C4	0.3813 (3)	0.5068 (2)	0.16646 (12)	0.0230 (3)
C10	0.3888 (3)	0.3119 (2)	0.23590 (12)	0.0227 (3)
C11	0.1773 (3)	0.2861 (2)	0.30087 (13)	0.0284 (4)
C12	0.1998 (3)	0.1016 (2)	0.36339 (13)	0.0318 (4)
C13	0.4302 (3)	−0.0611 (2)	0.36167 (13)	0.0290 (4)
C14	0.6399 (3)	−0.0330 (2)	0.29695 (13)	0.0294 (4)
C15	0.6214 (3)	0.1514 (2)	0.23510 (13)	0.0264 (4)
C16	0.4486 (4)	−0.2635 (3)	0.4268 (2)	0.0411 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C4	1.225 (2)	C10—C15	1.386 (2)
N1—C4	1.356 (2)	C10—C11	1.388 (2)
N1—C1	1.425 (2)	C11—C12	1.388 (2)
C1—C2	1.386 (2)	C12—C13	1.388 (2)
C1—C3	1.389 (2)	C13—C14	1.383 (2)
C2—C3^{i}	1.386 (2)	C13—C16	1.511 (2)
C4—C10	1.502 (2)	C14—C15	1.387 (2)
C4—N1—C1	126.32 (13)	N1—C4—C10	115.04 (13)
C2—C1—C3	119.50 (13)	C15—C10—C11	118.94 (13)
C2—C1—N1	122.67 (13)	C15—C10—C4	117.62 (14)
C3—C1—N1	117.77 (13)	C11—C10—C4	123.43 (14)
O1—C4—N1	123.78 (13)	C4—O1—H1N^{ii}	164.2 (4)
O1—C4—C10	121.18 (13)		
C4—N1—C1—C2	−30.7 (2)	O1—C4—C10—C15	−28.2 (2)
C4—N1—C1—C3	151.96 (15)	N1—C4—C10—C15	151.60 (14)
C1—N1—C4—O1	−0.9 (3)	O1—C4—C10—C11	151.1 (2)
C1—N1—C4—C10	179.29 (13)	N1—C4—C10—C11	−29.1 (2)

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $1+x, y, z$.

All C-, N- and O-atom positions were refined with anisotropic displacement parameters. All C—H hydrogens were located from the difference map, placed in idealized positions and refined with fixed isotropic displacement parameters $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) at the phenyl rings and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) at the methyl groups, using a riding model with C—H distances of 0.95 and 0.98 Å, respectively. The position and isotropic displacement parameter of the H atom bound to nitrogen were refined. The methyl hydrogens were found disordered over two positions and were placed accordingly, with fixed site-occupation factors of 0.5.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1219). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Tetrameric Macrocycle with 2,5-Dithio-1,3,4-thiadiazole Subunits

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Abstract

The centrosymmetric molecule 40<[OS(2,5)1,3,4-thiadiazolo,S]$_4$-coronand-16> (alternative name: 10,11,21,22,32,33,43,44-octaaza-5,16,27,38-tetraoxa-2,8,13,19,24,30,35,41,45,46,47,48-dodecathiapentacyclo[40.2.1.1^{9,12}.1^{20,23}.1^{31,34}]octatetracontane), $C_{24}H_{32}N_8O_4S_{12}$, has its 40-membered ring, in which no cavity exists, in an extended conformation, with its maximum dimension approximately three times that of its minimum. Linkage of one of the two independent thiadiazole rings to the remainder of the molecule is *syn* to nitrogen on both sides, with N—C—S—C torsion-angle magnitudes of 0.8 (3) and 13.6 (4)°. The other thiadiazole ring has one linkage *syn* to nitrogen and one *anti* to nitrogen, with torsion-angle magnitudes of 31.3 (3) and 177.9 (3)°.

Comment

We have reported previously the structures of monomeric and dimeric macrocycles containing the 2,5-dithio-1,3,4-thiadiazole subunit, and also the structures of several of their transition metal complexes (Evans *et al.*, 1988; Cho, Fronczek, Taylor & Watkins, 1988; Bonomo, Bottino, Fronczek, Mamo & Pappalardo, 1989). The

