Effects of Molecular Association in the Radical-Cations of 1,8-Bis(ethylenedithiotetrathiafulvalenyl)naphthalene[1]

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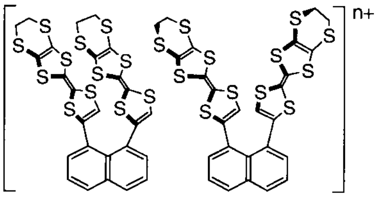
The π–π interaction of the tetrathiafulvalenyl groups in 1,8-bis(ethylenedithiotetrathiafulvalenyl)naphthalene was investigated. The novel electronic properties of neutral and cationic tetrathiafulvalenes have been revealed on the basis of the X-ray analysis, spectral analyses, and DFT calculations.

Tetrathiafulvalene (TTF) has attracted much interest because of the electron-donating ability that has been used for the synthesis of new organic metals and superconductors.[2,3] In particular, the most remarkable property of TTF and its derivatives is the great facility for molecular association both in the neutral state and in the radical-cation state, and the one-dimensional column of the radical-cations forms a conduction path in the organic metals.[4,5]

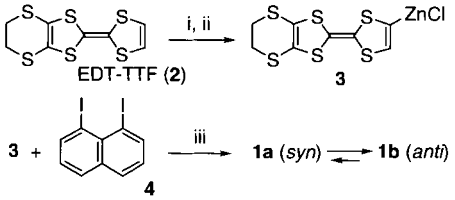
1,8-Diarylnaphthalenes have been investigated extensively,[6,7] because of the interaction of the close face-to-face arranged aromatic rings which rotate at ambient temperature. On the basis of these results, 1,8-bis(tetrathiafulvalenyl)naphthalenes[8] seem to be a good model system to investigate the interaction and self-assembly of TTF and its radical-cation as shown in Figure 1. We report here the molecular association of the radical-cation species $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$ derived from 1,8-bis(ethylenedithiotetrathiafulvalenyl)naphthalene **1**.



$\mathbf{1a}^{n+}$ (syn) $\mathbf{1b}^{n+}$ (anti)

Figure 1. 1,8-Bis(ethylenedithiotetrathiafulvalenyl)naphthalene **1**

The synthesis of **1** was carried out using the palladium-catalyzed cross-coupling reaction of an organozinc species with 1,8-diiodonaphthalene **4** as shown in Scheme 1. Thus, the reaction of EDT-TTF (2.8 equiv) with Bu^{n}Li (2.9 equiv), followed by treatment with $ZnCl_2$ (3.3 equiv) formed the zinc species **3**. The reaction of **3** thus prepared with **4** (1 equiv) in THF at –20 °C for 1 h and then at 45 °C for 12 h produced the coupling product **1** in 77% yield.[9] The cyclic voltammetric analysis indicates that **1** has three reversible redox waves at 0.28, 0.41, and 0.90 V vs SCE (0.1 M Bu$^n_4$NClO$_4$, PhCN). The first two waves correspond to two one-electron processes, whereas the third wave is a two-electron process. Since EDT-TTF shows oxidation potentials at 0.45 and 0.74 V under similar conditions, the first and second oxidation potentials of **1** for the formation of $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$ were lower than the first potential of EDT-TTF **2**. However, the third potential of **1** corresponding to the formation of the tetracation $\mathbf{1}^{4+}$ is much higher than the second potential of **2**, presumably due to the effect of the face-to-face interaction.



Scheme 1. Synthesis of **1**. Reagents and conditions: i) Bu^{n}Li (1.04 equiv), THF, –78 °C, 1 h; ii) $ZnCl_2$ (1.18 equiv), –65 °C, 1.5 h; iii) $Pd(PPh_3)_4$ (8 mol% to **3**), rt–45 °C, 12 h.

