

Oxidative Intramolecular Cyclization of 2,2'-Bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls affording Novel Bis(1,3-dithiole) Electron Donors

Akira Ohta and Yoshiro Yamashita*

Department of Structural Molecular Science, The Graduate University for Advanced Studies and Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

The title bis(1,3-dithiole) compounds containing a 3,3'-bithienyl unit undergo an intramolecular coupling reaction at the 6-positions of the dithiafulvenyl groups by oxidation to give cyclization products in high yields.

It is known that 1,4-dithiafulvene derivatives undergo oxidative intermolecular coupling reactions at the 6-position to give 1,2-bis(1,3-dithiol-2-ylidene)ethane derivatives.¹ Very recently, Lorcy *et al.*^{1a} and Benahmed-Gasmi *et al.*^{1b} pointed out the synthetic utility of such reactions. If this type of reaction is applied to intramolecular cyclization, it should give a new extended bis(1,3-dithiole) donor containing a 1,2-bis(1,3-dithiol-2-ylidene)ethano moiety with *cis* configuration. We report here the preparation and electrochemical properties of the title bis(1,3-dithiole) compounds **5** containing a 3,3'-bithienyl unit and the successful formation of the corresponding cyclization products.

The formyl groups of aldehyde **1** were protected as 1,3-dioxolane groups by a usual method (96%) prior to methylation with BuLi and methyl iodide to give a dimethyl derivative **2** (84%, mp 203–204 °C). Although the parent compound **5a** could not be isolated, the compounds **5b–f** were prepared by either a Wittig reaction of a phosphonium salt **3** (for **5d**) or Wittig–Horner reaction of phosphonate esters **4** with the corresponding aldehydes **1** and **2** in 69–93% yields.† The X-ray structural analysis‡ of **5e** reveals that the molecule twists around the central C–C bond and the two dithiafulvenylthiophene subunits are almost planar as shown in Fig. 1. The dihedral angle formed by the two thiophene rings is 56.0°. The interatomic distances between the sulfur atoms of the thiophene and the dithiole (3.11 and 3.23 Å) are shorter than the sum of the van der Waals radii (3.70 Å). According to PM3 calculations on **5a**,§ the carbon atoms at the 6-positions of the

dithiafulvenyl groups have large atomic orbital coefficients in the HOMO, suggesting that the coupling reaction occurs selectively at these positions.

The cyclic voltammograms (CV) of **5** reveal that they are irreversibly oxidized at peak potentials of E_{pa} to give new redox active products which show reversible waves at half-wave potentials of $E_{(new)1/2}$ by subsequent chemical reactions. The CV of **5b** is shown in Fig. 2 and the redox potentials are summarized in Table 1. The re-reduction peaks corresponding to the first oxidation peaks could be observed only at high scan rate ($>5 \text{ V s}^{-1}$), indicating that the subsequent chemical reactions are very fast. Since such electrochemical behaviours were not affected by α -substituents on the thiophene rings, the reactions seem to take place at the 6-positions of the dithiafulvenyl groups as predicted by the PM3 calculations. The E_{pa} values of **5** are close to those of the corresponding

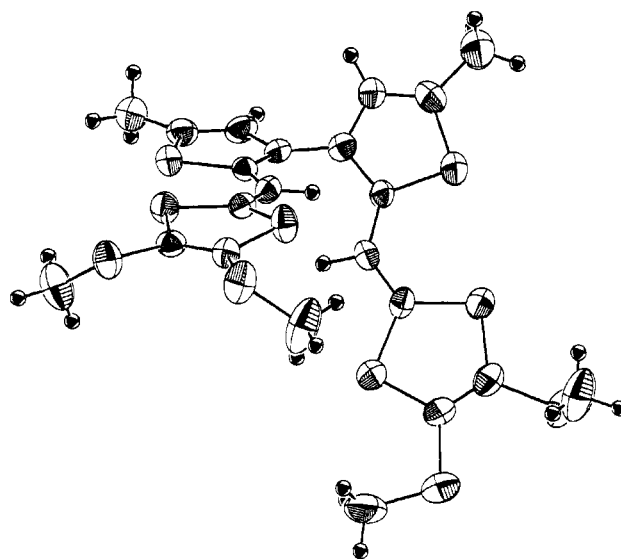
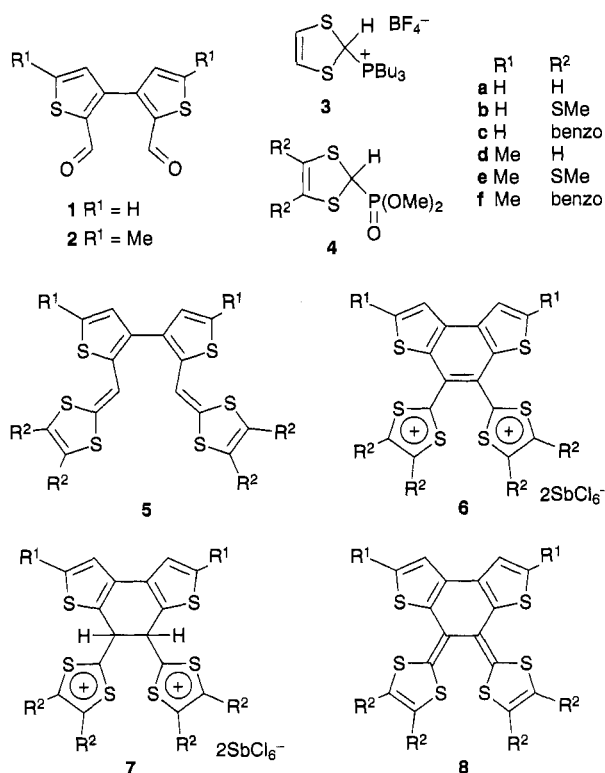


