

Tetrahedron Letters 40 (1999) 2807-2810

TETRAHEDRON LETTERS

1,1-Bis(tetrathiafulvalenyl)ethylene. A Unique Cross-Conjugated Dimeric Tetrathiafulvalene

Masahiko Iyoda,^{a*} Shigeru Sasaki,^a Mami Miura,^a Mitsuhiro Fukuda,^a and Jun Yamauchi^b

^aDepartment of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan ^bGraduate School of Human and Environmental Studies, Kyoto University, Yoshida, Kyoto 606-8501, Japan

Received 14 January 1999; revised 1 February 1999; accepted 5 February 1999

Abstract: 1,1-Bis(tetrathiafulvalenyl)ethylenes, synthesized using the palladium-catalyzed cross-coupling of 4trimethylstannyl-TTF with 2,2-disubstituted 1,1-dibromoethylenes, were converted into the corresponding CTcomplexes and cation-radical salts to determine the electric conductivities and magnetic properties. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: coupling reactions; electron donors; physical properties; X-ray crystal structures.

Since the discovery of the properties of tetrathiafulvalene (TTF) in 1970,¹ much effort has been devoted to designing new analogues of this π -donor in order to improve the electroconducting properties of the corresponding salts.² Fukutome reported theoretical calculations³ and predicted that the dication-diradical **2** derived from 1,1-bis(tetrathiafulvalenyl)ethylene **1** shows a high-spin ground state (i.e., a triplet ground state) which possesses somewhat lower energy as compared with a low-spin ground state. This presumption suggests that molecular materials containing both magnetic and electrical behavior may be constructed from TTF derivatives. An attempt along this line has been reported for bis(tetrathia-fulvalenyl)ketone **3** and its derivatives and the results show that the dication-diradical **4** derived from **3** possesses a singlet ground state, presumably due to the fairly stabilized singlet ground state in **4**.⁴ Since the triplet ground state in **2** has been calculated to be more stable than that in **4**, 1,1-bis(tetrathiafulvalenyl)ethylenes **5-9** have been synthesized to examine the spin-spin interaction and conducting properties of CT-complexes and cation-radical salts derived from new donors **5-9**.



The synthesis of 5-9 was carried out using the palladium-catalyzed cross-coupling reaction of 4trimethylstannyl-TTF 11 with 2,2-disubstituted 1,1-dibromoethylenes (Scheme 1).⁵ Thus, the reaction of 11 (2 equiv.) with 1,1-dibromo-2,2-diphenylethylene 12 (1 equiv.) in the presence of Pd(PPh₃)₄ (0.1 equiv.) proceeded smoothly in refluxing benzene for 24 h to produce 5 in 57% yield.⁶ Although the reaction of 11 with 1,1-dibromo-2-methylpropene 13 in the presence of Pd(PPh₃)₄ (0.1 equiv.) produced 6 in a low yield (19%), the yield of 6 was improved to 26% when the reaction was carried out in refluxing toluene. In a similar manner, the palladium-catalyzed reactions of 11 with 14, 15 and 16 in refluxing benzene or toluene afforded the corresponding products 7, 8 and 9 in 52, 41 and 28% yields, respectively.



Because of the low solubility of the aryl-substituted 5 and 7 in common organic solvents such as ether, CH_2Cl_2 , benzene, etc., we converted 5 and 7 into the hexamethylthio derivatives 17 and 18 (Scheme 2). The reactions of 5 and 7 with excess amounts of lithium diisopropylamide (LDA) in THF at -78 °C, followed by treatment with dimethyldisulfide (excess) at -78 °C to room temperature produced the corresponding fully thiomethylated 17 and 18 in 48 and 13% yields, respectively.



Table 1. Cyclic voltammetric data for 5-9 and 17-18.^a

Compound	E ¹ 1/2	E ² 1/2	ΔΕ	Compound	E ¹ 1/2	E ² 1/2	ΔE
TTF	0.36	0.73	0.37	8	0.48	0.82	0.34
5	0.40	0.79	0.39	9	0.39	0.73	0.34
6	0.39	0.72	0.33	17	0.53	0.79	0.26
7	0.45	0.80	0.35	18	0.56	0.77	0.21

^aExperimental conditions: *n*-Bu₄NClO₄ (0.1 mol dm⁻³) in dry benzonitrile at room temperature; Pt working and counter electrodes. Potentials were measured against an Ag/Ag⁺ electrode and converted to the value vs SCE (Fc/Fc⁺ = 0.31 V).

