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Hydrogen bonding and the zwitterion structure of taurine.

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Very recently Sutherland & Young (1963) described the results of their determination of the crystal and molecular structure of taurine, $H_2N.CH_2.CH_2.SO_3H$. Their refinement was carried out by three-dimensional least squares, and included the determination of individual isotropic temperature factors for the C, N, O, and S atoms. At an intermediate stage, a three-dimensional difference synthesis was computed, and it was stated that this synthesis clearly indicated the positions of the hydrogen atoms: the four attached to the carbon atoms were very close to the calculated positions; two more were attached to the nitrogen atom, and the seventh to an oxygen atom. After the inclusion of the hydrogen atoms, apparently at the positions of the peaks in the difference map, the least-squares refinement was continued, without, however, allowing the hydrogen parameters to vary. In the subsequent discussion of the results, only two hydrogen bonds were mentioned, namely, N–H · · · O(2), of length 2·78 Å and N–H · · · O(4), of length 2·89 Å, with C–N···O angles of 100° and 111° respectively.

I wish to point out that there is an alternate interpretation to this structure. Although Sutherland & Young stated that 'there was, however, no evidence in the three-dimensional difference Fourier synthesis for the existence of the "zwitterion" configuration', the zwitterion structure is, in fact, almost certainly the correct one for this high-melting (328 °C), alcohol-insoluble substance. It may be recalled that the zwitterion structure has been found for every amino acid yet studied, and that the sulfonic acid group is a much stronger acid than is the carboxyl group. Also, it is well known that difference maps prepared by the use of data in which the positions of the heavy atoms were incompletely refined, and for which only isotropic thermal motions were allowed, often show spurious peaks, or peaks which are far from the positions expected for hydrogen atoms. In the present case it is therefore reasonable to discount the evidence provided by the difference synthesis, and to examine the structure solely on the basis of the heavy atom positions.

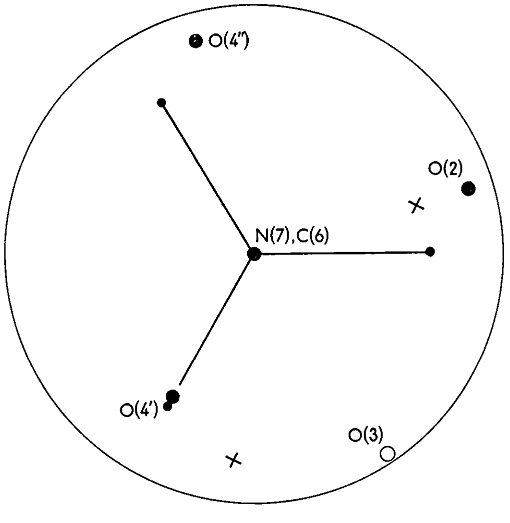

Fig. 1. Stereogram of the environment of the $-NH_3^+$ group, viewed down the N–C bond. Small black circles denote positions for hydrogen atoms in a regular tetrahedral $-NH_3^+$ group. Crosses denote positions for the hydrogen atoms given by Sutherland & Young. All of these, and the three oxygen positions denoted by large black circles, project in the upper hemisphere; O(3) projects in the lower hemisphere.

The close neighbors of the nitrogen atom were presented in Fig. 4 of Sutherland & Young. Examination of the geometry of these shows that an N · · · O(3) distance (of 3·03 Å), together with the two N · · · O distances mentioned above, comprise an entirely satisfactory system expected for an $-NH_3^+$ group forming three hydrogen bonds. This situation is clearly shown in Fig. 1, which is a stereographic projection of the surroundings of the nitrogen atom, as viewed down the N–C bond. The relevant angles are presented in Table 1. Both the distances and the angles are in the range of those found in amino acids and related compounds, as reported in the reviews by Donohue (1952) and Fuller (1959). The oxygen atom (O(3)), situated at 2·97 Å from the nitrogen atom, is seen to be unfavorably located for N–H · · · O interaction. An N · · · O distance of 3·0 Å is not unexpected for a simple van der Waals contact.

Table 1. *Angles related to* NH · · · O *hydrogen bonds*

C–N · · · O(2)	100°	O(2) · · · N · · · O(4')	127°
C–N · · · O(4')	111	O(2) · · · N · · · O(4'')	88
C–N · · · O(4'')	97	O(4') · · · N · · · O(4'')	127

C, N at (x, y, z); O(2) at $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$; O(4'') at $(1-x, \bar{y}, \bar{z})$; O(4') at $(\bar{x}, \bar{y}, \bar{z})$.

Additional evidence that the hydrogen atom under discussion is not part of the sulfonic acid group is found in the virtual equality reported for the three S–O distances: these are S–O(2) = 1·479 ± 0·008, S–O(3) = 1·453 ± 0·008, and S–O(4) = 1·463 ± 0·009 Å. If one of these oxygen atoms were covalently bonded to a hydrogen atom, the corresponding S–O distance would be expected to be about 0·1 Å longer than the other two; however, the coordinates given by Sutherland & Young for the hydrogen atoms lead to an O(3)–H bond — but the S–O(3) bond is the shortest of the three. Furthermore, these coordinates correspond to an O(3)–H bond distance og 0·79 Å and an S–O(3)–H bond angle of 76°, neither of which values is close to those expected.

All of the above evidence indicates that in the crystal taurine has the zwitterion structure, $H_3N^+–CH_2–CH_2–SO_3^-$, and that the hydrogen bonding scheme fits satisfactorily into the well established properties of such bonds.

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