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THE X-RAY ANALYSIS OF SPARTEINE-N_{16}-OXIDE SESQUIPERCHLORATE, $(C_{15}H_{26}N_2O)_2.3HClO_4$

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In 1964 P. Baranowski, J. Skolik and M. Wiewiorowski (1) proposed a structure for sparteine-N_{16}-oxide sesquiperchlorate on the basis of the chemical behaviour and IR spectra. They postulated the presence of symmetrical hydrogen bonding in the sesquication.

Since the evidence could not be considered as unequivocally establishing the structure, a detailed X-ray study was suggested by Dr. M. Wiewiorowski, who has supplied the crystals suitable for this investigation. They were found to belong to the space group of the orthorhombic system, $P2_12_12$. There are four molecules of the alkaloid and six perchlorate ions per unit cell. Four perchlorate groups were found in general positions, but the other two were placed on two-fold axes parallel to the c axis. The unit cell dimensions are: a = 18.01, b = 12.47 and c = 8.14 Å. The intensities of 1894 reflections were measured visually from equi-inclination Weissenberg photographs using the multiple film technique.

The positions of the chlorine atoms were obtained from the sharpened three dimensional Patterson synthesis. The molecular structure was solved from several Fourier summations having started with the heavy-atom method. No chemical assumptions were made. The atomic parameters were subsequently refined by block diagonal least squares calculations using the programs written by F.R. Ahmed for the IBM/360 system. All atoms were refined anisotropically with the exception of the hydrogen atoms.

A schematic representation of the (001) projection is given in Fig. 1.

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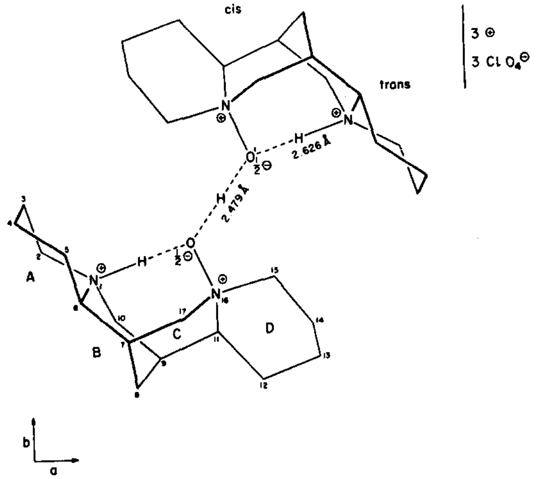

Fig. 1. The structure of sparteine-N_{16}-oxide sesquiperchlorate along the c axis, showing the hydrogen bonds.

The coordinates of the hydrogen atoms were calculated assuming the values of 1.07 and 1.03 Å for the C-H and N-H bond lengths respectively. The B factor was taken as 5.0 Å^2. The hydrogen atoms were used in structure factor calculations but their positions have not been refined, with the exception of the hydrogen between the oxygen atoms.

The final value of the reliability index, R, was 0.096.

The molecular structure of α-isosparteine, which is made up of two trans-quinolizidine systems, has been solved by X-rays in 1953 (2). This study represents the first analysis of a cis-trans C_{15} lupine alkaloid.

The oxygen atom was found to be attached to the nitrogen atom of the cis-quinolizidine system. This result, although indicated by chemical and physico-chemical studies, needed confirmation.

All the rings are in the chair conformation. This is in agreement with the postulate of P.J. Krueger and J. Skolik (3) who examined the NMR spectra. It is interesting that in sparteine and its derivatives in solution the inversion of N_{16} can readily take place transforming the ring C into a boat form (4,5).

The hydrogen between the oxygen atoms was found on electron density maps to be situated on the two-fold axis, which is parallel to the c axis and passes through the centre of the O...O' line. The hydrogen atom is displaced from the centre of the O...O' line by 0.19 Å. In view of the large estimated standard deviation of the z coordinate of the hydrogen atom (0.13 Å), this displacement is not significant, but it is of interest that it leads to a value of 113.4° for the N_{16}-O...H angle, which is closer to a tetrahedral value, than that of the N_{16}-O...O' angle of 116.7°.

The distance between the oxygen atoms is 2.479 Å with estimated standard deviation of 0.008 Å. J.C. Speakman obtained the weighted mean of 2.446 Å for seven crystallographically symmetrical O...H...O bonds (6). The deviation from Speakman's value can be taken as possibly significant as it corresponds to the probability smaller than 5% (7).

The existence of disorder with hydrogens with half occupancy on either side of the two-fold axis seems to be precluded, as the B factor has refined to a value of 2.66 $Å^2$. The r.m.s. amplitude of thermal vibration is therefore 0.18 Å, whereas a minimum value of 0.27 Å would be required by the presence of O-H bonds of 0.97 Å.

The N_1...O distance was found to be 2.626 Å (e.s.d. 0.007) and the hydrogen attached to the nitrogen atom was located on the three-dimensional difference synthesis.

The results of this investigation will be published in greater detail elsewhere.

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