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CRYSTAL AND MOLECULAR STRUCTURE OF 1-ACETONYL-1-THIONIA-5-THIACYCLOOCTANE PERCHLORATE[1]

Suzanne M. Johnson and Iain C. Paul[2]

Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois 61801

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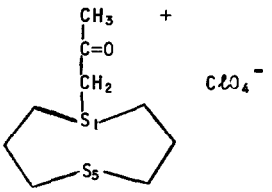
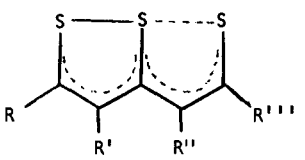
The reaction of acetone with the perchlorate of 1,5-dithiacyclooctane-1-oxide leads to a crystalline salt, $C_9H_{17}OS_2^+Cl\mathcal{O}_4^-$. Spectroscopic evidence led to the proposal of structure (I) for this salt and comparison of the mode of formation of the derivative with that for other acetonyl derivatives of sulfur compounds indicated a specific role for S(5) in the reaction.[3,4,5] An X-ray single crystal analysis has been carried out on the salt to verify the structural assignment, to provide information on any S---S interaction, which might cast light on the participation of S(5) in the reaction, and to study the conformation of the eight-membered ring.



(I)



(II)

The transparent needles of (I) belong to the orthorhombic system with $\underline{a}$ = 13.67 ± 03, $\underline{b}$ = 9.12 ± 0.04, and $\underline{c}$ = 21.09 ± 05 Å (MoK_{α}, λ = 0.7107 Å) at 25°C. The measured density,

$\underline{\rho}$ = 1.51 g cm^{-3}, indicates that there are eight molecules of $C_9H_{17}OS_2^+ \cdot C\ell O_4^-$ ($\underline{Fw}$ = 304.8) in the unit cell. Systematic absences, $\underline{h0\ell}$, when $\underline{\ell} = 2\underline{n} + 1$, $\underline{hk0}$, when $\underline{h} = 2\underline{n} + 1$, and $0\underline{k\ell}$ when $\underline{k} = 2\underline{n} + 1$, indicate that the space group is $\underline{Pbca}$ $\underline{D_{2h}^{15}}$ (No. 61). A total of 1270 independent reflexions was obtained by visual estimates of equi-inclination Weissenberg photographs ($\underline{CuK_\alpha}$ radiation). The structure was solved by symbolic addition methods[6] and has been refined, incorporating anisotropic temperature factors for the atoms of the anion, to an $\underline{R}$-factor of 0.14 on all observed reflexions. The structure of the cation is shown in Figure 1.

The structure (I) is confirmed for the salt and the eight-membered ring is seen to be in the boat-chair (BC) conformation[7]. While there are several instances where crystallographic disorder prevents definite conclusions from being drawn,[8,9,10] $\underline{trans}$-1,2-cyclooctanedicarboxylic acid,[11] dimeric cyclooctanone peroxide,[12] and a thiaazacyclooctane derivative[13] have been shown to exist in the BC conformation. A twisted crown conformation has been found in $\underline{trans,syn,trans}$-1,2,5,6-tetrabromocyclooctane.[14] There is evidence for only small energy differences among several conformations in the eight-membered ring series.[7,15,16]

The transannular S---S distance is 3.13 Å, which is considerably shorter than twice the van der Waals radius for sulfur (3.70 Å)[17], but is also much longer than the "long" S---S distances (2.47-2.57 Å) found in thiathiophthen derivatives (II)[18]. The intramolecular S---O contact is 2.80 Å; comparison with the sum (3.25 Å) of the van der Waals radii,[17] and the carbonyl group orientation, which minimises the S---O distance, would imply some attractive interaction between the sulfur and oxygen atoms. This distance is somewhat longer than the examples of S---O distances (2.38-2.70 Å) found in 5-atom conjugated systems[19], and may indicate simply a strong ion-dipole interaction. The bond lengths and angles in the acetonylthionia portion of the molecule correspond to the generally-accepted values for the various types of distance and angle.[20]

The full details of the analysis and the relevance of these structural results to the chemistry of the 1-acetonyl-1-thionia-5-thiacyclooctane cation will be published elsewhere.

