

C6—C7 bonds, although this axis cannot be exact since C2—C3 is a double bond and C10—C11 is single.

Molecular-mechanics calculations performed on cyclododecene rings with *XICAMM* (a program resembling standard main-frame programs with modifications to allow it to run on an IBM PC-AT desk computer; Bruger, 1986) supported the indications of flexibility in that several different conformational minima of similar energy were found. These conformers had torsion angles similar to the measured values for the bonds from C1 through C5 and also retained the near planarity of C5 through C8 but had different *gauche* conformations in the rest of the ring. An exhaustive search for all possible conformational energy minima seems beyond the scope of this paper. A model based on the observed crystal conformation changed somewhat after molecular-mechanics refinement in that the torsion angles of the C1—C2 and C3—C4 bonds became less nearly equal at 166 and 89°, respectively. The changes might be attributed to the omission of the camphanate moiety from the calculations but, since there are no close contacts between the ring and camphanate atoms in the crystal, intermolecular packing forces may also be important and may also make the choice of the crystal conformation from among the possible conformers. There could be a dynamic equilibrium among two or more conformations in the less restrictive environment of the solutions used for CD measurements. The conformation of the present (*E*)-cyclododecene is quite different from that calculated for the (*Z*) isomer by Anet & Rawdah (1979) which closely resembles the cyclododecane conformation described by Dunitz & Shearer (1960).

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## Structure of a 1-Oxa-6,6a $\lambda^4$ -dithia-2,5-diazapentalene

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**Abstract.** 5-Oxa-2,5a $\lambda^4$ ,6-trithia-4,7-diazacyclohexa-[*cd*]pentalene, C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>OS<sub>3</sub> (2),  $M_r = 204.3$ , triclinic,  $P\bar{1}$ ,  $a = 8.158$  (3),  $b = 8.892$  (2),  $c = 11.517$  (4) Å,  $\alpha = 68.11$  (2),  $\beta = 88.91$  (3),  $\gamma = 80.20$  (2)°,  $V = 763.0$  (4) Å<sup>3</sup>,  $Z = 4$  (two crystallographically independent molecules),  $D_x = 1.78$  Mg m<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda =$

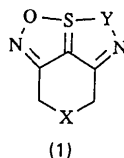
1.54178 Å,  $\mu = 8.33$  mm<sup>-1</sup>,  $F(000) = 416$ , room temperature,  $R = 0.051$  for 1773 observed reflections with  $|F_o| > 3\sigma(|F_o|)$ . On comparing the structure of (2) with those of related heteropentalenes, the gross molecular structure remains virtually unperturbed. However, the replacement of one of the O atoms in the fused

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heteropentalene by an S atom results in a dramatic increase in the S—O bond length from 1.85 to 2.08 Å. The layered crystal structure of (2) contains short intralayer intermolecular non-bonded N...S distances.

**Introduction.** Recently, we have reported the electrochemical properties of a number of dioxathiadiaza heteropentalenes (Camilleri, Clark, Gilmore & Cole-Hamilton, 1985) and oxadithiadiaza heteropentalenes (Camilleri, Gilmore & Cole-Hamilton, 1985). We have also investigated (Camilleri, Rzepa, Slawin & Williams, 1989) the X-ray crystal structures of three heteropentalene derivatives of type (1), having  $X = S$ , SO and  $SO_2$  and  $Y = O$ .



Here we report the X-ray crystal structure of (2) ( $X = Y = S$ ) and compare the structural features of this molecule with those of the corresponding dioxathiadiaza derivative (3) ( $X = S$ ,  $Y = O$ ) (Camilleri *et al.*, 1989). The half-peak reduction potentials (*vs* Ag—AgCl) of (2) and (3) have been measured as  $-473$  and  $-643$  mV, respectively (Camilleri, Clark, Gilmore & Cole-Hamilton, 1985; Camilleri, Gilmore & Cole-Hamilton, 1985). We have tried to interpret this difference in the electrochemical reduction of these molecules in terms of their chemical structure.

