Synthesis, structure and redox reactions of a new crowded benzodithiolium salt: first isolation and characterization of a stable dithiolyl radical with a 7π electron framework

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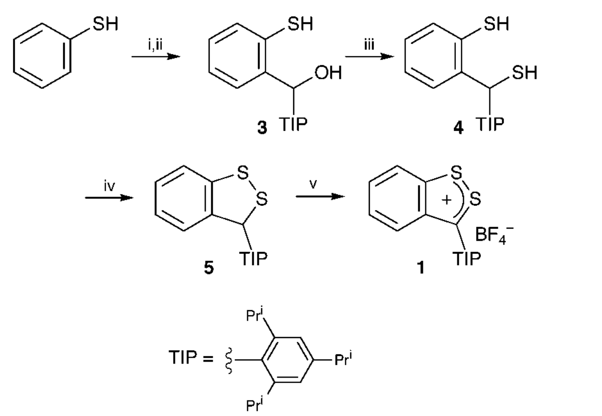
The molecular structure of the sterically crowded 3-(2,4,6-triisopropylphenyl)-1,2-benzodithiolium cation has been determined by crystallographic studies on the BF_4^- salt and the corresponding novel 1,2-dithiolyl radical with a 7π electron framework has been isolated by one-electron reduction.

The unusual 7π electron structure of certain five-membered rings has allowed the construction of a unique reversible one-electron redox system. Recently, we reported reversible one-electron redox couples by the use of 4,7-disubstituted benzotrichalcogenoles and found by EPR spectroscopy that their radical cation salts obtained on treatment with a one-electron oxidant had unusual 7π frameworks.[1] However, to date, dithiolyl radicals with 7π electrons have so far only been obtained in solution as unstable species by electrochemical reduction or laser flash photolysis.[2] Herein we present the synthesis and structural determination by X-ray crystallographic analysis of the new sterically crowded dithiolium salt, 3-(2,4,6-triisopropylphenyl)-1,2-benzodithiolium tetrafluoroborate **1**, and the first isolation of a stable 7π radical, 3-(2,4,6-triisopropylphenyl)-1,2-benzodithiolyl **2**, by one-electron reduction. In addition, we have succeeded in the construction of a new type of one-electron redox system between **1** and **2** by means of both chemical and electrochemical methods.

3-(2,4,6-Triisopropylphenyl)-1,2-benzodithiolium tetrafluoroborate **1** was synthesized as follows (Scheme 1). We employed commercially available thiophenol as a starting material to prepare the desired cyclic disulfide compound. 2-Mercapto-2′,4′,6′-triisopropylbenzhydrol **3** was obtained in 59% yield by *ortho* lithiation[3] of thiophenol followed by the addition of 2,4,6-triisopropylbenzaldehyde, which was readily prepared by general methods.[4] Thiolation was performed upon treatment of the benzhydrol with P_2S_5 and *in situ* cyclization of the resulting dithiol **4** was carried out in the presence of I_2/Et_3N after displacement of the solvent from toluene to CH_2Cl_2. After usual work-up, the crude product was purified by column chromatography (silica gel, *n*-hexane) to give 3-(2,4,6-triisopropylphenyl)-3*H*-1,2-benzodithiole **5** quantitatively. The corresponding dithiolium salt **1** was prepared by a two-electron oxidation of dithiole **4** with 2 equiv. of $NOBF_4$ in quantitative yield.†

The structure of new dithiolium salt **1** has been fully characterized by physical and spectroscopic means, and its solid-state structure (recrystallized from benzene) was determined by single-crystal X-ray diffraction (Fig. 1).‡ In the solid state, the benzodithiolium unit is almost coplanar (the torsion angles $S_2S_1C_8C_7$ and $S_2C_3C_9C_4$ are 178.9 and −178.9°, respectively), with the 2,4,6-triisopropylbenzene ring very nearly orthogonal to the planar unit (the torsion angle $S_2C_3C_{10}C_{11}$ is 89°), which may arise from the steric repulsion between the bulky 2,6-isopropyl groups on benzene and the *ortho* proton on the benzene ring fused to the dithiolium ring. This conformation plays an important role in blocking radical dimerization, which is adopted *via* a cofacial alignment, resulting in the isolation of the corresponding radical (*vide infra*).

Cyclic voltammetry of **1** in MeCN at 20 °C under an Ar atmosphere exhibited well-defined reversible one-electron redox waves at $E_{1/2}$ = −0.51 V *vs.* Ag / 0.01 mol dm^{-3} $AgNO_3$.§ This result implies that dithiolium **1** provides a stable



Scheme 1 *Reagents and conditions:* i, TMEDA (2.2 equiv.), BuLi (2.2 equiv.), cyclohexane, ii, 2,4,6-$Pr^i_3C_6H_2CHO$; iii, P_2S_5, toluene; iv, I_2, Et_3N, CH_2Cl_2; v, $NOBF_4$ (2.0 equiv.), THF–MeCN.