Recrystallization of **1** from CH_2Cl_2–$(CH_3)_2CHOCH(CH_3)_2$ gave single crystals, and the X-ray crystallographic analysis revealed the molecular structure of **1** (Figure 2). The molecule has a crystallographic C_2 symmetry with a 2-fold axis passing through the C(1)–C(2) bond to form an *anti*-conformation **1b**. The structure of **1b** is essentially similar to that of 1,8-diphenylnaphthalene, and the molecular strain is released by the deformation of the naphthalene ring and by the *anti*-conformation of TTF rings.[10] The dihedral angle between the naphthalene and TTF rings is 54.6(3)°. Interestingly, the intramolecular distances C(6)···C(6*) and C(7)···C(7*) are 2.50 and 2.76 Å, respectively. Thus, these intramolecular distances are 3% and 8–9% shorter than those of 1,8-diarylnaphthalene.[7]

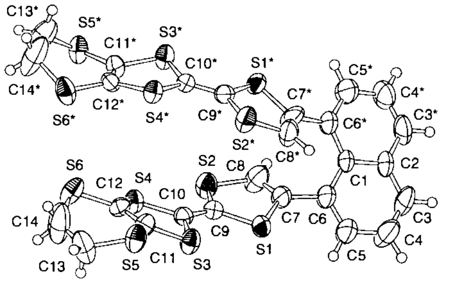


Figure 2. ORTEP diagram of **1b**.

Compound **1** showed temperature-dependent NMR spectra due to the interconversion between the two isomers **1a** and **1b**. The ^{1}H NMR spectrum at 25 °C gave averaged signals because of the fast isomer interconversion, which decoalesced at ca. –75 °C, and two sets of signals were observed below –80 °C reflecting the presence of two isomers in a ratio of 93:7. Taking into account the results of the X-ray analysis of **1**, the *anti*-form **1b** was assigned to the major isomer and the *syn* **1a** to the minor. The isomer ratio corresponds to the free energy difference of 0.94 kcal/mol between **1a** and **1b** at –90 °C. The B3LYP/3-21G* calculations[11] show that the energy difference between **1a** and **1b** is 3.44 kcal/mol, which is in agreement with the experimental value. Lineshape analysis revealed that the activation free-energy ($\Delta G^{\ddagger}$) from **1b** to **1a** is 11.0 kcal/mol at –75 °C.

Although the solid-state properties of the radical-cation TTF$^{\bullet+}$ have been widely studied upto now, the spectroscopic behavior of TTF$^{\bullet+}$ and its derivatives in solution seems to remain equivocal due to the equilibrium between the monomer and the dimer. Since **1**, **1**$^{\bullet+}$, and **1**$^{2+}$ impart information on the dimeric state of TTFs, reflecting their structures, the chemical oxidation of **1** was investigated using $Fe(ClO_4)_3$. Thus, **1** was oxidized with 1–7.5 equiv of $Fe(ClO_4)_3$ in CH_2Cl_2/CH_3CN (1:1). The concentrations of **1** used for the measurements were very low, and hence a further aggregation of **1**$^{\bullet+}$ or **1**$^{2+}$ can be ruled out. The oxidation of **1** with 1.2 equiv of $Fe(ClO_4)_3$ gave **1**$^{\bullet+}$, and the electronic spectrum reveals three absorption maximums at 312 (log ε = 4.42), 816 (3.87), and 1800 nm (ca. 3.5). The very broad absorption at around 1800 nm is assigned to the mixed-valence absorption of **1**$^{\bullet+}$ between the neutral and radical-cation moieties. The absorption at 1800 nm disappeared when **1** was oxidized with 2.4 equiv of $Fe(ClO_4)_3$, and new absorption maxima of **1**$^{2+}$ were observed at 296 (4.36), 402 (4.39), 732 (4.26), and 858 nm (4.12). The face-to-face interaction between the two TTF$^{\bullet+}$ was observed as a separation of the longest absorption of TTF$^{\bullet+}$. Thus, the absorption at 732 nm can be assigned to that of the π-dimer with Davydov blue shift, and that of 858 nm is a charge-transfer absorption.[5a,12] Although the oxidation of **1** with 4–5 equiv of $Fe(ClO_4)_3$ revealed no clear change, **1**$^{4+}$, which may adopt an *anti*-form **1b**$^{4+}$, was formed when oxidized with excess amounts (7.5 equiv) of $Fe(ClO_4)_3$. The tetracation **1**$^{4+}$ showed the maximum at 652 nm (4.47), which is similar to the dicationic absorption of other TTF derivatives.[13]