**Experimental.** Single crystals of (2), suitable for X-ray crystallography, were grown at room temperature from a solution in cyclohexane and had m.p. 414 K. Crystal size  $0.04 \times 0.05 \times 0.11$  mm. Refined unit-cell parameters obtained from setting angles of 15 reflections with  $8 \leq \theta \leq 27^\circ$ . Nicolet R3m diffractometer. 2062 independent reflections ( $\theta \leq 58^\circ$ ) measured, Cu  $K\alpha$  radiation (graphite monochromator),  $\omega$  scan. 1773 [ $|F_o| > 3\sigma(|F_o|)$ ] considered observed, index range  $h -8/8$ ,  $k -8/8$ ,  $l 0/12$ ; two check reflections measured every 50 reflections, net count constant; Lorentz and

Table 1. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*$
S(1)	750 (2)	372 (2)	-3300 (1)	53 (1)
C(2)	683 (7)	1959 (7)	-2666 (5)	51 (2)
C(3)	-716 (6)	1951 (6)	-1811 (4)	43 (2)
C(4)	-2274 (6)	1554 (6)	-2027 (4)	40 (2)
C(5)	-2613 (7)	1076 (7)	-3040 (4)	45 (2)
C(6)	-1360 (7)	979 (7)	-3974 (5)	54 (2)
N(7)	-534 (5)	2336 (6)	-825 (4)	53 (2)
S(8)	-2185 (2)	2354 (2)	13 (1)	57 (1)
S(9)	-3809 (2)	1629 (2)	-1034 (1)	48 (1)
O(10)	-5072 (4)	869 (5)	-2207 (4)	60 (2)
N(11)	-4089 (6)	697 (6)	-3114 (4)	56 (2)
S(1')	5076 (2)	4349 (2)	3768 (1)	55 (1)
C(2')	5562 (7)	3018 (8)	2884 (5)	56 (3)
C(3')	4106 (6)	3173 (6)	2042 (5)	43 (2)
C(4')	2458 (6)	3388 (6)	2429 (4)	38 (2)
C(5')	2005 (6)	3595 (6)	3559 (4)	41 (2)
C(6')	3249 (7)	3541 (8)	4501 (5)	54 (2)
N(7')	4373 (5)	3043 (6)	962 (4)	51 (2)
S(8')	2707 (2)	3115 (2)	153 (1)	57 (1)
S(9')	889 (2)	3429 (2)	1456 (1)	46 (1)
O(10')	-566 (4)	3845 (5)	2860 (3)	54 (2)
N(11')	403 (5)	3866 (6)	3759 (4)	51 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

polarization corrections, analytical absorption correction (face-indexed crystal) with minimum and maximum transmission factors of 0.34 and 0.51. Structure solved by heavy-atom method; non-H atoms refined anisotropically; positions of all H atoms calculated ( $C-H = 0.96$  Å); H atoms assigned isotropic thermal parameters,  $U(H) = 1.2 U_{eq}(C)$ , and allowed to ride on parent C atoms. An empirical extinction correction was applied [ $g = 0.004$  (1)]. Refinement using  $F$  magnitudes by block-cascade full-matrix least squares;  $R = 0.051$ ;  $wR = 0.054$  [ $w^{-1} = \sigma^2(F) + 0.00078F^2$ ],  $S = 1.63$ ,  $(\Delta/\sigma)_{max} = 0.050$ ; residual electron density in difference map within  $-0.46$  and  $0.47$  e Å $^{-3}$ ; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

**Discussion.** The structure of (2) with atom numbering is shown in Fig. 1. Table 1\* lists the fractional atomic coordinates of the non-H atoms and Table 2 compares the bond lengths and angles of (2) with those of (3). The geometries of the two independent molecules do not differ significantly; the r.m.s. deviation for the fit of the non-H atoms in one molecule against those in the other is 0.017 Å. Excluding S(1), both molecules are essentially planar with a maximum deviation from their mean

