

2,4,6-Tris(4,5-diisopropyl-1,3-dithiol-2-ylidene)cyclohexane-1,3,5-trione: Synthesis, X-Ray Crystal Structure and Amphoteric Redox Properties of a Highly Delocalised Heterocyclic π -System

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The title compound **1** is synthesised by treatment of 1,3,5-trihydroxybenzene with 2-methylthio-4,5-di-*n*-propyl-1,3-dithiolium iodide in the presence of pyridine; the X-ray crystal structure of **1** reveals a highly delocalised π -system with strongly bonding intramolecular S \cdots O interactions; four-stage, amphoteric redox behaviour is observed by cyclic voltammetry.

Organic molecules that possess multi-stage, amphoteric redox properties (*i.e.* the ability to undergo both anodic oxidation and cathodic reduction) within a relatively small range of potentials are rare.¹ Notable examples, all of which contain a highly delocalised π -electron framework, include cyclobuta[b]quinoxaline-1,2-dione,² 9,9'-bianthryl-10,10'-dicarbonitrile³ and extended quinones.^{4,5} In these molecules both the π -donor and π -acceptor ability are enhanced by aromatic stabilisation of the charged species and by judicious choice of functional groups attached to the molecule. An extended quinone is claimed to exhibit the smallest value of E^{sum} *viz* 0.75 V⁴ [$E^{\text{sum}} = E^{\text{ox}} + (-E^{\text{red}})$].

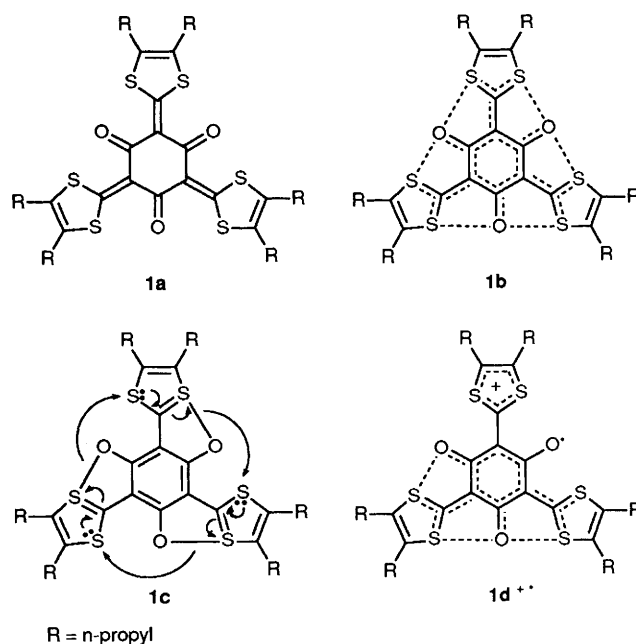
We were attracted by system **1**, for which heteroaromatic, 6 π , 1,3-dithiolium cations and phenoxy anions could participate in stabilising oxidised and reduced states, respectively. Furthermore, hexasubstituted benzene derivatives that have threefold symmetry and can be readily oxidised, are prime candidates for achieving ferromagnetic interactions in organic materials, as the dication may be a ground state triplet owing to orbital degeneracy.^{6–10}

The reaction of 1,3,5-trihydroxybenzene (0.62 mmol) with 2-methylthio-4,5-di-*n*-propyl-1,3-dithiolium iodide¹¹ (1.8 mmol) in acetonitrile (20 ml) with pyridine (0.35 ml) as base,¹² afforded the target compound **1** [30% yield, m.p. 312–315 °C, after column chromatography on silica, eluent dichloromethane–cyclohexane (1 : 1 v/v) and recrystallisation from ethanol]. The carbonyl absorption frequency of compound **1** occurs at 1530 cm^{–1}; this low value indicated strong S \cdots O interactions in the structure.¹³ [The unsubstituted system **1** (R = H)¹⁴ and the hexamethyl analogue **1** (R = Me) are intractable solids, which could not be recrystallised. We, therefore, prepared the hexa-*n*-propyl analogue described herein, to increase the solubility.]

