A Novel Macrocycle containing the 4,5-dithio-1,3-dithiole-2-thione Unit and a Related Macrocycle incorporating the Tetrathiafulvalene Moiety

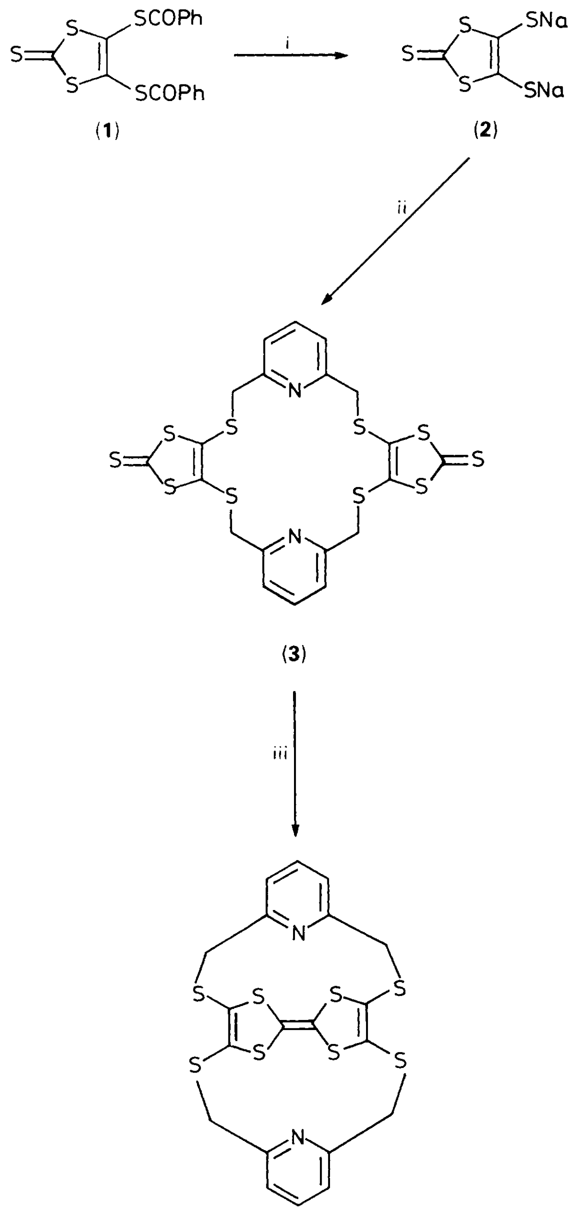
B. Girmay,[a] J. D. Kilburn,[a]* A. E. Underhill,[a] K. S. Varma,[a] M. B. Hursthouse,[b] M. E. Harman,[b] J. Becher,[c] and G. Bojesen[c]

[a] *Department of Chemistry, University College of North Wales, Bangor LL57 2UW, Gwynedd, Wales, U.K.*
[b] *Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.*
[c] *Department of Chemistry, Odense University, Odense M, Denmark*

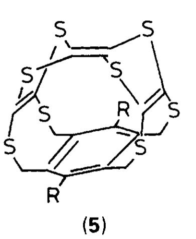
A novel macrocycle (**3**) incorporating the 4,5-dithio-1,3-dithiole-2-thione unit has been prepared from 2,6-bis(bromomethyl)pyridine and 4,5-bis(benzoylthio)-1,3-dithiole-2-thione: intramolecular triethylphosphite coupling of (**3**) leads to a novel macrocyclic π-donor (**4**) incorporating a non-planar tetrathiafulvalene moiety; the crystal structures of (**3**) and (**4**) are reported.

Organic π-donors and their cation radical salts have been extensively studied because of their potential as molecular conductors and superconductors.[1] The most successful to date have incorporated the tetrathiafulvalene (TTF) moiety.[2]

The dimercapto disodium salt (**2**) is an excellent synthon for entry into the TTF system[3] and it is readily prepared by the sodium metal reduction of carbon disulphide in the presence of *N*,*N*-dimethylformamide.[4]



Scheme 1. *Reagents*: i, NaOEt, EtOH, 20 °C; ii, 2,6-bis(bromomethyl)pyridine; iii, P(OEt)$_3$.