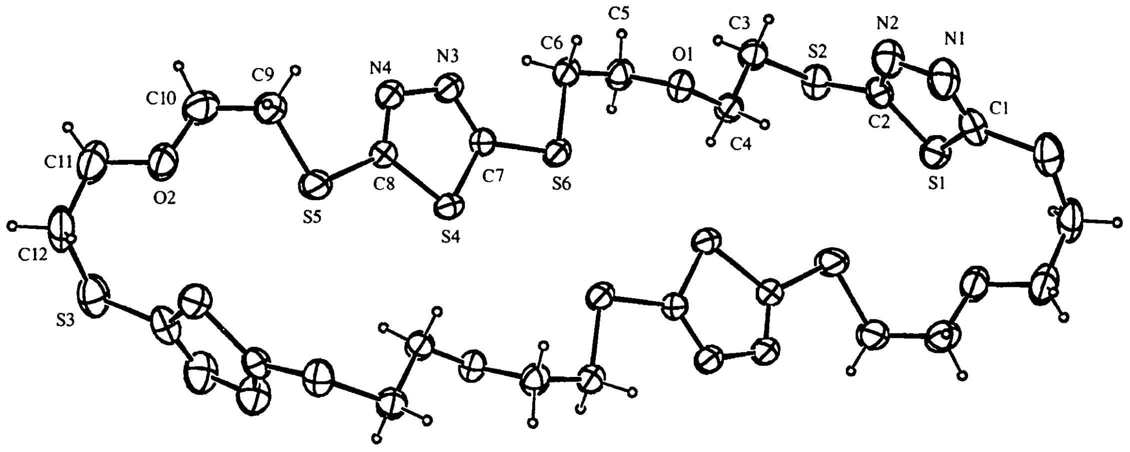
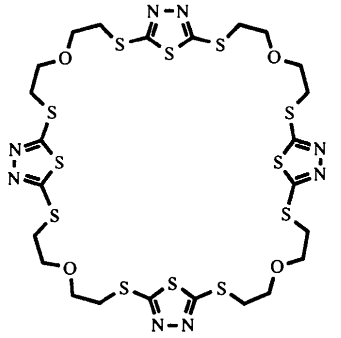


Fig. 1. The molecular structure of (I), with 30% probability ellipsoids and H atoms of arbitrary radii.

metal complexes are either monodentate through an N atom or bridging through both N atoms (Evans *et al.*, 1988; Bonomo *et al.*, 1989). Others have reported the structures of metal complexes of non-macrocyclic ligands containing this subunit (Castano *et al.*, 1989; Tandon, Thompson & Bridson, 1993; Tandon, Chen, Thompson & Bridson, 1994). Macrocycles in which the 2,5-dithio-1,3,4-thiadiazole subunits are joined by ethereal linkages have been prepared as dimers, trimers and tetramers (Pappalardo, Bottino, Tringali & Fronczek, 1987). The crystal structure of the dimer (Evans *et al.*, 1988) exhibits an extended conformation in which no cavity exists, while the trimer forms a cavity and stacks to form channels which serve as hosts for solvent molecules (Fronczek, Watkins & Pappalardo, 1987). We have determined the crystal structure of the tetramer, (I), containing a 40-membered ring, in order to determine which type of behavior it exhibits in the solid.



(I)

The structure of (I) is illustrated in Fig. 1. The molecule is centrosymmetric and exists in an elongated conformation with no cavity. The O—C bond distances are in the range 1.396 (5)–1.425 (3) Å, with a mean of 1.414 Å. The C—C distances are in the range 1.478 (5)–1.510 (4) Å, with a mean of 1.494 Å. Atom S6 has an intramolecular distance of 3.666 (1) Å to its inversion-related equivalent S6′ and a shorter distance of 3.551 (1) Å to S4′. Here and elsewhere, the prime refers to the symmetry operation $1-x$, $1-y$, $1-z$ [(i) in Table 2]. The molecule is approximately three times as long as it is wide. The C12· · ·C12′ distance is 20.888 (6) Å, while the C6· · ·C6′ distance is 7.148 (4) Å. The analogous dimer has a similar conformation, with no cavity (Evans *et al.*, 1988). In that structure, the elongated conformation is enabled by both *syn*- and *anti*-N—C—S—C linkages to the heterocyclic ring. Molecule (I) also exhibits this conformation for one of its heterocyclic rings. The N2—C2—S2—C3 torsion angle is −31.3 (3)°, while the N1—C1—S3′—C12′ torsion angle is 177.9 (3)°. The other independent heterocyclic ring has both linkages *syn* to the N atom, with torsion angles N3—C7—S6—C6 of −0.8 (3)° and N4—C8—S5—C9 of −13.6 (4)°. Mean bond distances involving the heterocyclic ring are N—N 1.389 (3), C=N 1.290 (2), C—S (endocyclic) 1.724 (2) and C—S (exocyclic) 1.741 (2) Å. The C—S—C angles within the thiadiazole are identical at 86.7 (1)°. These values agree well with those seen in related macrocycles.

The packing is illustrated in Fig. 2. The long axis of the molecule (C12· · ·C12′) is inclined at an angle of 29.57 (1)° from the **b** direction, which, in combination with the 2_1, yields the long symmetry axis.