Fig. 1 X-Ray molecular structure of **5e**

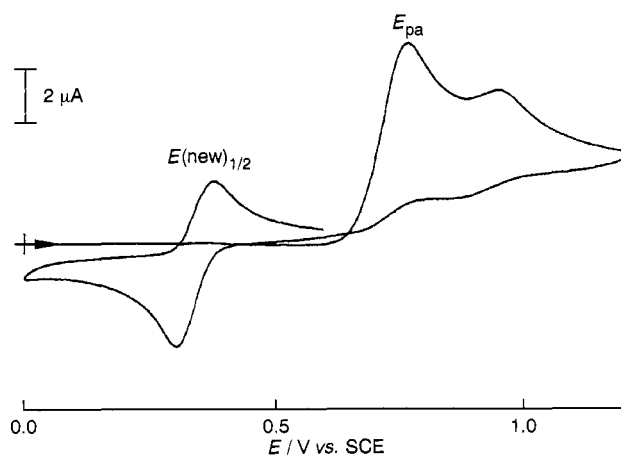


Fig. 2 Cyclic voltammogram of **5b** in PhCN

2-(1,4-dithiafulven-6-yl)thiophenes,^{1a} suggesting that the molecules consist of two independent dithiafulvenylthiophene units due to the twisted structure.

Chemical oxidation of **5** with 2 equiv. of tris(4-bromophenyl)aminium hexachloroantimonate in dichloromethane gave cyclization products **6b–f** as dication salts in 86–95% yields. The formation of the dications can be explained by oxidation of the intermediates **7** with formation of an additional aromatic ring. The dications **6** showed reversible redox waves and the potentials are in complete agreement with the $E(\text{new})_{1/2}$ values of **5**. Any products arising from intermolecular reactions were not detected. Chemical reduction of the dications with zinc in refluxing acetonitrile gave neutral bis(1,3-dithiole) donors **8b–f** in 68, 69, 24, 86 and 96% yields, respectively. On the other hand, attempted preparation of **8f** using the Wittig–Horner reaction of **4** with the corresponding quinone² resulted in recovery of the quinone. This result indicates the usefulness of the cyclization reaction described here to prepare such bis(1,3-dithiole) donors.

Donors **8b–f** are air-stable reddish orange crystals. The X-ray molecular structure of **8e** is shown in Fig. 3. The two 1,3-dithiole rings deviate largely from the plane of the tricyclic

system to avoid the steric interaction between the sulfur atoms of the dithiole rings. The central six-membered ring adopts a slightly twisted conformation. Short intramolecular S...S contacts (3.01 Å) are observed. The donors **8b–f** showed reversible one-stage two-electron redox waves and the oxidation potentials (**8b**, 0.34; **8c**, 0.41; **8d**, 0.18; **8e**, 0.29; **8f**, 0.35 V vs. SCE) are fairly low. The presence of methyl groups on the thiophene rings slightly lower oxidation potentials. Although the donors **8** have low oxidation potentials, their ability to form charge-transfer (CT) complexes is poor, probably due to their nonplanar structure which is unfavourable for molecular stacking. Among them **8d** gave a CT complex with TCNQ which showed a conductivity of $1.7 \times 10^{-5} \text{ S cm}^{-1}$ as a compressed pellet.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

Received, 1st June 1995; Com. 5/03489B

Table 1 Redox potentials of **5**^a

Compound	E_{pa}/V	$E(\text{new})_{1/2}/\text{V}$
5b	0.75	0.34
5c	0.88	0.41
5d	0.58	0.18
5e	0.69	0.29
5f	0.83	0.35

^a Bu_4NBF_4 (0.1 mol dm^{-3}) in PhCN, Pt electrode, scan rate 100 mV s^{-1} , E/V vs. saturated calomel electrode (SCE).

