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LIBRATIONAL MOBILITY OF THE METHYL GROUP IN N-ACETYLGLYCINE

by

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Refinement by Donohue and Marsh (1) of the earlier X-ray film data (2) on N-acetylglycine permitted derivation of a three-dimensional difference synthesis which placed the non-methyl hydrogen atoms in specific locations. For the remaining three hydrogen atoms of the methyl group, the evidence was interpreted as indicative of rotational disorder about the bond, C(3) - C(4), Fig. 1. [In (1), this situation was approximated by disposing 12 one-quarter hydrogen atoms at equal separations around the circle corresponding to the disorder path of the H atoms.] Similar conclusions appear to have been reached by Peterson, Levy and Schomaker (3) from analysis of neutron diffraction data, although no subsequent detailed account of this work has appeared.

As part of a proposed study of the detailed electron-density distribution of N-acetylglycine, a new set of neutron diffraction data has been measured and the analysis of this data allows a clearer identification of the state of the methyl group hydrogens.

The three-dimensional neutron intensity data, judged from the measurement of the equivalent reflexions to be of reasonable precision, were collected on single-crystal diffractometers, installed on the HIFAR reactor at the Australian Atomic Energy Commission Establishment. Intensities for 977 of a possible 1149 terms, equivalent to the CuKα limit for X-rays, having values above the incoherent scattering background, were measured from a crystal of volume, $24.8 \times 10^{-3} cm^3$. An approximate linear absorption coefficient, $\mu = 1.73\ cm^{-1}$, was determined and applied to the measured intensities to take account of absorption and incoherent scattering by the N-acetylglycine crystal. Starting from the positional parameters for C, N and O in (1), these were refined with the neutron data using a standard least-squares procedure. Difference synthesis then revealed the sites of all hydrogen atoms and further refinement with anisotropic temperature factors yielded a final index, $R = \sum|F_o|-|F_c|/\sum|F_o|$, of 0.044 for the observed terms.

While the heavy atom and non-methyl hydrogen atom features are in accord with the earlier studies (the molecule, apart from the five tetrahedral hydrogen atoms, was found to be planar to within ± 0.07 Å), the detail concerning the three methyl hydrogen atoms, H(5), H(6) and H(7) is different. These are clearly defined in space about the C(3) - C(4) bond. They are not freely rotating as presumed earlier, although there is some evidence of libration of relatively limited range. Examples of other fixed methyl hydrogen atoms in relation to comparable acetyl groups are provided in the X-ray crystal structures of N,N-diphenylacetamide (4) and acetanilide (5,6).

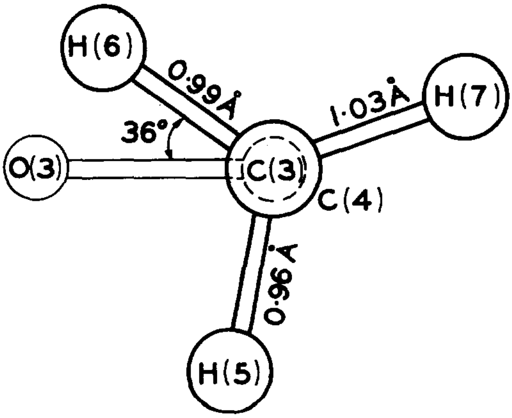

Fig. 1. View of the acetyl group in N-acetylglycine looking down the C(3) - C(4) bond showing bond lengths involving H atoms. These values have not been corrected for anisotropic thermal vibrations.

It is of interest to note that H(7), with the highest peak value of the three methyl hydrogens, is close to an acetyl oxygen and a carbonyl oxygen of the carboxyl group of two adjacent molecules, with approach distances of 2.62 and 2.52 Å respectively, indicative of non-bonded interactions. H(5) and H(6) have no corresponding close approaches and appear to have greater mean vibrational amplitude to judge from the peak values, both approximately 2/3 that of H(7). As shown in Fig. 1, the conformation of the methyl group is such that the dihedral angle O(3)C(3)C(4)H(6) is 36.0°, i.e. intermediate between eclipsed and staggered. The result is somewhat different from that expected on the basis of the ideas of Owen and Sheppard (7,8) on intramolecular interactions in such groups which may be more applicable to the isolated molecule whereas the details in N-acetylglycine may reflect the additional factor of intermolecular packing forces.

Microwave spectral studies of a number of organic compounds including propionaldehyde (9) and methyl vinyl ketone (10) have led to estimations of the height of the potential barrier hindering the internal rotation of methyl groups in the related molecule. Typical values range from 1070 - 2280 cal/mole (11). The existence of barriers of this magnitude in the gas phase, compounded in the crystal by intermolecular forces, would suggest that freely rotating methyl groups are likely to be rather exceptional in crystal structures at room temperature. The present evidence, in rectifying the impression of earlier work, lends support to this view.

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