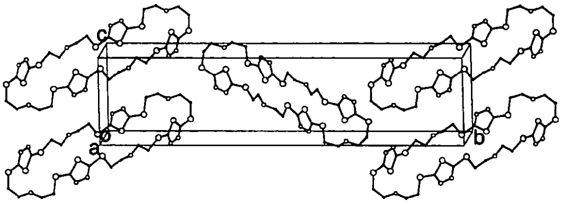


Fig. 2. View of the packing approximately down the **a** direction.

Experimental

The synthesis of the title compound has been described previously (Pappalardo *et al.*, 1987). Crystals were grown from a chloroform–ethyl acetate (9:1) solution (m.p. = 397.5–399.0 K).

Crystal data

$C_{24}H_{32}N_8O_4S_{12}$
$M_r = 881.3$
Monoclinic
$P2_1/n$
$a = 5.2230\ (7)$ Å
$b = 38.371\ (5)$ Å
$c = 9.417\ (1)$ Å
$\beta = 96.98\ (1)°$
$V = 1873.3\ (8)$ Å^3
$Z = 2$
$D_x = 1.562$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 17–29°$
$\mu = 6.9$ mm^{-1}
$T = 298$ K
Plate fragment
$0.40 \times 0.36 \times 0.18$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.221$, $T_{\max} = 0.288$
4167 measured reflections
3865 independent reflections

3454 observed reflections $[I > \sigma(I)]$
$R_{\rm int} = 0.037$
$\theta_{\max} = 74.90°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 48$
$l = -11 \rightarrow 11$
3 standard reflections frequency: 166 min intensity variation: increased 3.6%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.062$
$S = 1.731$
3454 reflections
218 parameters
H atoms: see below
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $3.1\ (1) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	−0.3630 (2)	0.31754 (2)	0.64658 (9)	0.0653 (2)
S2	−0.5732 (1)	0.36506 (2)	0.40645 (9)	0.0636 (2)
S3	0.9512 (2)	0.73949 (2)	0.2680 (1)	0.0892 (3)
S4	0.6537 (2)	0.55717 (2)	0.36122 (7)	0.0599 (2)
S5	0.9258 (2)	0.61195 (2)	0.21392 (9)	0.0866 (3)
S6	0.2641 (2)	0.49966 (2)	0.33909 (7)	0.0571 (2)
O1	−0.0078 (4)	0.42866 (5)	0.3023 (2)	0.0535 (5)
O2	1.0397 (6)	0.67735 (6)	0.0524 (3)	0.0853 (8)
N1	−0.0178 (6)	0.29754 (8)	0.4963 (4)	0.0840 (9)
N2	−0.1651 (6)	0.32173 (7)	0.4132 (3)	0.0766 (9)
N3	0.4150 (6)	0.53792 (6)	0.1224 (3)	0.0646 (7)
N4	0.5767 (6)	0.56501 (6)	0.0913 (3)	0.0679 (7)
C1	−0.0990 (6)	0.29240 (7)	0.6192 (4)	0.0667 (9)
C2	−0.3498 (6)	0.33382 (7)	0.4772 (3)	0.0543 (7)
C3	−0.3795 (6)	0.39006 (8)	0.2976 (3)	0.0639 (8)
C4	−0.1721 (5)	0.41064 (7)	0.3867 (3)	0.0529 (7)
C5	−0.1282 (6)	0.45816 (8)	0.2306 (3)	0.0604 (8)
C6	0.0708 (6)	0.48176 (7)	0.1835 (3)	0.0590 (8)
C7	0.4341 (5)	0.53146 (6)	0.2575 (3)	0.0486 (6)
C8	0.7088 (6)	0.57750 (7)	0.2046 (3)	0.0547 (7)
C9	0.9735 (8)	0.61737 (9)	0.0282 (4)	0.079 (1)
C10	0.8915 (9)	0.6522 (1)	−0.0270 (4)	0.088 (1)
C11	0.990 (1)	0.7116 (1)	−0.0005 (5)	0.104 (1)
C12	1.1118 (9)	0.73674 (8)	0.1098 (5)	0.096 (1)

