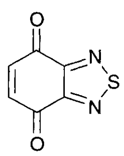

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Table 1 Oxidation potentials[a] of donors **1**

Donor	$E_{1/2}$/V	($E_1 - E_2$)/mV	log K_{sem}[b]
1a	0.73[c]	40	0.68
1b	0.71[c]	60	1.01
1c	0.68[c]	52	0.88
1d	0.76, 0.85	90	1.53
TTF	0.46, 0.87	410	6.95

[a] Bu_4NBF_4 (0.1 mol dm^{-3}) in PhCN, Pt electrode, scan rate 100 mV s^{-1}, V *vs.* saturated calomel electrode (SCE). [b] log $K_{\text{sem}} = (E_1 - E_2)/0.059$. [c] Two-electron oxidation.

Table 2 Conductivities of the PF_6 cation radical salts of **1**

Donor	Solvent	Molar ratio[a]	σ/S cm^{-1} [b]	E_a/eV
1a	THF	1 : 1 : 1	2.5×10^{-2}	0.16
1b	THF	2 : 1 : 1	6	0.03
1c	THF	2 : 1 : 1	10	metal
1c	DHF	2 : 1 : 1	10	0.19
1c	DO	2 : 1 : 1	10	0.03

[a] Donor : PF_6 : solvent. [b] Measured by a four-probe technique on single crystals at room temperature.

attempted to replace them with other molecules to investigate their effects. When electrolytic oxidation of **1c** was carried out in various solvents, 2,5-dihydrofuran (DHF)- and 1,3-dioxolane (DO)-included salts with the composition of 2 : 1 : 1 (**1c** : PF_6 : solvent) were obtained as single crystals. Their conductivities at room temperature were the same as that of the THF included salt as shown in Table 2. However, they showed semiconducting behaviour where the activation energy (E_a) of $(\mathbf{1c})_2(PF_6)(DO)$ was much smaller than that of $(\mathbf{1c})_2(PF_6)(DHF)$. This result indicates that the physical properties are strongly dependent on the included solvent molecules. In order to examine the difference in structures, the X-ray analyses of the DO- and DHF- incorporated salts were carried out. The crystal data indicate that the cell parameters are very similar to each other.† In the crystal structures, no distinctive difference except for the different solvent molecules was observed. This is in contrast to the effect of incorporated solvent molecules found in BEDT–TTF conductors, where different structures were observed.[9] It is interesting that a small structural change results in a large difference in the physical properties. The stability of the metallic state decreases in the included solvent order: THF < DO < DHF. This solvent effect may be related to the ordering of the solvent molecules, because the ease of the ordering increases in the order: THF < DO < DHF. Further studies are in progress to clarify this point.

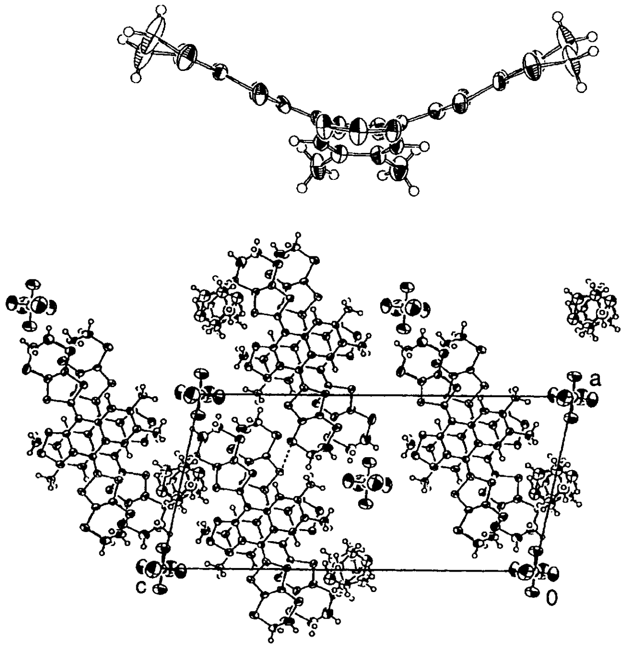

Fig. 1 X-Ray molecular and crystal structure of $(\mathbf{1c})_2(PF_6)(THF)$ [broken line S···S interaction 3.689(6) Å]

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Footnote

† No polymorphism of crystals was observed. *Crystal data* for $(\mathbf{1c})_2(PF_6)(THF)$: $C_{48}H_{40}N_4OS_{18}PF_6$, M = 1410.91, monoclinic, space group $P2_1/n$, Z = 2, a = 13.111(3), b = 8.0111(6), c = 27.328(2) Å, β = 102.19(1)°, V = 2805(1) Å^3, D_c = 1.670 g cm^{-3}. The final R value was 0.065 for 2853 reflections with $I > 3\sigma(I)$. For $(\mathbf{1c})_2(PF_6)(DHF)$: $C_{48}H_{38}N_4OS_{18}PF_6$, M = 1408.90, monoclinic, space group $P2_1/n$, Z = 2, a = 13.100(1), b = 8.0096(6), c = 27.227(2) Å, β = 101.804(5)°, V = 2796.4(3) Å^3, D_c = 1.673 g cm^{-3}. The final R value was 0.046 for 3944 reflections with $I > 3\sigma(I)$. For $(\mathbf{1c})_2(PF_6)(DO)$: $C_{47}H_{38}N_4O_2S_{18}PF_6$, M = 1412.89, monoclinic, space group $P2_1/n$, Z = 2, a = 13.1049(8), b = 8.0139(5), c = 27.162(1) Å, β = 101.614(4)°, V = 2794.2(3) Å^3, D_c = 1.679 g cm^{-3}. The final R value was 0.055 for 4243 reflections with $I > 3\sigma(I)$. The non-hydrogen atoms except those in the solvent molecules were refined anisotropically. The disordered solvent molecules were treated as rigid groups of 0.5 occupancy with restraints and refined isotropically. Hydrogen atoms were included at calculated positions but not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and reference number 182/178.

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