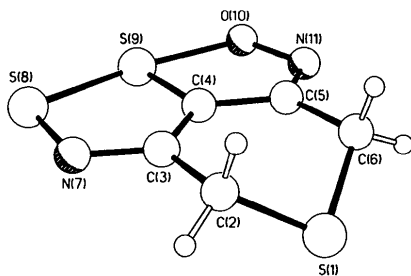


Fig. 1. The molecular structure of (2) giving the atom numbering.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51482 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

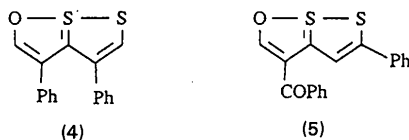
Table 2. Comparative bond lengths (Å) and angles (°) for (2) and (3) with e.s.d.'s in parentheses

In both compounds atoms denoted by primes refer to crystallographically independent molecules.

	(2)	(3)		(2)	(3)		(2)	(3)
S(1)—C(6)	1.810 (6)	1.810 (4)	S(1)—C(2)	1.808 (7)	1.816 (4)	C(2)—C(3)	1.492 (8)	1.492 (5)
C(3)—C(4)	1.425 (8)	1.393 (5)	C(3)—N(7)	1.319 (8)	1.321 (5)	C(4)—C(5)	1.428 (9)	1.407 (5)
C(4)—S(9)	1.690 (5)	1.665 (3)	C(5)—C(6)	1.486 (8)	1.494 (5)	C(5)—N(11)	1.317 (8)	1.308 (5)
N(7)—S(8)	1.643 (5)	1.346 (5)	S(8)—S(9)	2.134 (2)	1.849 (3)	S(9)—O(10)	2.078 (5)	1.849 (3)
O(10)—N(11)	1.343 (7)	1.358 (5)	S(1')—C(6')	1.821 (6)	1.830 (4)	S(1')—C(2')	1.822 (8)	1.818 (4)
C(2')—C(3')	1.503 (8)	1.490 (5)	C(3')—C(4')	1.413 (7)	1.400 (4)	C(3')—N(7')	1.302 (8)	1.312 (4)
C(4')—C(5')	1.415 (8)	1.404 (4)	C(4')—S(9')	1.704 (5)	1.659 (3)	C(5')—C(6')	1.481 (8)	1.483 (4)
C(5')—N(11')	1.320 (7)	1.313 (4)	N(7')—S(8')	1.641 (5)	1.350 (4)	S(8')—S(9')	2.149 (2)	1.849 (3)
S(9')—O(10')	2.093 (4)	1.843 (3)	O(10')—N(11')	1.322 (7)	1.351 (4)			
C(2)—S(1)—C(6)	97.3 (3)	99.6 (2)	S(1)—C(2)—C(3)	111.7 (4)	110.1 (3)	C(2)—C(3)—C(4)	122.1 (5)	121.2 (3)
C(2)—C(3)—N(7)	119.9 (5)	124.3 (3)	C(4)—C(3)—N(7)	118.1 (5)	114.5 (3)	C(3)—C(4)—C(5)	123.5 (5)	128.2 (3)
C(3)—C(4)—S(9)	118.9 (4)	116.1 (3)	C(5)—C(4)—S(9)	117.6 (4)	115.7 (3)	C(4)—C(5)—C(6)	122.1 (5)	120.3 (3)
C(4)—C(5)—N(11)	117.5 (5)	115.0 (3)	S(1)—C(6)—C(5)	112.4 (4)	111.0 (2)	C(6)—C(5)—N(11)	120.4 (6)	124.8 (3)
C(3)—N(7)—S(8)	115.3 (4)	110.7 (3)	N(7)—S(8)—S(9)	98.5 (2)	113.8 (2)	C(4)—S(9)—S(8)	89.1 (2)	84.8 (2)
C(4)—S(9)—O(10)	82.1 (2)	85.0 (1)	S(8)—S(9)—O(10)	171.2 (1)	169.9 (1)	S(9)—O(10)—N(11)	110.2 (3)	113.7 (2)
C(5)—N(11)—O(10)	112.6 (5)	110.6 (3)	C(2')—S(1')—C(6')	97.1 (3)	100.9 (2)	S(1')—C(2')—C(3')	111.3 (4)	111.3 (2)
C(2')—C(3')—C(4')	120.9 (5)	121.8 (3)	C(2')—C(3')—N(7')	119.4 (5)	123.5 (3)	C(4')—C(3')—N(7')	119.6 (5)	114.7 (3)
C(3')—C(4')—C(5')	124.9 (5)	128.2 (3)	C(3')—C(4')—S(9')	117.8 (4)	116.1 (2)	C(5')—C(4')—S(9')	117.3 (4)	115.7 (2)
C(4')—C(5')—C(6')	122.7 (4)	121.2 (3)	C(4')—C(5')—N(11')	117.8 (5)	114.8 (3)	S(1')—C(6')—C(5')	111.6 (4)	111.4 (2)
C(6')—C(5')—N(11')	119.6 (5)	124.0 (3)	C(3')—N(7')—S(8')	115.6 (4)	110.5 (3)	N(7')—S(8')—S(9')	97.8 (2)	113.9 (2)
C(4')—S(9')—S(8')	89.1 (2)	84.8 (1)	C(4')—S(9')—O(10')	81.8 (2)	85.1 (1)	S(8')—S(9')—O(10')	170.5 (1)	169.9 (1)
S(9')—O(10')—N(11')	109.9 (3)	113.9 (2)	C(5')—N(11')—O(10')	113.3 (5)	110.5 (3)			