In order to estimate the donor ability and the interactions between two TTF moieties in 5-9 and 17-18, redox potentials of these new donors were measured by cyclic voltammetry. All 1,1-bis(tetrathiafulvalenyl)-ethylenes show the reversible two two-electron redox waves. As shown in Table 1, the potentials of 5, 6, and 9 show similar values for the first and second oxidations as unsubstituted TTF does, whereas the electron-withdrawing cyclopentadienylidene unit in 7 and 8 decreases the donor ability of the TTF moieties.⁷ In the case of 17 and 18, the first and second oxidation potentials are similar to those of tris(methylthio)-TTF.⁸ These results indicate that the redox processes of 5-9 and 17-18 display no separation of each two-electron transfer in their cyclic voltammograms, presumably due to the weak interaction between the two TTF moieties in these molecules. The weak interaction in the neutral state of 5-9 and 17-18 may reflect the twisted structure which has been elucidated by the X-ray analysis of 5 and 17 (Figs. 1 and 2).⁹



Figure 1. ORTEP Drawings of 5. (a) Top View. (b) Side View. Figure 2. ORTEP Drawing of 17.

All 1,1-bis(tetrathiafulvalenyl)ethylenes can be expected to form CT-complexes and cation-radical salts. Therefore, solutions of 5 and 17 in CH₂Cl₂ were mixed with solutions of DDQ and TCNQF₄ in CH₃CN to produce the corresponding CT-complexes 19 and 21, respectively (Scheme 3). Similarly, treatment of 5 and 17 with I₂ yielded the cation radical salts 20 and 22, respectively. Although 19, 20 and 22 were fine crystals or an amorphous solid, the CT-complex 21 gave black single crystals, whose crystal structure was determined by X-ray analysis (Fig. 3). The cation-radical salt 20 and the CT-complex 21 show the electric conductivities of 1 x 10^{-5} and 7.1 x 10^{-6} S cm⁻¹, respectively, whereas 19 and 22 are insulators.



As shown in Fig. 3, the CT-complex 21 consists of 17 and two TCNQF₄ molecules (1:2 complex) together with an equimolar amount of CH₃CN to 17. The two TCNQF₄ molecules adopt an anion-radical form and are stacked face to face. The average exocyclic C-C bond length (1.412 Å) of TCNQF₄ in 21 is closely related to that of the TCNQF₄ anion-radical [1.407(9) Å]¹⁰ but clearly different from that of the neutral TCNQF₄ [1.372(2) Å].¹¹ Similarly, the lengths of the central and peripheral C-C double bonds of the two TTF moieties in 21 are elongated as compared with 17 (Fig. 2), reflecting the cation-radical structure of the TTF cores. Interestingly, the environment around the two TTF⁺⁺ moieties of 17^{2++} is clearly different. One forms a dimeric structure with the TTF⁺⁺ moiety of the neighboring 17^{2++} , and the other does not have significant intermolecular contacts. The unique crystal structure of 21 is related to the magnetic properties. The field dependence of magnetization below 10 K shown in Fig. 4 is in good agreement with the Brillouin function for the one S = 1/2 spin per 17•(TCNQF₄)₂•CH₃CN unit, which can be rationalized by antiferromagnetic cancellation of the three of the four S=1/2 spins in 17•(TCNQF₄)₂•CH₃CN unit, due to the two types of dimeric structures revealed by X-ray crystallography, and the remaining one S = 1/2 spin of TTF⁺⁺. It is worth noting that the paramagnetic radical salt 21 is a semi-conductor.

Although the crystal structure of the cation-radical salt 20 is still unknown, 20 showed interesting magnetic and electrical behavior. Thus, the EPR spectra of the powdered sample of 20 at low temperatures consist of a broad signal at the center and a fine structure (g = 2.0074, D = 108 G at 163 K) along with $\Delta m_s = 2$ signals due

to a triplet species. The distance between the two spins estimated from the D value by the point dipole approximation (6.36 Å) seems to be comparable to the distance between the two TTF units in 20. The structure of 20 is now under investigation.





Figure 4. Field dependence of magnetization of 21 at 3 (O), 5 (\diamond), and 10 (Δ) K. Brillouin function for S = 1/2 is shown as a solid line.

normal demonter Financial summart by a Cront in Aid for Sai

Acknowledgment: Financial support by a Grant-in-Aid for Scientific Research on Priority Areas from Ministry of Education, Science and Culture Japan (06243105) is gratefully acknowledged.