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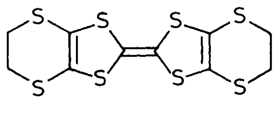

(6)

As part of our search for novel organic conducting materials and our interest in metal cation complexation we have explored the possibility of incorporating the 4,5-dithio-1,3-dithiole-2-thione unit and the tetrathiafulvalene unit into macrocyclic structures. The complexation of metal cations by such macrocycles would provide a mechanism for fine-tuning the electronic properties of the macrocycle in the solid state. A number of sulphur containing macrocycles has been reported and macrocycles incorporating both sulphur and the pyridine ring have been studied in some detail together with their metal complexes.[5] We now report the synthesis of macrocycle (**3**), the first aza-macrocyclic ligand incorporating a 4,5-dithio-1,3-dithiole-2-thione unit.[6]

Synthesis of (**3**) was both straightforward and high yielding† (Scheme 1). Slow addition of 2,6-bis(bromomethyl)pyridine[7] to the disodium salt (**2**) [generated *in situ* from the benzoylated derivative[3,4] (**1**)] gave the macrocycle (**3**) in >90% yield, as a yellow solid. The macrocycle was recrystallised from chloroform and the crystal structure‡ shown in Figure 1, indicates that (**3**) crystallises with one molecule of chloroform per molecule of macrocycle.

The solid state conformation of the macrocycle presumably results from the avoidance of the lone pair repulsions between heteroatoms. Thus the two pyridine rings are angled to avoid an unfavourable interaction between the two nitrogen lone pairs and the sulphur-containing rings are twisted to minimise the sulphur lone pair interactions.

In view of our interest in incorporating the tetrathiafulvalene unit into macrocyclic structures, and a recent synthesis of a caged donor molecule (**5**),[8] we then investigated the possibility of intramolecular coupling of the 4,5-dithio-1,3-dithiole-2-thione units in macrocycle (**3**).

Reaction of (**3**) with triethylphosphite in refluxing xylene[9] gave on isolation the macrocycle (**4**) in 20—25% yield§

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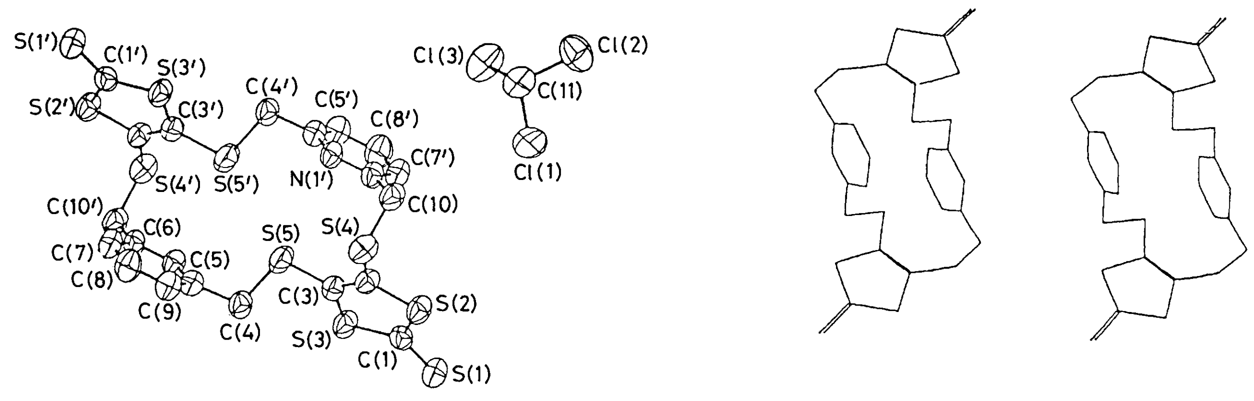
† Sodium (0.60 g, 26 mmol) was added to dry ethanol (45 ml) and the resulting solution of sodium ethoxide was added to a stirred suspension of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione[3,4] (**1**) (4.1 g, 10.1 mmol) in ethanol (180 ml), under an argon atmosphere, at room temperature to give a deep red solution of the disodium salt (**2**). A solution of 2,6-bis(bromomethyl)pyridine[7] (2.7 g, 10.1 mmol) in ethanol (100 ml) was added over 12 h and stirring continued for a further 6 h. The resulting yellow precipitate was filtered, washed with ethanol and air dried to give the macrocycle (**3**) (2.9 g, 95%) as a yellow solid which could be recrystallised from $CHCl_3$; m.p. 84—86 °C (decomp.); i.r. (KBr) 3058, 1629, 1589, 1572, 1453, 1064, and 1038 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 4.09 (s, 8H), 7.15 (d, 4H), and 7.65 (t, 2H); u.v. ($CHCl_3$) λ_{max} 240 (log ε 4.36), 273 (4.34), and 381 nm (4.38); *m/z* (EI) M^+ 602.