Table 2. *Selected geometric parameters (Å, °)*

S1—C1	1.728 (3)	S5—C9	1.808 (4)
S1—C2	1.722 (3)	S6—C6	1.810 (3)
S2—C2	1.747 (3)	S6—C7	1.742 (3)
S2—C3	1.802 (3)	N1—N2	1.386 (4)
S3—C1$^{\rm i}$	1.738 (3)	N1—C1	1.296 (5)
S3—C12	1.799 (5)	N2—C2	1.285 (4)
S4—C7	1.723 (3)	N3—N4	1.393 (4)
S4—C8	1.724 (3)	N3—C7	1.288 (4)
S5—C8	1.736 (3)	N4—C8	1.290 (4)
C1—S1—C2	86.7 (2)	S1—C1—N1	113.7 (2)
C2—S2—C3	100.8 (1)	S3$^{\rm i}$—C1—N1	118.9 (3)
C1$^{\rm i}$—S3—C12	104.3 (2)	S1—C2—S2	120.1 (2)
C7—S4—C8	86.7 (1)	S1—C2—N2	114.9 (2)
C8—S5—C9	101.8 (2)	S2—C2—N2	125.0 (2)
C6—S6—C7	100.0 (1)	S4—C7—S6	119.4 (2)
N2—N1—C1	112.8 (3)	S4—C7—N3	114.6 (2)
N1—N2—C2	112.0 (3)	S6—C7—N3	126.0 (2)
N4—N3—C7	112.1 (2)	S4—C8—S5	118.5 (2)
N3—N4—C8	112.3 (2)	S4—C8—N4	114.3 (2)
S1—C1—S3$^{\rm i}$	127.2 (2)	S5—C8—N4	127.2 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The title structure was solved by direct methods. As individual refinement of H atoms did not lead to acceptable results in all cases, H atoms were placed in calculated positions with a C—H distance of 0.95 Å and $B_{\rm iso} = 1.3B_{\rm eq}$ for the bonded C atom.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN*.

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1223). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,5-Dibromocycloocta-1,5-diene

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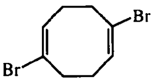
Abstract

The molecule of the title compound, $C_8H_{10}Br_2$, lies on a crystallographic twofold axis. The eight-membered ring has a twist-boat conformation in which the two olefin planes form a dihedral angle of 74.7 (1)° with one another. The C—Br distance is 1.928 (3) Å and the C=C distance is 1.314 (3) Å.

Comment

1,5-Dibromocycloocta-1,5-diene, (I), is a key intermediate in the preparation of the highly reactive 1,5-cyclooctadiyne. The crystal structure of the title compound was determined in order to confirm its identity, as well as to determine the conformation of its eight-membered ring.



(I)

The molecular structure of (I) is shown in Fig. 1. The molecule lies on a crystallographic twofold axis. The cyclooctadiene ring has a twist-boat conformation, identical to that of *syn*-3,7-dibromocycloocta-1,5-diene, which also lies on a twofold axis in the crystal (MacKenzie, MacNicol, Mills, Raphael, Wilson & Zabkiewicz, 1972). The mean difference in the four endocyclic torsion angles defining the eight-membered ring conformation is 1.7° when comparing the structure of (I) with that of MacKenzie *et al.* This is less than the uncertainties of their determination, which was based on film data. There is also excellent agreement with the twist-boat conformation found for unsubstituted cycloocta-1,5-diene by gas-phase electron diffraction (Hagen, Hedberg & Hedberg, 1982). The mean endocyclic torsion-angle deviation when (I) is compared with unsubstituted cycloocta-1,5-diene is 2.7°, well within the limits of error of that experiment.

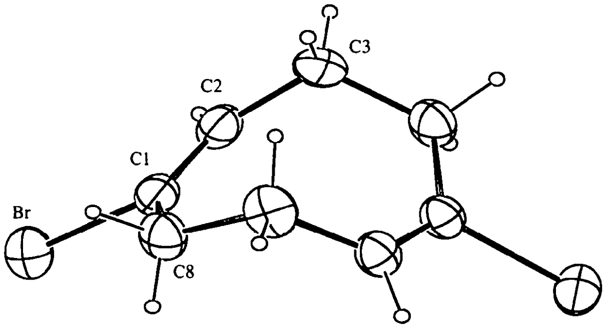


Fig. 1. The molecular structure of (I) shown with 40% probability ellipsoids and H atoms of arbitrary radius.

The five atoms defining the olefin plane (C_4Br) are coplanar within a maximum deviation of 0.013 (4) Å (for C3). This plane is tilted at an angle of 37.4 (1)° to the **b** direction and, thus, the two olefin planes related by the twofold axis form a dihedral angle of 74.7 (1)°. This angle is identical to the value of 74° reported for *syn*-3,7-dibromocycloocta-1,5-diene (MacKenzie *et al.*, 1972).

The C—Br distance in (I) is longer than expected. The standard value for C_{sp^2}—Br distances found by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) is 1.883 Å and the upper quartile is 1.894 Å. Kaftory (1983) finds an average value of 1.888 Å for bromoolefins. Our distance is thus 0.043 (3) Å longer than the expected value. We have, however, found a number of well determined structures containing the C=C—Br moiety for which the C—Br distances agree well with ours. Examples are 1.922 (5) Å in 11-bromo-