planes of 0.03 and 0.05 Å respectively. S(1), S(1') are 0.89 Å from these planes.

The S—S bond length in (2) [2.134 (2) and 2.149 (2) Å]\* is close to the value 2.10 Å, usually associated with an S—S single bond in a *cis* planar sulfide group (Hordvik, 1966). However, the S—O distance [2.078 (5) and 2.093 (4) Å] is more than 20% greater than the sum of the covalent radii of S and O, 1.71 Å (Hordvik, 1966). Furthermore, it is considerably greater than the equivalent S—O distance in (3) [1.849 (3) Å] (Camilleri *et al.*, 1989). Similar long S—O distances have been reported for related structures, such as (4) and (5) (Hansen, Hordvik & Sæthre, 1975).



The effect of replacing O(8) in (3) by S to give (2), and the associated significant increases in the S(9)—X(8) and S(9)—O(10) distances, gives rise to predictable changes in the angles in the two fused five-membered rings: reduction of the angles at O(10) and S(8), and increases in angles at N(7), N(11), C(3), C(5) and C(4). However, the overall changes in the conformation of the six-membered ring are small, there being only a small reduction in the non-bonded C(2)···C(6) distance, 2.72, 2.73 Å *cf.* 2.77, 2.81 Å in (3) and no change in the transannular S(1)—C(4) distance.

\* The two values of bond lengths refer to the two crystallographically independent molecules of (2) in the asymmetric unit. The same is also the case for (3).

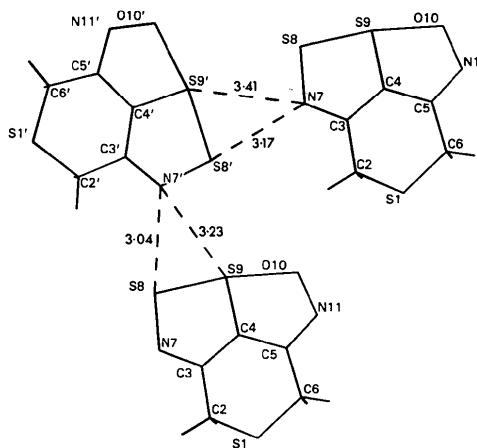


Fig. 2. Short intrasheet intermolecular N...S contacts (Å) in the structure of (2).