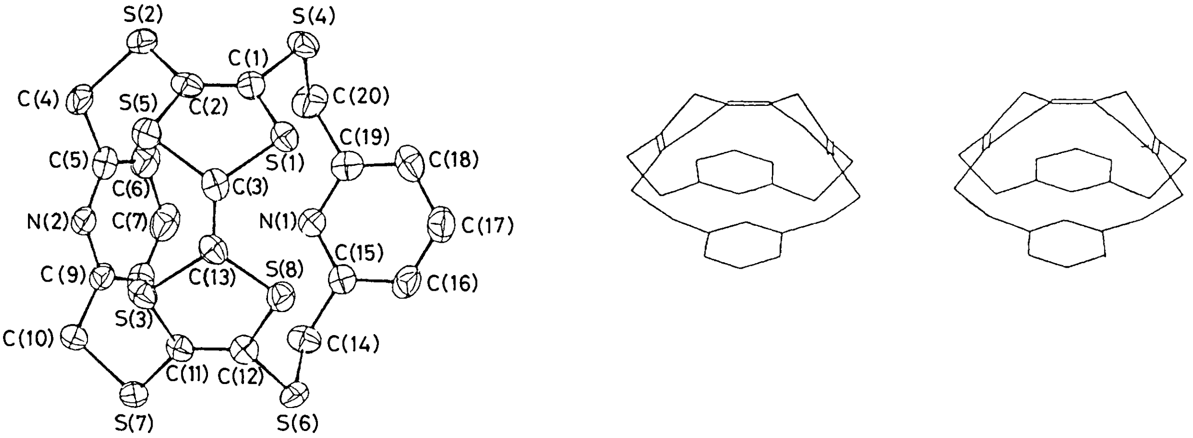
‡ *Crystal data* for (**3**): $C_{20}H_{14}N_2S_{10}\cdot CHCl_3$, M = 722.32, monoclinic, space group $P2_1/c$, a = 8.985(5), b = 18.942(2), c = 10.114(1) Å, β = 104.40 (1)°, Z = 4, D_c = 2.88 g cm^{-3}, U = 1666.62 Å^3, $F(000)$ = 1464. The structure was solved by direct methods and refined by least-square using 2245 observed data [$F_0 > 3\sigma(F_0)$] out of a total of 2929, measured using a CAD4 diffractometer, operating in the $\omega/2\sigma$ scan mode with graphite monochromated Mo-K_α radiation. The final R, R_w values were 0.051, 0.076 for 201 parameters (non-hydrogens anisotropic, hydrogens isotropic). (**4**): $C_{20}H_{14}N_2S_8$, M = 538.82, monoclinic, a = 7.889 (1), b = 15.261 (1), c = 18.672 (1) Å, β = 100.80 (1)°, U = 2208.2 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.62 g cm^{-3}, μ(Cu-K_α) = 75.07 cm^{-1}, $F(000)$ = 1104. 4232 reflections measured, $1.5 < \theta < 65.0°$, CAD4 diffractometer, Cu radiation, λ(Cu-K_α) = 1.5418 Å, 3749 unique, 2434 observed [$I > 1.5\sigma(I)$]. Structure solved by direct methods, refined by least squares, non-hydrogens anisotropic, hydrogens isotropic, 307 parameters, weights $\omega = [\sigma^2(F_0) + 0.0009F_0^2]^{-1}$, R = 0.064, R_w = 0.078. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Triethyphosphite (1 ml) was added to macrocycle (**3**) (100 mg) in dry, degassed xylene (30 ml) and the mixture refluxed for 3 h. After cooling the resulting brown precipitate was collected, washed with ethanol, and air dried, to give (**4**) (20 mg, 22%) as a light brown solid which could be recrystallised from CH_2Cl_2; m.p. 90—92 °C (decomp.); i.r. (KBr) 2976, 2922, 1631, 1589, 1572, and 1451 cm^{-1}, ^{1}H n.m.r. ($CDCl_3$) δ 3.85 (d, 4H), 4.16 (d, 4H), 7.47 (d, 4H), and 7.77 (t, 2H): u.v. ($CHCl_3$) λ_{max} 240 (log ε 4.21), 262 (4.22), and 340 nm (3.85); *m/z* (EI) M^+ 538.