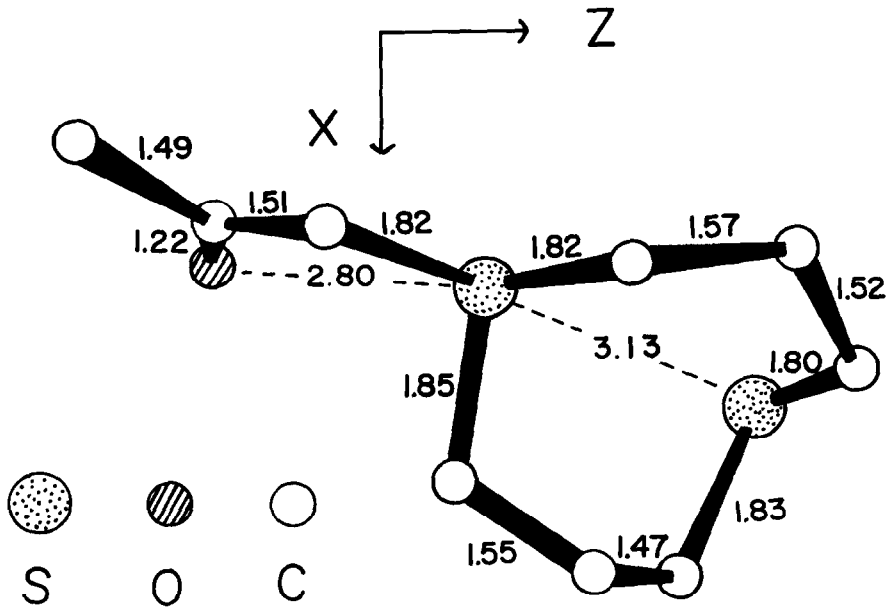


FIG. 1

View of the 1-acetonyl-1-thionia-5-thiacyclooctane cation looking down the b-axis. Bond distances (Å) are marked.

REFERENCES AND NOTES

(1) Work supported by USPH GM 12470-04 and NSF GP-8407 X.

(2) Alfred P. Sloan Research Fellow.

(3) A. E. Yethon, Ph.D. Thesis, University of Illinois, 1963.

(4) N. J. Leonard, J. A. Klainer, and A. E. Yethon, in preparation.

(5) Carbonyl-heteroatom interactions have been indicated in phosphorus ylids, A. W. Johnson and R. T. Amel, Can. J. Chem., 46, 461 (1968), and implicated in sulfur ylids, A. F. Cook and J. G. Moffatt, J. Am. Chem. Soc., 90, 740 (1968); see also D. Darwish and R. L. Tomilson, J. Am. Chem. Soc., 90, 5938 (1968).

(6) J. Karle and I. L. Karle, Acta Cryst., 21, 849 (1966).

(7) See, for example, J. B. Hendrickson, J. Am. Chem. Soc., 86, 4854 (1964).

(8) D. E. Sands and V. W. Day, Acta Cryst., 19, 278 (1965).

(9) J. D. Dunitz and V. Prelog, Angew. Chem., 72, 896 (1960). Further examination of the X-ray results on azacyclooctane hydrobromide suggests that the structure is disordered, J. D. Dunitz, personal communication.

(10) An X-ray study of the structure of diazacyclooctane dihydrobromide indicates crystallographic disorder, J. S. McKechnie and I. C. Paul, unpublished data.

(11) J. D. Dunitz and A. Mugnoli, Chem. Commun., 166 (1966); M. Dobler, J. D. Dunitz and A. Mugnoli, Helv. Chim. Acta, 49, 2492 (1966).

(12) P. Groth, Acta Chem. Scand., 19, 1497 (1965); 21, 2695 (1967).

(13) K. T. Go and I. C. Paul, Tetrahedron Letters, 4265 (1965); I. C. Paul and K. T. Go, J. Chem. Soc. Sect. B, in press.

(14) G. Ferguson, D. D. MacNicol, W. Oberhansli, R. A. Raphael, and J. A. Zabkiewicz, Chem. Commun., 103 (1968).

(15) J. B. Hendrickson, J. Am. Chem. Soc., 89, 7036 (1967).

(16) F. A. L. Anet and M. St. Jacques, ibid., 88, 2585, 2586 (1966).

(17) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N. Y., 1960, 3rd Ed., p. 260.

(18) A. Hordvik, E. Sletten, and J. Sletten, Acta Chem. Scand., 20, 2001 (1966); S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, Chem. Commun., 1170 (1967).

(19) For a discussion of such structures, see J. A. Kapecki, J. E. Baldwin, and I. C. Paul, J. Am. Chem. Soc., 90, 5800 (1968).

(20) O. Kennard, "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1962, volume III, pp. 275-276.