Double-Layered Tetrathiafulvalene as a Novel Electron Donor

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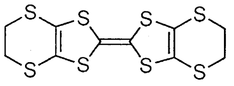
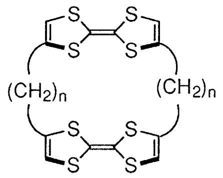
A double-layered tetrathiafulvalenophane with four alkylenedithio spacers has been synthesized as a novel electron donor. Its structure has been elucidated by an X-ray crystal analysis to have a pair of face-to-face tetrathiafulvalenes with a small cavity in the center. Its electronic spectrum and cyclic voltammetry show a transannular interaction between both TTF units.

Double-layered tetrathiafulvalenophanes are of particular interest as intramolecularly interactive electron donors forming charge-transfer complexes with controlled stoichiometry. In addition, they might provide some important information on the electronic interaction of the dimeric TTF structure of κ-type of superconductive molecular complexes based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), which are characterized by the packing of dimeric TTF units in the crystal structure.[1] Such phanes, however, have been so far scarcely studied: Staab et al. reported [2.2]- and [3.3]-tetrathiafulvalenophanes (**1**) as the first examples,[2] but these and related dimeric TTF phanes[3] were indicated to favor a step-by-step *cis*-configuration. Müllen et al. reported a cage phane (**2**) which consisted of a dimeric TTF unit linked with two bulky *p*-hydroquinone spacers.[4] As one of simple face-to-face TTF phanes, we report here the synthesis, structure, and properties of novel tetrathiafulvalenophane (**3**) linked with four alkylenedithio bridges.



BEDT-TTF



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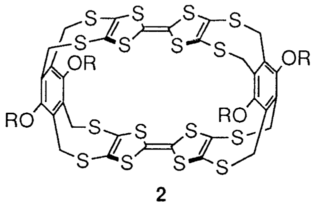

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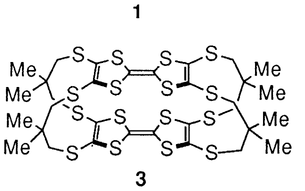

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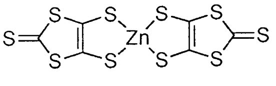
2,2-Dimethylpropane-1,3-diol (**4**) was treated with equimolar *p*-toluenesulfonyl chloride in pyridine at 0 °C to give monotosylate (**5**) in 78% yield. The substitution reaction of **5** with sodium iodide in *N,N*-dimethylformamide (DMF) at 90 °C afforded 3-iodo-2,2-dimethyl-1-propanol (**6**) in 73% yield, which was then coupled with bis(tetrabutylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate (**7**)[5] in DMF at 110 °C to give 4,5-bis(3-hydroxy-2,2-dimethylpropylthio)-1,3-dithiole-2-thione (**8**) in 52% yield. Subsequently, the alcohol (**8**) was quantitatively converted into diiodo compound (**10**) via ditosylate (**9**) in a similar manner. A coupling reaction of **7** and **10** in DMF at 85 °C gave the cyclic bis(dithiole-dithione) (**11**) in 23% yield, which on treatment with mercuric acetate in acetic acid-chloroform was converted to diketone (**12**) in a quantitative yield. The dimeric coupling reaction of **12** with triethylphosphite in toluene under reflux gave the desired tetrathiafulvalenophane (**3**) in 26% yield.

$HOCH_2C(CH_3)_2CH_2X$

4 X=OH
5 X=OTs
6 X=I



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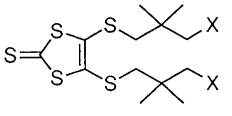
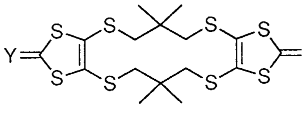


8 X=OH
9 X=OTs
10 X=I



11 Y=S
12 Y=O

Compound **3** was fully characterized by spectroscopic analyses,[6] and the exact molecular structure was elucidated by an X-ray crystallographic analysis.[7] Recrystallization from carbon disulfide provided a good single crystal containing four carbon disulfide molecules per **3**, which was used for the structural analysis. Figure 1 shows that the TTF planes are slightly bent into a boat shape and overlapped with each other. The face-to-face overlap, however, somewhat slides in the transverse direction. The bridged alkylenedithio chains stand perpendicular to the TTF moieties, rather drifting apart both TTF units so as to make a small cavity in the center of the