Orange crystals of compound **1**, grown from toluene solution, were suitable for X-ray analysis.[†] The crystal structure of **1** is shown in Fig. 1. The molecule is almost planar (with the exception of the propyl chains) with a slight deviation from D_{3h} symmetry. Analysis of the bond lengths (Fig. 1) reveals a fascinating electron distribution in the neutral molecule, which is best represented by the highly delocalised structure **1b**. Contributing canonical structures

include **1a** and **c**, and other structures with positive charge placed on the sulfur atoms. The central ring, which has pronounced benzenoid character, can be considered to be covalently embedded within a 24 π electron milieu. All the C–C bonds that radiate from the 'benzene' ring are intermediate in length between single and double bonds, while the C–O distances are close to the accepted value for a carbon–oxygen double bond. The intramolecular S–O separations are all in the range 2.57–2.60 Å, which is considerably shorter than the sum of their van der Waals radii (3.25 Å), indicating significant S \cdots O \cdots S bonding interactions in the structure. The peripheral C–C distances within the 1,3-dithiole rings, *e.g.* C(8)–C(9), are all consistent with a normal carbon–carbon double bond, which implies that these π -electrons are not delocalised to any extent.

The electrochemical behaviour of compound **1** has been studied by cyclic voltammetry. These experiments required rigorous exclusion of oxygen, water and other protic impurities. A variety of solvents were investigated and the best quality data were obtained in propionitrile solution at low temperatures (<0 °C), where four-stage amphoteric behaviour is observed (Fig. 2). Compound **1** can be oxidised in three, successive, one-electron transfer steps: E_1^{ox} (*i.e.* the formation of the radical cation) and E_2^{ox} (*i.e.* the formation of the dication) occur at +0.65 and +0.80 V, respectively, and both are reversible processes within the scan range 0.0 to +1.1 V. If a higher potential range is scanned, a third irreversible oxidation is seen at +1.25 V and E_2^{ox} now becomes irreversible. The oxidised redox stages will, presumably, be stabilised by the involvement of 6 π dithiolium



[†] Crystal data for **1**: C₃₃H₄₂O₃S₆, $M = 679.1$, triclinic, space group $P\bar{1}$, $a = 8.878(2)$, $b = 12.914(2)$, $c = 15.175(2)$ Å, $\alpha = 82.96(1)$, $\beta = 86.70(1)$, $\gamma = 87.20(1)^\circ$, $U = 1722.3$ Å³, $Z = 2$, $D_x = 1.309$ g cm^{–3}, $\lambda(\text{Cu-K}\alpha) = 1.54184$ Å, $\mu = 3.86$ mm^{–1}, $F(000) = 720$, $T = 295$ K. Data were measured with on-line profile fitting¹⁷ on a Stoe-Siemens diffractometer. The structure was determined by direct methods and refined¹⁸ to a minimum of $\Sigma w\Delta^2$ [$\Delta = F_o - F_c$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 9 + 89G - 59G^2 - 30H + 21H^2 - 61GH$, $G = F_o/F_{\text{max}}$, $H = \sin \theta / \sin \theta_{\text{max}}$]¹⁹ from 3554 reflections with $2\theta < 120^\circ$ and $F > 4\sigma_c(F)$ (σ_c from counting statistics only). Anisotropic thermal parameters were refined for all non-H atoms; H atoms were constrained. Final $R = 0.0607$, $R_w = (\Sigma w\Delta^2 / \Sigma wF_o^2)^{1/2} = 0.0757$, $S = 1.04$, for 390 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