In order to determine the structure of **1**$^{\bullet+}$, electrochemical oxidation was attempted to prepare single crystals of **1**$^{\bullet+}$. Thus, the cationic species was prepared in chlorobenzene in the presence of $Bu^n{}_4NI_3$ by controlled electrolysis at a constant potential and was characterized by X-ray analysis.[14] The crystal lattice contains the two different types of radical-cations, together with I_3^- anion, I_2, I^-, and chlorobenzene (Figure 3). Taking into account that the ratio of the molecules of **1** and the anionic charges based on I_3^- and I^- is 4:3, the radical cation possesses the average +0.75 charges per one molecule of **1**. The two types of radical-cations $(\mathbf{1}_2)^{1.5(\bullet+)}$ adopt a *syn*-conformation, reflecting the stability of the face-to-face stacking structure. Interestingly, these dimeric TTFs are aligned in an edge-to-face mode to form a two-dimensional sheet structure. The dihedral angles between the naphthalene and TTF rings are 52–56°. Although one TTF ring adopts a planar structure with the maximun derivations of 0.1 Å from the least squares plane, the other three TTF rings have bent 1,3-dithiole rings. In spite of only one short S···I contact (3.53 Å), there are a number of intermolecular S···S short contacts, and these S···S contacts result in the formation of a unique sheet structure. The room temperature conductivity of the radical salt $(\mathbf{1})_2{\cdot}C_6H_5Cl{\cdot}I_{3.5}$ was found to be 5.0×10^{-5} S cm^{-1}, in spite of its κ-like structure.

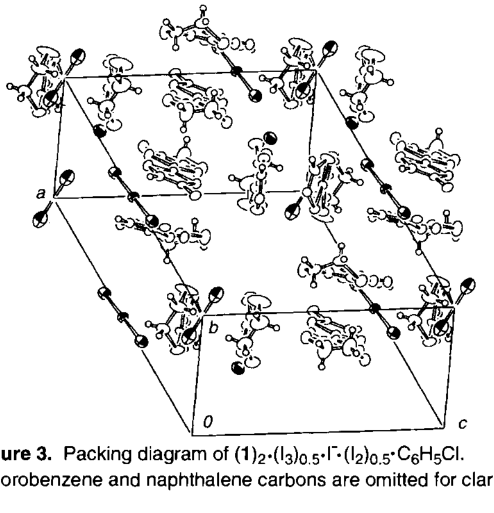


Figure 3. Packing diagram of $(\mathbf{1})_2{\cdot}(I_3)_{0.5}{\cdot}I^-{\cdot}(I_2)_{0.5}{\cdot}C_6H_5Cl$. Chlorobenzene and naphthalene carbons are omitted for clarity.

On the basis of the B3LYP/3-21G* calculations of **1**$^{\bullet+}$ and **1**$^{2+}$, the *syn*-forms **1a**$^{\bullet+}$ and **1a**$^{2+}$ are the more favorable conformation as compared to the *anti*-forms **1b**$^{\bullet+}$ and **1b**$^{2+}$. The energy differences between *syn*- and *anti*-forms in **1**$^{\bullet+}$ and **1**$^{2+}$ are 0.22 and 1.10 kcal/mol, respectively. Therefore, the preferential structures in the ground state are **1a**$^{\bullet+}$ and **1a**$^{2+}$ for the radical-cation and bis(radical-cation) species. The electronic spectra of **1**$^{\bullet+}$ and **1**$^{2+}$ reflect the strong interactions of the mixed valence state in **1a**$^{\bullet+}$ and of the π-dimer in **1a**$^{2+}$. Our results reported here have disclosed novel electronic properties of the mixed-valence dimer $(TTF)_2^{\bullet+}$ and the π-dimer $(TTF)_2^{2+}$ in the solid state and in solution.