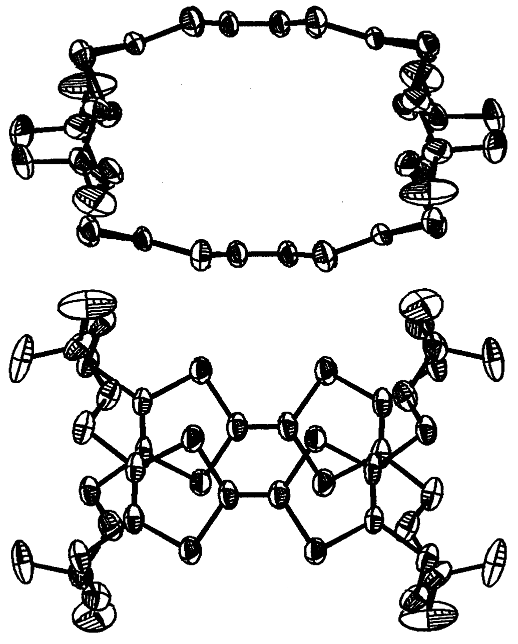


Figure 1. A side view (upper) and a top view (lower) of **3**.

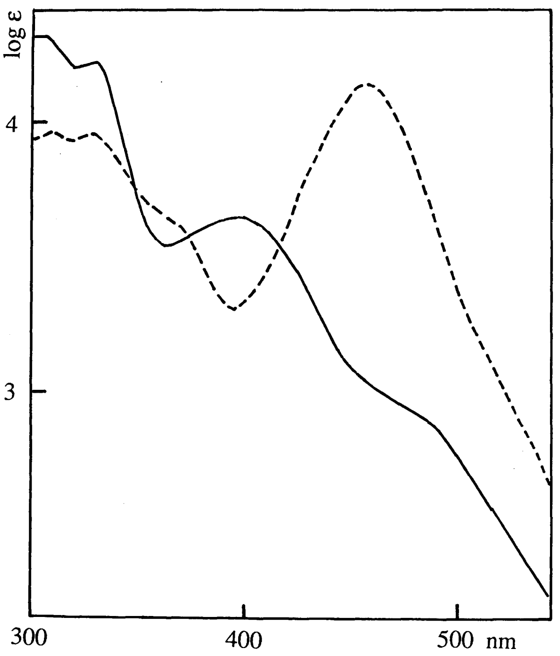
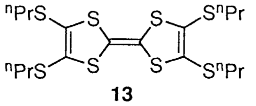


Figure 2. Electronic spectra of **3** (——) and **13** (------) in tetrahydrofuran.

molecule. On the other hand, the electronic absorption spectrum of **3** in tetrahydrofuran demonstrated a large spectral change involving brodening as compared with that of tetrakis(propylthio)tetrathiafulvalene (**13**) as a reference (Fig. 2), suggesting a marked electronic interaction of both TTF chromophores in solution as seen in layered cyclophane series.[8] The cyclic voltammogram of **3** showed two reversible redox waves in 1:1 CS_2-benzonitrile, which each correspond to two-electron transfer. The first and second half-wave oxidation potentials (+0.68 and +1.00 V vs. Ag/AgCl) are elevated as compared with the corresponding ones of **13** (+0.61 and +0.82 V). This result is explainable by transannular electrostatic repulsion between both TTF units in the higher oxidation states. The low solubilities of **3** in common solvents prevented a study on its complexation, but treatments of **3** with $TCNQF_4$, DDQ, and iodine in the solid state formed black complexes, which had conductivities of the order of 10^{-5} Scm^{-1}.



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A modification of **3** by controlling the lengths of the alkylene chains might lead to the design of novel tetrathiafulvalenophane donors with a more interactive dimeric TTF unit or with a large cavity encapsulating a counter ion. Further study along this line is under progress.