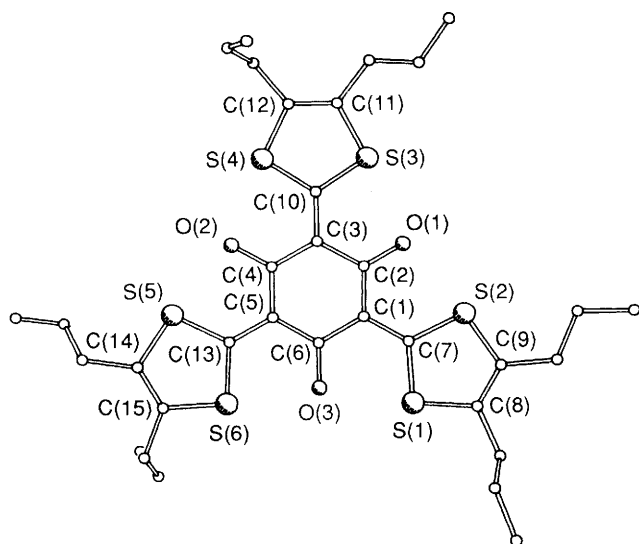


Fig. 1 View of **1** along the normal to the central C_6 ring, showing the atom labelling scheme. Bond lengths (\AA), excluding n-propyl substituents, are: S(1)–C(7) 1.718(5), S(1)–C(8) 1.744(5), S(2)–C(7) 1.718(5), S(2)–C(9) 1.746(5), S(3)–C(10) 1.715(5), S(3)–C(11) 1.753(5), S(4)–C(10) 1.717(4), S(4)–C(12) 1.738(5), S(5)–C(13) 1.726(5), S(5)–C(14) 1.756(5), S(6)–C(13) 1.729(5), S(6)–C(15) 1.748(5), O(1)–C(2) 1.240(6), O(2)–C(4) 1.257(5), O(3)–C(6) 1.257(6), C(1)–C(2) 1.442(6), C(1)–C(6) 1.445(6), C(1)–C(7) 1.399(6), C(2)–C(3) 1.456(6), C(3)–C(4) 1.439(6), C(3)–C(10) 1.397(6), C(4)–C(5) 1.452(6), C(5)–C(6) 1.444(6), C(5)–C(13) 1.389(6), C(8)–C(9) 1.321(7), C(11)–C(12) 1.335(7), C(14)–C(15) 1.324(7), O(1)–S(2) 2.595, O(1)–S(3) 2.597, O(2)–S(4) 2.581, O(2)–S(5) 2.570, O(3)–S(1) 2.584, O(3)–S(6) 2.586.

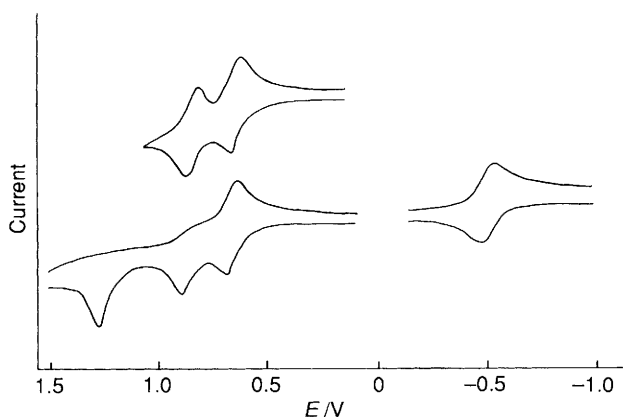


Fig. 2 Cyclic voltammograms of compound **1**, ca. $1 \times 10^{-4} \text{ mol dm}^{-3}$, electrolyte $\text{Et}_4\text{N}^+\text{PF}_6^-$ (ca. $1 \times 10^{-1} \text{ mol dm}^{-3}$) in dry propionitrile under argon, -10°C , vs. Ag/AgCl, Pt electrode. The values of E_1^{ox} , E_2^{ox} and E_1^{red} quoted in the text were calculated by averaging the anodic and cathodic peak potentials [*i.e.* $E = (E_p^a + E_p^c)/2$]; for E_3^{ox} , where the reduction process is not observed on the return sweep, the value quoted is for E_p^{ox} .

cations, *e.g.* canonical structure **1d** $^{+}$. The π electrons of the peripheral C=C double bonds would be delocalised in this structure, which contrasts with their localisation in the neutral system (X-ray data discussed above). The difference, ΔE , between E_1^{ox} and E_2^{ox} (0.15 V) is significantly less than that between E_2^{ox} and E_3^{ox} (0.45 V); this is a reflection of increased coulombic repulsion in the trication.