From ESR measurements (Camilleri, Gilmore & Cole-Hamilton, 1985) it appears that reduction of the heteropentalene ring system involves the acceptance of an electron by C(4). Although the replacement of one of the O atoms in the fused five-membered moiety of (2) by S does not appear to introduce much strain into the six-membered ring system, it is noticeable that significant changes in the bond angles occur around C(4). The three bond angles about C(4) in (2) are closer to 120° than the corresponding angles in (3). These differences are expected to make delocalization in the eight- $\pi$ -electron system more facile in (2) than in (3). This conclusion is also supported by the red shift observed in the wavelength of maximum absorption of the two molecules. Heteropentalene (2) absorbs visible light at 451 nm in methanol/water (3:1 v/v) whereas molecule

(3) absorbs at 353 nm under the same conditions (Camilleri, Gilmore & Cole-Hamilton, 1985).

The more positive reduction potential for (2) in relation to (3) may be due to the S in the heteropentalene moiety being more electron withdrawing than O. This is consistent with Hammett  $\sigma$  values for substituents such as SH ( $\sigma_p = 0.15$ ) and OH ( $\sigma_p = -0.37$ ) or SCH<sub>3</sub> ( $\sigma_p = 0.00$ ) or OCH<sub>3</sub> ( $\sigma_p = -0.27$ ).

The molecules in crystals of (2) pack in parallel sheets but with no short interlayer contacts. There are, however, some notable intrasheet non-bonded intermolecular S...N contacts (Fig. 2) between crystallographically independent molecules. The shortest contacts are S(8)...N(7')\*, 3.04 Å, and S(8')...N(7)\*, 3.17 Å. These can be ascribed to weak  $d\pi-\pi$  interactions.

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## Structural Studies of Some Benzodiazepines. I. The Structure of 3-(Benzylamino)-4,5-dihydro-1H-2,4-benzodiazepine Hydrochloride (1)

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**Abstract.** C<sub>16</sub>H<sub>18</sub>N<sub>3</sub><sup>+</sup>.Cl<sup>-</sup>,  $M_r = 287.8$ , orthorhombic,  $P2_12_12_1$ ,  $a = 11.474$  (2),  $b = 22.212$  (2),  $c = 5.810$  (1) Å,  $V = 1480.7$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $\lambda(\text{Cu K}\alpha) = 1.54178$  Å,  $\mu = 22 \text{ cm}^{-1}$ ,  $D_x = 1.2909$  (3) g cm<sup>-3</sup>,  $F(000) = 624$ . Diffractometer data at room temperature.  $R = 6.15\%$  for 1641 reflections with  $I > 3\sigma(I)$ , max.  $\Delta/\sigma = 1.772$ . The benzodiazepine ring has an envelope conformation; both diazepine N atoms are protonated – compound (1) exists in the ionic form, stabilized by hydrogen bonds between all N atoms and the Cl ion.

**Introduction.** The wide range of biological activity of derivatives of 3-amino-2,4-benzodiazepine (2) is the main reason for the many chemical and pharmacological studies of these compounds. For example, 3-amino-4,5-dihydro-1H-2,4-benzodiazepine (Rodríguez, Zitho & de Stevens, 1968) and its derivatives

(Ciba Ltd, 1970) act on coronary vasa and show bacteriostatic activity. Other compounds of this type, synthesized by Schnettler & Suh (1975), had in pharmacological tests a depressive effect on the central nervous system. This variety of properties of these and similar compounds prompted our studies of several new benzodiazepines, which should enable us to design the most pharmacologically favourable derivative of (2).

The title compound, (1), was obtained with good efficiency by the method described by Schnettler & Suh (1975), introducing necessary modifications (Brzezińska, unpublished data). In preliminary pharmacological tests it acted as tranquilizer and also showed some neuroleptic activity.

**Experimental.** Colourless needle-shaped crystals (0.3 × 0.5 × 0.8 mm) from ethanol at room temperature. Diffraction data measured on a CAD-4 dif-