(a) (b)

Figure 1. Crystal structure of macrocycle (**3**). (a) ORTEP plot; (b) stereo view.



(a) (b)

Figure 2. Crystal structure of (**4**). (a) ORTEP plot; (b) stereo view.

(Scheme 1). There was no evidence of intermolecular coupling and, indeed, attempted reaction of (**3**) with 4,5-ethylenedithio-1,3-dithiole-2-thione gave none of the cross-coupled material and only macrocycle (**4**) and bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) (**6**) were isolated.

Colourless crystals of (**4**) were obtained from dichloromethane. The result of the crystal structure analysis‡ is shown in Figure 2 and indicates that, as in the parent macrocycle (**3**), the pyridine rings are oriented presumably to avoid nitrogen–nitrogen lone-pair interactions. The tetrathiafulvalene moiety is necessarily non-planar due to considerable ring strain. The planes defined by C(1), C(2), S(1), and S(5) and by C(11), C(12), S(3), and S(8) are inclined to the double bond C(3)–C(13) by approximately 45°. Despite this non-planarity cyclic voltammetry of (**2**) in 1,1,2-trichloroethane (0.1 M $\mathrm{Bu^t_4NClO_4}$, Pt working electrode, 200 mV s^{-1}) shows two reversible one-electron oxidation waves at +0.27 V and +0.57 V (*vs.* silver/silver chloride electrode). Interestingly, although Mullen *et al*[8] report a similar distortion of the tetrathiafulvalene unit in (**5**) (similarly defined planes to those described above being inclined at 49.5° and 47.6° to the central double bond), they also report that (**5**) shows one irreversible one-electron oxidation at 1.09 V.

The strained conformation of (**4**) necessitates that the sulphur lone pairs point out of the macrocycle making 1 : 1 metal ion complexation unlikely. For macrocycle (**3**), despite the apparent lack of pre-organisation, studies with molecular models suggest that re-organisation and subsequent metal cation complexation should be straightforward. Investigations into the metal complexing ability and the electronic properties of these novel macrocycles and related systems are continuing.

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References

1 G. Schukat, A. M. Richter, and E. Fanghanel, *Sulfur Reports*, 1987, **7**, 155; J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, and A. J. Schultz, *Prog. Inorg. Chem.*, 1987, **35**, 51.

2 K. Kikuchi, K. Murata, Y. Honda, T. Namiki, K. Saito, K. Kobayashi, T. Ishiguro, and I. Ikemoto, *J. Phys. Soc. Jpn.*, 1987, **56**, 4241, and references cited therein.

3 K. S. Varma, A. Bury, N. J. Harris, and A. E. Underhill, *Synthesis*, 1987, 837.

4 G. Steimecke, H. J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus Sulfur*, 1979, **7**, 49.

5 C. A. Salata, D. Van Engen, and C. J. Burrows, *J. Chem. Soc., Chem. Commun.*, 1988, 579; A. Carroy and J.-M. Lehn, *ibid.*, 1986, 1232; D. Parker, J.-M. Lehn, and J. Rimmer, *J. Chem. Soc., Dalton Trans.*, 1985, 1517; M. J. Gunter, L. N. Mander, K. S. Murray, and P. E. Clark, *J. Am. Chem. Soc.*, 1981, **103**, 6784; J.-M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441.

6 Tetrathiafulvalenes fused with crown ethers have been prepared, albeit in extremely low yield, by T. Otsubo and F. Ogura, *Bull. Chem. Soc. Jpn.*, 1985, **85**, 1343. Our own work on crown ether–tetrathiafulvalene cage molecules will be published shortly.

7 2,6-Bis(bromomethyl)pyridine was prepared in over 30% yield from 2,6-pyridine dicarboxylic acid according to the method of Cram *et al.*; M. Newcomb, J. M. Timko, D. M. Walba, and D. J. Cram, *J. Am. Chem. Soc.*, 1977, **99**, 6392.

8 J. Rohrich, P. Wolf, V. Enkelmann, and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1377.

9 A. Krief, *Tetrahedron*, 1986, **42**, 1209.