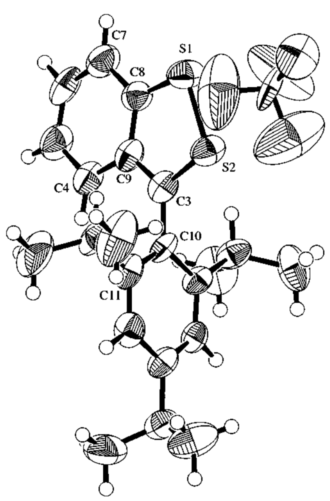
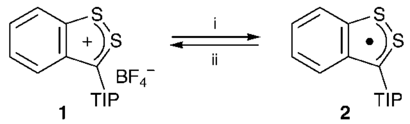


Fig. 1 ORTEP view of **1**. Benzene molecule is omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)–S(2) 2.020(4), S(1)–C(8) 1.70(1), S(2)–C(3) 1.69(1), C(3)–C(9) 1.38(1), C3–C10 1.47(1), C(8)–C(9) 1.44(2); S(1)–S(2)–C(3) 97.8(4), S(2)–S(1)–C(8) 95.3(4), S(2)–C(3)–C(9) 115.0(9), S(1)–C(8)–C(9) 115.0(8), C(3)–C(9)–C(8) 116(1); S(2)–S(1)–C(8)–C(7) 178.9(10), S(2)–C(3)–C(9)–C(4) −178.9(8), S(2)–C(3)–C(10)–C(11) 89(1).



Scheme 2 *Reagents and conditions*: i, Na (1.0 equiv), THF; ii, $NOBF_4$ (1.0 equiv), THF–MeCN.

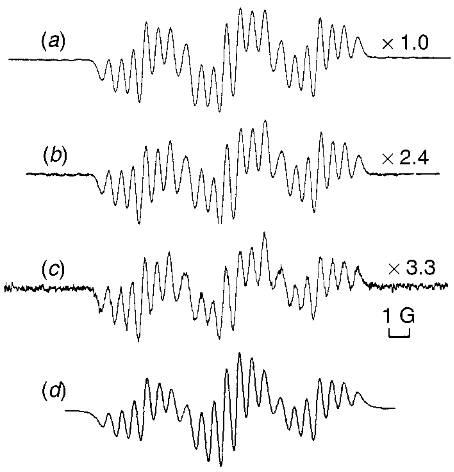
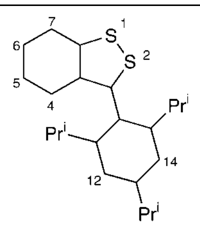


Fig. 2 VT-EPR spectra of **2** at (*a*) 18, (*b*) −50, (*c*) −81 °C, and (*d*) simulated spectrum.

neutral radical even at room temperature. The novel dithiolyl radical **2**¶ was isolated in the one-electron reduction of **1** with sodium metal in THF (Scheme 2). The structure of the first isolable dithiolyl radical **2**, a green solid, was determined by high-resolution MS and EPR spectroscopy. The EPR spectra of **2** in THF solution showed the multiple signals (g = 2.0049 G) attributable to a radical, and the a_H values were evaluated by the fitting of simulated spectra to the experiment spectrum (Fig. 2). In addition, the experimental values of the unpaired π spin density from the hyperfine splitting are in good agreement with those calculated by the simple Hückel and McLachlan's methods (Table 1). Using variable-temperature EPR spectra normalized by the Mn^{2+} on MgO standard, the intensities of the

Table 1 Unpaired spin populations (ρ^π) of **2**



		ρ^π		
Position	Atom	Exp.	Hückel	McLachlan
1	S	—	0.146	0.210
2	S	—	0.244	0.335
3	C	0.175	0.149	0.180
4	C	0.055	0.107	0.089
5	C	0.054	0.012	−0.019
6	C	0.205	0.176	0.200
12,14	C	0.029	0.004	−0.007

signals gradually decreased at low temperatures, but their hyperfine structure was unchanged, which suggests that the bulky substituent serves as an efficient protective group for spin-dimerization even at low temperature. Although it has not yet been possible to grow single crystals suitable for X-ray diffraction, unpaired π-electron density was delocalized over both the coplanar benzene and the five-membered heterocycle. Interestingly, the salt **2** undergoes one-electron oxidation to give **1** quantitatively by treatment with 1 equiv. of $NOBF_4$ (Scheme 2). Thus, the facile interconversion in the redox reactions of **1** and **2** has been ascribed to the unusual stabilization of the radical by the 7π electron framework.