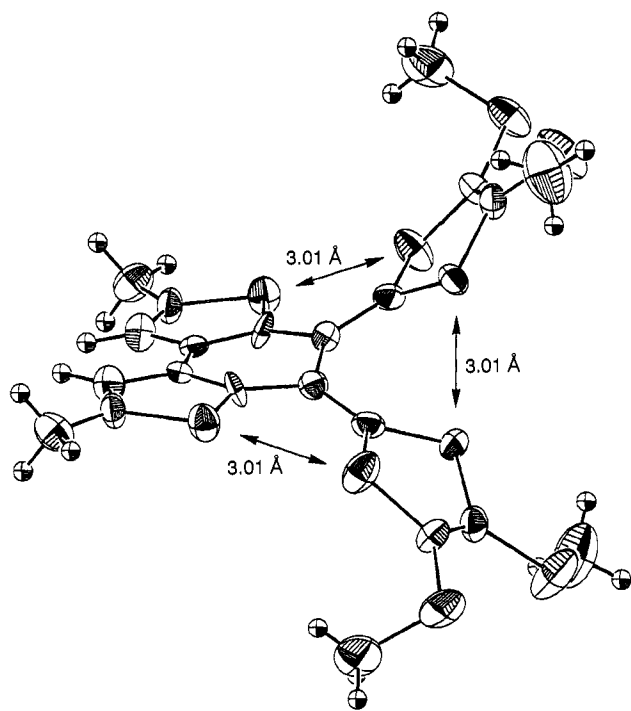


Fig. 3 X-Ray molecular structure of **8e**

Footnotes

† The structures of all new compounds were determined from their spectroscopic data.

Selected data for **5b**: mp 179–180 °C; ¹H NMR [(CD₃)₂SO] δ 2.42 (6H, s, SMe), 2.44 (6H, s, SMe), 6.42 (2H, s, –CH=), 7.03 (2H, d, *J* 5.3 Hz, Th-H), 7.62 (2H, d, *J* 5.3 Hz, Th-H); UV–VIS (CH₂Cl₂) λ_{max}/nm (log ε) 250 (4.35), 378 (4.41). For **6b**: mp 115 °C (decomp.); ¹H NMR (CD₃CN) δ 2.87 (12H, s, SMe), 8.10 (2H, d, *J* 5.6 Hz, Th-H), 8.19 (2H, d, *J* 5.6 Hz, Th-H); UV–VIS (CH₂Cl₂) λ_{max}/nm (log ε) 256 (4.68), 499 (4.14). For **8b**: mp 213–214 °C; ¹H NMR [(CD₃)₂SO] δ 2.45 (6H, s, SMe), 2.50 (6H, s, SMe), 7.63 (2H, d, *J* 5.3 Hz, Th-H), 7.75 (2H, d, *J* 5.3 Hz, Th-H); UV–VIS (CH₂Cl₂) λ_{max}/nm (log ε) 266 (4.37), 278 (4.37), 342 (4.28), 471 (4.08).

‡ Crystal data for **5e**: C₂₂H₂₂S₁₀, *M* = 607.02, monoclinic, space group *P*2₁/*n*, *Z* = 4, *a* = 13.179(3), *b* = 7.864(5), *c* = 26.690(3) Å, β = 93.45(1)°, *V* = 2761(1) Å³, *D*_c = 1.460 g cm⁻³. The final *R* value was 0.048 for 1872 reflections with *I* > 3σ(*I*). For **8e**: C₂₂H₂₀S₁₀, *M* = 605.00, orthorhombic, space group *F*dd2, *Z* = 8, *a* = 15.104(6), *b* = 36.944(7), *c* = 9.416(6) Å, *V* = 5254(3) Å³, *D*_c = 1.530 g cm⁻³. The final *R* value was 0.048 for 697 reflections with *I* > 3σ(*I*). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions but not refined. Atomic coordinates, bond lengths and angles, and thermal parameters for both **5e** and **8e** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The calculations were performed (MOPEC⁵) by using the geometry determined from the X-ray analysis.

References

- (a) D. Lorc, R. Carlier, A. Robert, A. Tallec, P. Le Maguerès and L. Ouahab, *J. Org. Chem.*, 1995, **60**, 2443; (b) A. Benahmed-Gasmi, P. Frère, J. Roncali, E. Elandaloussi, J. Orduna, J. Garin, M. Jubault and A. Gorgues, *Tetrahedron Lett.*, 1995, **36**, 2983; (c) A. Ohta and Y. Yamashita, *Heterocycles*, 1995, **40**, 123; (d) M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson and P. Batail, *J. Am. Chem. Soc.*, 1993, **115**, 3752; (e) U. Schöberl, J. Salbeck and J. Daub, *Adv. Mater.*, 1992, **4**, 41; (f) Von R. Mayer and H. Kröber, *J. Prakt. Chem.*, 1974, **316**, 907.
- H. Wynberg and H. J. M. Sinnige, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 1244.
- K. Takahashi, T. Nihira, M. Yoshifuji and K. Tomitani, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2330.
- K. Akiba, K. Ishikawa and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2674.
- MOPAC program: J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209, 221.