One reductive wave was observed for compound **1** at $E^{\text{red}} = -0.51 \text{ V}$, which corresponds to the formation of the radical anion **1** $^{\cdot-}$: controlled potential coulometry confirmed this to be a single-electron process. This is a reversible wave, but further reduction could not be clearly identified, even upon sweeping to -2.5 V . The negative charge in reduced states of **1**, will, presumably, be localised predominantly on the oxygen atoms and it seems that their close proximity inhibits dianion formation. The oxidation of compound **1** is reminiscent of 2,4,6-(4,5-dimethyl-1,3-dithiol-2-ylidene)-1,3,5-trithiane, which also forms a trication in electrochemical experiments,¹⁵ and hexakis(1,3-dithiol-2-ylidene)cyclohexane derivatives, which display three oxidation waves leading to a tetracation;¹⁶ however, neither of these systems undergoes electrochemical reduction.

In conclusion, compound **1** has been shown by X-ray analysis to comprise a highly delocalised π -electron system, and four-stage, amphoteric, redox behaviour has been observed. The value of E_1^{sum} (*viz.* 1.16 V) is low in comparison with most other closed-shell organic compounds. The preparation of electrochemically and chemically generated salts of system **1** is underway.

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References

- 1 K. Deichert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1978, **90**, 927.
- 2 S. Hünig and H. Putter, *Chem. Ber.*, 1979, **110**, 2524.
- 3 J. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 202.
- 4 K. Takahashi and T. Suzuki, *J. Am. Chem. Soc.*, 1989, **111**, 5483.
- 5 K. Takahashi and M. Ogiyama, *J. Chem. Soc., Chem. Commun.*, 1990, 1196.
- 6 T. J. LePlage and R. Breslow, *J. Am. Chem. Soc.*, 1987, **109**, 6412.
- 7 L. Y. Chiang and H. Thomann, *J. Chem. Soc., Chem. Commun.*, 1989, 172.
- 8 R. Lapouyade and J.-P. Morand, *J. Chem. Soc., Chem. Commun.*, 1987, 223.
- 9 P. J. Krusic and E. Wasserman, *J. Am. Chem. Soc.*, 1991, **113**, 2322.
- 10 Other workers have pointed out that an appropriately substituted dianion can, theoretically, also lead to a triplet species: D. A. Dixon and J. S. Miller, *Mol. Cryst. Liq. Cryst.*, 1989, **176**, 211.
- 11 This compound was synthesised starting from butyraldehyde (six steps, 11% overall yield) based on the route described previously for 4-hexyl-1,3-dithiole-2-thione: A. S. Dhindsa, M. R. Bryce, M. C. Petty, K. Kobayashi and H. Tukada, *Synth. Metals*, 1989, **31**, 379.
- 12 For related chemistry see: R. Gompper and E. Kutter, *Chem. Ber.*, 1965, **98**, 1365.
- 13 N. Lozac'h in *Organosulfur Chemistry*, ed. M. J. Janssen, Wiley, New York, 1967, pp. 179–201.
- 14 M. Kimura, W. H. Watson and J. Nakayama, *J. Org. Chem.*, 1980, **45**, 3719.
- 15 R. R. Schumaker, S. Rajeswari, M. V. Joshi, M. P. Cava, M. A. Takassi and R. M. Metzger, *J. Am. Chem. Soc.*, 1989, **111**, 308.
- 16 T. Sugimoto, Y. Misaki, T. Kajita, Z. Yoshida, Y. Kai and N. Kasai, *J. Am. Chem. Soc.*, 1987, **109**, 4106.
- 17 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
- 18 G. M. Sheldrick, SHELXS86, program for crystal structure determination, University of Göttingen, 1986; SHELXTL, an integrated system for solving, refining and displaying crystal structures from diffraction data, revision 5, 1985.
- 19 Wang Hong and B. E. Robertson, *Structure and Statistics in Crystallography*, ed. A. J. C. Wilson, Adenine Press, New York, 1985, 125.