Notes and references

† *Selected data* for **1**: yellow plates (CH_2Cl_2–*n*-hexane); mp 219–225 °C (decomp.) (Found C, 59.41; H, 5.90. $C_{22}H_{27}S_2BF_4$ requires C, 59.73; H, 6.15%); ν_{max}(KBr)/cm^{-1} 3449, 2959, 2871, 1593, 1458, 1431, 1380, 1084, 1035, 877, 761, 722; δ_H(400 MHz, CD_3CN) 1.02 (d, 6H, *J* 6.7, *o*-CH_3), 1.15 (d, *J* 6.7, 6H, *o*-CH_3), 1.32 (d, *J* 6.9, 6H, *p*-CH_3), 2.18 (sept, *J* 6.7, 1H, *o*-C*H*), 3.06 (sept, *J* 6.9, 1H, *p*-C*H*), 7.39 (s, 2H, *m*-Ar*H*), 7.85 (dd, *J* 8.5, 0.7, 1H, 4-Ar*H*), 7.91 (ddd, *J* 8.6, 6.8, 0.7, 1H, 6-Ar*H*), 8.30 (ddd, *J* 8.5, 6.8, 1.3, 1H, 5-Ar*H*), 8.67 (d, *J* 8.6, 1.3, 1H, 7-Ar*H*); δ_C(101 MHz, CD_3CN) 24.0 (*o*-CH_3), 24.1 (*o*-CH_3), 24.9 (*p*-CH_3), 32.5 (*o*-CH), 35.3 (*p*-CH), 121.5, 123.6, 126.5, 129.8, 131.3, 138.9, 143.8, 150.0, 155.4, 163.7, 197.4 (3-*C*).

‡ *Crystal data* for **1**: $C_{22}H_{27}S_2BF_4{\cdot}C_6H_6$, M = 520.49, monoclinic, space group *C*2/*c* (no. 15), a = 26.387(8), b = 13.177(7), c = 19.851(7) Å, β = 122.91(2)°, U = 5794(4) Å^3, T = 293 K, Z = 8, D_c = 1.193 g cm^{-3}, μ(Cu-Kα) = 20.03 cm^{-1}, F(000) = 2192. A yellow prismatic crystal of dimensions 0.40 × 0.30 × 0.20 mm was used. 4659 reflections were measured of which 4544 were unique using a Rigaku AFC7R diffractometer with Cu-Kα radiation using ω–2θ scans. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package. The final cycle of full-matrix least-squares refinement was based on 2083 observed reflections [$I > 1.50\sigma(I)$] and 316 variable parameters with R = 0.105, R_w = 0.151. CCDC 182/1370. See http://www.rsc.org/suppdata/cc/1999/1891/ for crystallographic data in .cif format.

§ Cyclic voltammograms of **1** (2.0 mmol dm^{-3}) were measured in MeCN at 20 °C containing 0.1 mol dm^{-3} NBu_4ClO_4 as a supporting electrolyte using a glassy-carbon working electrode and Ag/0.01 mol dm^{-3} $AgNO_3$ couple in MeCN as a reference electrode; scan rate in the range from 50 to 500 mV s^{-1}.

¶ *Selected data* for **2**: green crystals (*n*-hexane); mp 76 °C (decomp.) (Found: M$^+$ 355.1565. $C_{22}H_{27}S_2$ requires 355.1554); X-band EPR (THF) g = 2.0049, a_{H1} = 0.461 mT, a_{H2} = 0.394 mT, a_{H3} = 0.123 mT, a_{H4} = 0.121 mT, a_{H5} = 0.065 mT.

1 S. Ogawa, T. Kikuchi, S. Niizuma and R. Sato, *J. Chem. Soc., Chem. Commun.*, 1994, 1593; S. Ogawa, T. Kikuchi, A. Sasaki, S. Chida and R. Sato, *Tetrahedron Lett.*, 1994, **35**, 5469; S. Ogawa, S. Saito, T. Kikuchi, Y. Kawai, S. Niizuma and R. Sato, *Chem. Lett.*, 1995, 321; S. Ogawa, S. Nobuta, R. Nakayama, Y. Kawai, S. Niizuma and R. Sato, *Chem. Lett.*, 1996, 757; S. Ogawa, T. Ohmiya, T. Kikuchi, Y. Kawai, S. Niizuma and R. Sato, *Heterocycles*, 1995, **43**, 321; D. Schröder, H. Schwarz, B. Löbrecht, W. Koch and S. Ogawa, *Eur. J. Inorg. Chem.*, 1998, 983.

2 C. T. Pedersen and C. Lohse, *Tetrahedron Lett.*, 1972, 5213; K. Bechgaard, V. D. Parker and C. T. Pedersen, *J. Am. Chem. Soc.*, 1973, **95**, 4373; C. T. Pedersen and C. Lohse, *Acta Chem. Scand., Ser. B*, 1975, **29**, 831.

3 G. D. Figuly, C. K. Loop and J. C. Martin, *J. Am. Chem. Soc.*, 1992, **111**, 645; E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **111**, 658; K. Smith, C. M. Lindsay and G. J. Pritchard, *J. Am. Chem. Soc.*, 1992, **111**, 665.

4 B. B. Wayland, A. E. Sherry, G. Paszmik and A. G. Bunn, *J. Am. Chem. Soc.*, 1992, **114**, 1673.

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