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References and Notes

1 For a recent review, see J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M. -H. Whangbo, "Organic Superconductor," Prentice Hall, New Jersey (1992).

2 J. Ippen, C. Tao-pen, B. Starker, D. Schweitzer, and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, **19**, 67 (1980).

3 F. Bertho-Thoraval, A. Robert, A. Souizi, K. Boubekeur, and P. Batail, *J. Chem. Soc., Chem. Commun.*, **1991**, 843.

4 M. Adam, V. Enkelmann, H. -J. Räder, J. Röhrich, and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, **31**, 309 (1992).

5 G. Steimecke, H. -J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus Sulfur*, **7**, 49 (1979).

6 All new compounds gave satisfactory elemental analyses. Selective spectral data of **3**: yellow crystals from carbon disulfide; mp >300 °C; MS *m/z* 936 (M^+); ^{1}H-NMR (CS_2-$CDCl_3$) δ 1.13 (s, 12H, CH_3), 1.25 (s, 12H, CH_3), 2.60 (d, J=12.7 Hz, 8H, CH_2S); 3.27 (d, J=12.7 Hz, 8H, CH_2S). **5**: colorless oil; IR (neat) 3555 (OH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.89 (s, 6H, CH_3),1.65 (bs, 1H, OH), 2.46 (s, 3H, CH_3), 3.40 (s, 2H, CH_2OH), 3.84 (s, 2H, CH_2OTs), 7.36 (d, J=8.2 Hz, 2H, ArH), and 7.80 (d, J=8.2 Hz, 2H, ArH). **6**: pale yellow oil; IR (neat) 3350 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ 1.04 (s, 6H, CH_3), 1.56 (bs, 1H, OH), 3.22 (s, 2H, CH_2I), and 3.44 (s, 2H, CH_2OH). **8**: yellow needles from dichloromethane-hexane; mp 74-75 °C; MS *m/z* 370 (M^+); IR (KBr) 3300 (OH) and 1051 (C=S) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.02 (s, 12H, CH_3), 3.00 (s, 4H, CH_2S), and 3.47 (s, 4H, CH_2OH). **9**: orange oil; IR (neat) 1066 (C=S) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.02 (s, 12H, CH_3), 2.46 (s, 6H, CH_3), 2.88 (s, 4H, CH_2S), 3.85 (s, 4H, CH_2OTs), 7.39 (d, J=8.2 Hz, 4H, ArH), and 7.83 (d, J=8.2 Hz, 4H, ArH). **10**: orange oil; MS *m/z* 590 (M^+); IR (neat) 1064 and 1026 (C=S) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.20 (s, 12H, CH_3), 3.04 (s, 4H, CH_2S), and 3.30 (s, 4H, CH_2I). **11**: yellow needles from carbon disulfide; mp 272-273 °C; MS *m/z* 532 (M^+); IR (KBr) 1034 and 1055 (C=S) cm^{-1}; ^{1}H-NMR (CS_2-$CDCl_3$) δ 1.18 (s, 12H, CH_3) and 3.10 (s, 8H, SCH_2). **12**: pale yellow crystals from dichloromethane-hexane; mp 233-234 °C; MS *m/z* 500 (M^+); IR (KBr) 1666 (C=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.16 (s, 12H, CH_3) and 3.08 (s, 8H, CH_2S); ^{13}C-NMR ($CDCl_3$) δ 27.1, 36.8, 47.6, 127.9, and 189.5.

7 Crystal data for **3**: $C_{36}H_{40}S_{24}$ ($C_{32}H_{40}S_{16}$ + $4CS_2$), FW=1242.16, triclinic $P\bar{1}$, a=10.496(1), b=14.650(2), c=10.213(1) Å, α=103.75(1), β=100.60(1), γ=107.54(1)°, V=1398.0(3) Å^3, Z=1, D_c=1.475, graphite-monochromated Cu-$K\alpha$ radiation, crystal dimensions 1.38 x 0.46 x 0.45 mm, unique reflections 3620 ($|Fo| \geq 3\sigma(|Fo|$). The final R factor was 9.4%.

8 J. Ferguson, *Chem. Rev.*, **86**, 958 (1986).