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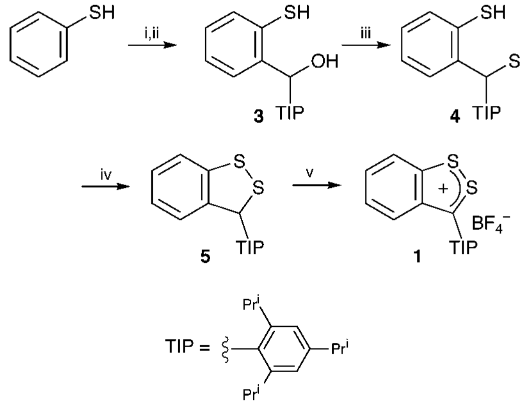
The molecular structure of the sterically crowded 3-(2,4,6-triisopropylphenyl)-1,2-benzodithiolium cation has been determined by crystallographic studies on the BF_4^- salt and the corresponding novel 1,2-dithiolyl radical with a 7π electron framework has been isolated by one-electron reduction.

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.

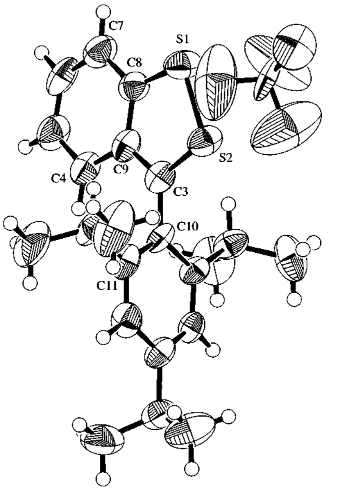
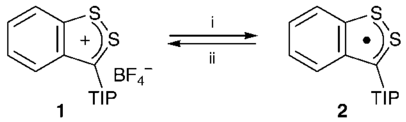


Fig. 1 ORTEP view of **1**. Benzene molecule is omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)–S(2) 2.020(4), S(1)–C(8) 1.70(1), S(2)–C(3) 1.69(1), C(3)–C(9) 1.38(1), C3–C10 1.47(1), C(8)–C(9) 1.44(2); S(1)–S(2)–C(3) 97.8(4), S(2)–S(1)–C(8) 95.3(4), S(2)–C(3)–C(9) 115.0(9), S(1)–C(8)–C(9)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

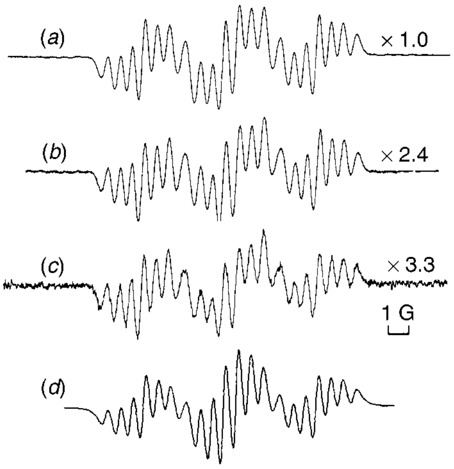
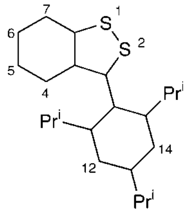


Fig. 2 VT-EPR spectra of **2** at (*a*) 18, (*b*) −50, (*c*) −81 °C, and (*d*) simulated spectrum.

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 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.

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

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*-C*H*$_3$), 1.15 (d, *J* 6.7, 6H, *o*-C*H*$_3$), 1.32 (d, *J* 6.9, 6H, *p*-C*H*$_3$), 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*-*C*H$_3$), 24.1 (*o*-*C*H$_3$), 24.9 (*p*-*C*H$_3$), 32.5 (*o*-*C*H), 35.3 (*p*-*C*H), 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**: $C_{22}H_{27}S_2BF_4$•C_6H_6, M = 520.49, monoclinic, space group $C2/c$ (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.

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