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References and Notes

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1 This paper is dedicated to Emeritus Professor Masazumi Nakagawa on the occasion of his 85th birthday.

2 a) F. Wudl, G. M. Smith, and E. J. Hufnagel, *J. Chem. Soc., Chem. Commun.*, **1970**, 1453. b) F. Wudl, D. Wobshall, and E. J. Hufnagel, *J. Am. Chem. Soc.*, **94**, 670 (1972). c) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Rerlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).

3 For a general review, see: J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. H. Whangbo, “Organic Superconductors (Including Fullerenes),” Prentice Hall: Engelwoods Cliffs (1992).

4 a) L. L. Miller and K. R. Mann, *Acc. Chem. Res.* **29**, 417 (1996). b) T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann, and F. Wudl, *J. Am. Chem. Soc.*, **111**, 3108 (1989). c) A. M. Kini, B. D. Gates, M. A. Beno, and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, **1989**, 169. d) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 301 (1986).

5 a) J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, *Phys. Rev. B.*, **19**, 730 (1979). b) L. Huchet, S. Akoudad, E. Levillain, J. Roncali, A. Emge, and P. Bäuerle, *J. Phys. Chem. B*, **102**, 7776 (1998). c) H. Spanggaard, J. Prehn, M. B. Nielsen, E. Levillain, M. Allain, and J. Becher, *J. Am. Chem. Soc.*, **122**, 9486 (2000).

6 For a review, see, P. König, *Topics in Current Chem.*, **196**, 91 (1998).

7 For recent examples, see: a) M. Iyoda, T. Kondo, K. Nakao, K. Hara, Y. Kuwatani, M. Yoshida, and H. Matsuyama, *Org. Lett.*, **2**, 2081 (2000). b) Y. Nakamura, M. Matsumoto, Y. Hayashida, and J. Nishimura, *Tetrahedron Lett.*, **38**, 1983 (1997).

8 U. Kux and M. Iyoda, *Chem. Lett.*, **1994**, 2327. 1,8-Bis(tetrathiafulvalenyl)naphthalene is rather unstable in solution, presumably due to its high donor ability.

9 **1**: red cryst.; FAB-MS: *m/z* 712 (M$^+$); ^{1}H NMR ($CDCl_3/CS_2$ 1:1) δ 3.29 (s, 8H), 6.03 (s, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.85 (dd, *J* = 7.5, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 30.5, 105.4, 114.2, 114.8, 118.4, 125.4, 129.5, 130.4, 131.0, 133.2, 135.2; UV-vis λ_{max} (CH_2Cl_2–CH_3CN 1:1, log ε) 312 (4.53), 336sh (4.40) nm, the absorption tails up to 550 nm.

10 Crystal data for **1**: $C_{26}H_{16}S_{12}$, M_W = 713.13, space group *C2/c* (# 15), a = 17.712(7), b = 16.313(3), c = 11.963(3) Å, β = 121.78(2)°, V = 2938 (1) Å^3, Z = 4, D_C = 1.612 g cm^{-3}, R_1 = 0.048, R_W = 0.068, GOF = 1.25.

11 All calculations were carried out using the Gaussian 98 program.

12 M. Iyoda, K. Hara, Y. Kuwatani, and S. Nagase, *Org. Lett.*, **2**, 2217 (2000).

13 G. Schukat and E. Fanghänel, *J. prakt. Chem.*, **327**, 767 (1985).

14 Crystal data for **1**$^{\bullet+}$: $(C_{26}H_{16}S_{12})_2{\cdot}C_6H_5Cl{\cdot}I_{3.5}$, M_W = 1982.99, space group $P\bar{1}$ (# 2), a = 15.5971(7), b = 17.858(1), c = 14.3447(7) Å, α = 95.272(1)°, β = 116.992(2)°, γ = 75.435(1)°, V = 3444.7(3) Å^3, Z = 2, D_C = 1.912 g cm^{-3}, R_1 = 0.065, R_W = 0.188, GOF = 1.04.