References and Notes

- (a) Wudl, F.; Smith, G. M.; Hufnagel, E. J. J. Chem. Soc., Chem. Commun., 1970, 1453.
 (b) Wudl, F.; Wobshall, D.; Hufnagel, E. J. J. Am. Chem. Soc., 1972, 94, 670.
 (c) Ferraris, J.; Cowan, D. O.; Walatka, Jr., V.; Rerlstein, J. H. J. Am. Chem. Soc., 1973, 95, 948.
- For general reviews, see (a) Sandman, D. J.; Ceasar, G. P. Isr. J. Chem., 1986, 27, 293. (b) Bryce, M. R. Aldchim. Acta 1985, 18, 73. (c) Bryce, M. R.; Murphy, L. C. Nature, 1984, 309, 119. (d) Perlstein, J. H. Angew. Chem., Int. Ed. Engl., 1977, 16, 519.
- 3. Mizouchi, H.; Ikawa, A.; Fukutome, H. Mol. Cryst. Liq. Cryst. 1993, 233, 127; J. Am. Chem. Soc., 1995, 117, 3260.
- Sugimoto, T.; Yamaga, S.; Nakai, M.; Nakatsuji, H.; Yamauchi, J.; Fujita, H.; Fukutome, H.; Ikawa, A.; Mizouchi, H.; Kai, Y. Kanehisa, N. Adv. Mater., 1993, 5, 741.
- (a) Iyoda, M.; Fukuda, M.; Yoshida, M.; Sasaki, S. Chem. Lett., 1994, 2369.
 (b) Iyoda, M.; Kuwatani, Y.; Ueno, N.; Oda, M. J. Chem. Soc., Chem. Commun., 1992, 158.
- All new compounds described in this communication were fully characterized by spectroscopic analyses. Selected data were as follows. 5: dark red needles, mp 213-214 °C (decomp.), FAB-MS (positive, m-nitrobenzyl alcohol) m/z 585 (M+1); ¹H NMR (CDCl₃) δ 7.29-7.28 (m, 6H), 7.21-7.20 (m, 4H), 6.27 (s, 4H), 6.06 (s, 2H); ¹³C NMR (CD₂Cl₂) δ 147.4, 141.2, 135.3, 131.1, 128.2, 121.8, 119.2, 118.8. 6: yellow fine cryst., mp 59-60 °C, FAB-MS (positive, m-nitrobenzyl alcohol) m/z 461 (M+1); ¹H NMR (CDCl₃) δ 6.33 (s, 4H), 6.21 (s, 2H), 1.47 (s, 6H); ¹³C NMR (CD₂Cl₂) δ 143.4, 134.0, 119.6, 119.2, 118.9, 117.3, 110.2, 110.1, 22.7. 17: red cryst., mp 81-82 °C, FAB-MS (positive, m-nitrobenzyl alcohol) m/z 861 (M+1); ¹H NMR (CD₂Cl₂) δ 7.32-7.27 (m, 10H), 2.43 (s, 6H), 2.41 (s, 6H), 2.05 (s, 6H); ¹³C NMR (CDCl₃) δ 153.4, 140.5, 133.2, 129.6, 128.1, 127.6, 127.3, 127.0, 126.0, 111.4, 107.1, 18.9, 18.8, 18.3.
- 7. Cf., Iyoda, M.; Okabe, T.; Kondo, T.; Sasaki, S.; Matsuyama, H.; Kuwatani, Y.; Katada, M. Chem. Lett., 1997, 103.
- 8. Cf., Iyoda, M.; Kuwatani, Y.; Hara, K.; Ogura, E.; Suzuki, H.; Ito, H.; Mori, T. Chem. Lett., 1997, 599.
- 9. X- Ray diffraction data were collected on a Rigaku AFC7R diffractometer. The structures were solved by direct methods and refined using full-matrix least-squares analyses using reflections with I > 3.00σ(I). Anisotropic thermal parameters were used for non-hydrogen atoms. Crystal data for 5: C₂₆H₁₆S₈, Mw = 584.89, triclinic, space group P1 (#2), a = 10.171(1), b = 21.257(2), c = 6.3169(8) Å, α = 93.196(8)°, β = 100.66(1)°, γ = 102.074(8)°, V = 1306.2(3) Å³, Z = 2, Dc = 1.487 g cm⁻³, R = 0.038, Rw = 0.027 for 4392 observed reflections out of 6040 unique reflections. Crystal data for 17: C₃₂H₂₈S₁₄, Mw = 861.41, monoclinic, space group C2/c (#15), a = 21.089(2), b = 15.768(2), c = 13.144(2) Å, β = 117.483(6)°, V = 3877.7(7) Å³, Z = 4, Dc = 1.475 g cm⁻³, R = 0.083, Rw = 0.082 for 2207 observed reflections out of 3017 unique reflections. Crystal data for 21: C5gH₂₈N₉F₈S₁₄, Mw = 1451.75, monoclinic, space group P2₁/n (#14), a = 9.165(1), b = 34.473(2), c = 19.575(2) Å, β = 94.62(1)°, V = 6164.7(10) Å³, Z = 4, Dc = 1.564 g cm⁻³, R = 0.052, Rw = 0.058 for 6548 observed reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
- 10. Iyoda, M.; Suzuki, H.; Sasaki, S.; Yoshino, H.; Kikuchi, K.; Saito, K.; Ikemoto, I.; Matsuyama, H.; Mori, T. J. Mater. Chem., 1996, 6, 501.
- 11. Emge, T. J.; Maxfield, M.; Cowan, D. O.; Kistenmacher, T. J. Mol. Cryst. Liq. Cryst., 1981, 65, 161.