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THE CONFORMATION OF A CONSTRAINED EIGHT-MEMBERED RING.[1]

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An X-ray investigation was undertaken on 5-methyl-1-thia-5-azacyclooctane-1-oxide perchlorate (1) (I), in order to ascertain the nature of the hydrogen bonding, and also to determine the conformation of the eight-membered ring. At at early stage in the investigation, we discovered that there is an alteration in crystal structure in going from room temperature (25°) to the temperature of a cold room (3°). We have determined the crystal structure under each set of conditions. Further details of these analyses and the relationship between the two forms will be given elsewhere (2). At present, we shall describe those of our results which will be of most general interest and shall limit our remarks to the crystal form existing at 3°, as the more accurate analysis has been possible on this form.

At 3°, 5-methyl-1-thia-5-azacyclooctane-1-oxide perchlorate crystallizes in the monoclinic system, with

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a = 9.87 Å., b = 8.78 Å., c = 13.26 Å., and β = 97°54'. These dimensions correspond to a unit cell volume of 1138.5 x 10^{-24} c.c., and there are four molecules of $C_7H_{16}O_5NSCl$ in the unit cell. Systematically absent reflexions indicate that the space group is $P2_1/c$ (C^5_{2h}). Intensity data were collected by photographic methods (CuK_α radiation) and 1298 non-zero intensities were recorded. The progress of the analysis will be described in full later (2). Least squares refinement gave an R-factor of 0.115, and, at this stage, a three-dimensional difference map was computed and peaks were found at or near the expected locations of the hydrogen atoms. Inclusion of hydrogen atoms at these positions gave a final discrepancy index of 0.092.

The bond distances involving the atoms other than hydrogen are given in Table II, and agree within experimental error with accepted values (3). The estimated standard deviation for a S-C bond is 0.013 Å., for a C-C bond is 0.017 Å., and for a Cl-O bond is 0.010 Å. A line drawing of the molecule is given in Fig. 1. This shows that the conformation of the eight-membered ring in this compound is best described as a "boat-chair" (BC) form (4,5) (II), rather than the "extended crown" form (III) found by Dunitz and Prelog (6) for azacyclooctane hydrobromide (IV), and postulated by Sands and Day (7) for cyclooctane at 0° on the basis of low order X-ray reflexions. A definite peak in the difference map was found between the nitrogen atom and the oxygen of the sulfoxide. The position of this peak suggests that the hydrogen atom is almost symmetrically placed between O and N, and the N-H-O angle

TABLE I

Atomic Coordinates in Fractions of the Unit Cell Edge

	x	y	z
S(1)	0.6850	0.0641	0.5220
C(2)	0.8618	0.1447	0.5426
C(3)	0.8676	0.3117	0.5509
C(4)	0.8297	0.4107	0.4582
N(5)	0.6762	0.3969	0.4145
C(6)	0.6502	0.3143	0.3143
C(7)	0.7144	0.1571	0.3168
C(8)	0.6647	0.0366	0.3849
O(9)	0.5920	0.1988	0.5418
C(10)	0.6048	0.5493	0.4027
Cl	0.1702	0.2652	0.3192
O(11)	0.0789	0.3723	0.2665
O(12)	0.1267	0.2271	0.4153
O(13)	0.3015	0.3321	0.3388
O(14)	0.1751	0.1270	0.2638

TABLE II

	Bond Length (Å)	Torsion Angle (τ)	Symbol
S(1) - C(2)	1.869 ± 0.012	+98°40'	+ac
C(2) - C(3)	1.472 ± 0.020	-72°36'	-sc
C(3) - C(4)	1.510 ± 0.017	+65°48'	+sc
C(4) - N(5)	1.551 ± 0.013	-109°23'	-ac
N(5) - C(6)	1.504 ± 0.014	+54°45'	+sc
C(6) - C(7)	1.518 ± 0.018	+64°9'	+sc
C(7) - C(8)	1.515 ± 0.018	-62°21'	-sc
C(8) - S(1)	1.818 ± 0.012	-41°48'	-sc
S(1) - O(9)	1.542 ± 0.008		
N(5) - C(10)	1.511 ± 0.015		
Cl - O(11)	1.419 ± 0.012		
Cl - O(12)	1.439 ± 0.008		
Cl - O(13)	1.414 ± 0.010		
Cl - O(14)	1.423 ± 0.011		

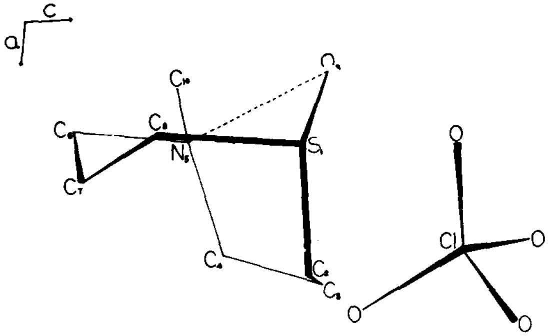


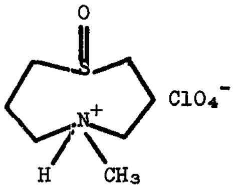
FIG. I

Line Drawing of the Molecule, viewed down the b-axis. The hydrogen bond is indicated by the discontinuous line.

is 157°. The location of hydrogen atoms in this analysis must be considered imprecise, but we feel that there is some evidence for a rather symmetrical hydrogen bond in this molecule which is in keeping with the low frequency (1) for the $\overset{+}{N}$-H vibration observed in the infrared spectrum. The transannular $\overset{+}{N}$----O distance is 2.64 Å, which is shorter than most reported values for $\overset{+}{N}$----O hydrogen bonds (8), although a few such short distances have been recorded (9,10). There are several possible causes for the difference in conformation between the present compound and azacyclooctane. The long bonds involving the sulfur atom and the presence of the intramolecular hydrogen bond are two factors not present in azacyclooctane.

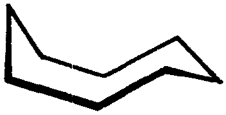
A virtually identical conformation was found in the crystal form stable at 25°, although the molecular packing has altered considerably. It would seem unlikely, therefore, that crystal forces are an important factor in determining the conformation of this molecule in the solid state.

In order to define the conformation of the ring, we have calculated the equations of various important planes by a least squares technique (11), and also calculated various angles of importance. The angle between the plane containing the atoms C_4, N_5, and C_6 and the plane containing the atoms C_8, S_1, and C_2 is 33°54'. The average standard deviations for the least squares plane containing the atoms S_1, C_2, C_4, N_5, and for the plane containing the atoms S_1, C_6, N_5, C_8 are 0.027 Å. in each case. These are the planes corresponding to the four supposedly near-planar atoms in the constituent "boat" and "chair" forms making up conformation II. The atoms C_{10}, N_5, S_1, and O_9 lie on a plane with an estimated standard deviation of 0.023 Å. The hydrogen atom of the hydrogen bond should lie on or near this plane. Finally, adopting the notation of Klyne and Prelog (12), we have calculated the angle of torsion (τ) between the substituents on each pair of bonded atoms in the ring. These values and the appropriate symbol are given in the second and third columns of Table I.

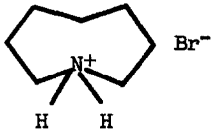


I

III



II



IV

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