

slightly higher than those at the other sampling sites. This may be the result of a temperature effect, that is, a warming of the rain as it falls through the atmosphere. This warming effect did not occur to any great extent in the mountain rain samples of Hawaii, or at the NRL sampling site. A measurable degree of warming was observed for some of the CPO daytime rain samples, however. To determine the possible effect of this warming on the precision of our field data, a series of six consecutive rain samples was collected at CPO during a 1-hour heavy rainfall. Treating these as replicate samples, we obtained relative standard deviations of ± 8 and ± 30 percent for the methane and carbon monoxide results, respectively. However, the recorded temperature spread in these samples at the time of sampling was 21° to 26°C . It is clear that this warming effect, when it occurs, introduces an additional source of variability in the rainwater data. This warming effect is sufficient to explain the variations in the methane results, but not in the carbon monoxide data. The wide spread of the latter values in Table 1 must be attributed to other causes.

In the case of the atmospheric samples collected in the vicinity of cities, pollution is the most probable cause of the widespread variations in the carbon monoxide data. In the case of the unpolluted Pacific air, however, the range of values shown is significantly greater than what can be explained in terms of the precision of our method; we believe this to be due to diurnal variations in the quantity of carbon monoxide released to the atmosphere by the ocean (1, 4). The atmospheric concentrations of carbon monoxide in the interior of Hawaii upwind of active volcanic sites appear to be typical of unpolluted marine air.

The high degree of carbon monoxide supersaturation in the rainwater is difficult to explain. Since a progressive decrease in the degree of supersaturation can be expected as the rain falls through the atmosphere, we suggest that the sources of the excess carbon monoxide are in the region where the rain is first formed in the clouds.

Recent investigations indicate the presence of organic matter in rainwater at concentrations between 2 and 12 mg/liter (9). Wilson *et al.* have shown (10) that the photochemical oxidation of organic matter in seawater leads to the formation of carbon monoxide. The highest concentration of car-

bon monoxide found in our Hawaiian rainwater samples was 6×10^{-4} mg/liter. It is evident that there is an abundant excess (more than a thousand-fold) of dissolved organic carbon in rain available for photochemical reactions which could lead to the production of carbon monoxide.

Electric discharges within the clouds may also lead to a slight dissociation of carbon dioxide. It is well known that ion recombination processes and corona discharges from charged droplets occur within the precipitation regions of clouds (11), and that chemical dissociation of carbon dioxide takes place in an electric discharge. Although it is unlikely that the dissociation of carbon dioxide in itself could account for the amounts of carbon monoxide found in the rainwater, the process may nevertheless be a contributing factor. However, in the absence of supporting data, these suggestions must be regarded as highly speculative, and further field investigations are required to confirm or refute such mechanisms.

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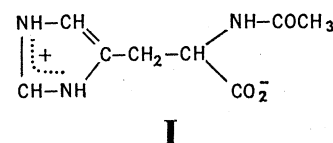
Crystal Structure of L-N-Acetylhistidine Monohydrate: An Open and Closed Case

Abstract. L-N-Acetylhistidine crystallizes from aqueous solution as the monohydrate. The crystals are triclinic, space group $P1$, with two formula units per cell. The structural solution was accomplished by direct methods. The two independent molecules have very different conformations, one open and one closed. These two conformations are compared with those found in other histidine structures.

The amino acid histidine is of particular importance in enzyme chemistry because of the frequency with which it is found to be associated with active sites. In particular, histidine seems to be directly involved in the proteolysis mechanisms of papain, subtilisin (subtilopeptidase A), chymotrypsin, trypsin, and other proteolytic enzymes. With crystal-structure results for several of these enzymes becoming available, it is now feasible to study the mechanism of proteolysis by model building based on electron density Fourier maps. For such purposes, reliable knowledge of the geometry of the histidine residue, including its conformational features, is necessary.

The crystal structures of L-histidine

hydrochloride (1), L-histidine (2), and DL-histidine hydrochloride (3) have previously been reported. The histidine moieties in these structures show major conformational differences, being in an extended, "open" form in crystals of L-histidine and DL-histidine hydrochloride and in a compact, "closed" form in L-histidine hydrochloride. We here report briefly on a derivative of histidine, L-N-acetylhistidine (I), which crystallizes as a mixture of two conformers, one open and one closed.



Crystals of L-N-acetylhistidine, as the monohydrate, were obtained from aqueous solution. The crystal system is triclinic, space group *P*1, with the following cell constants: $a = 8.865$ Å, $b = 9.097$ Å, $c = 7.346$ Å, $\alpha = 102.24^\circ$, $\beta = 90.30^\circ$, $\gamma = 117.73^\circ$, and cell volume (V) = 508.75 Å³. There are two independent molecules per cell. Intensity data were collected with nickel-filtered copper K α radiation on a Dtex-automated General Electric quarter-circle diffractometer. A total of 2152 independent intensities were measured.

The structural solution was obtained by the use of direct methods. An initial E-map based on a symbolic addition-

tangent refinement sequence indicated the position of 13 atoms (of which eight turned out to be correct). Further analysis with the use of this partial structure information, tangent refinement, and Fourier and difference Fourier techniques successfully produced the complete structure. Full-matrix least-squares analysis has led to an *R* value (4) of 0.029.

The molecules exist in the solid as zwitterions with protonation of the imidazole rings (I). With some minor exceptions, the bond distances and angles in the two molecules are in agreement to within the experimental error (about 0.005 Å and 0.1° for the heavy atoms). However, the two molecules

have grossly different conformations.

If the acetyl function is excluded, there are three single bonds which permit conformational freedom: C₁–C₂, C₂–C₃, and C₃–C₄. Views along these three bonds are shown in Fig. 1. For both molecules the torsion angle about C₁–C₂ lies in the range found in other histidine compounds (1–3) and in most amino acids [see, for example, (5)]. Similarly, the torsion angles about C₃–C₄ are nearly equal and the conformation is the expected one with C₂ displaced from the plane of the imidazole ring. It is the torsion angle about C₂–C₃ that differentiates between the two conformers. The angle of -44° found in molecule A, which gives rise to the “closed” conformation of the molecule, is close to the value -52° found in L-histidine hydrochloride (1); “open” conformations, with torsion angles similar to that of molecule B, are found in L-histidine [180° (2)] and DL-histidine hydrochloride [179° (3)].

We see, then, that there are at least two principal conformations of the histidine molecule. Moreover, the occurrence of both conformers in the same crystal gives clear indication that there can be little energy difference between the two—surely no more than could be gained by packing and hydrogen bonding interactions. Model-building studies should take this conformational freedom into careful account (6).

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4. The *R* value is defined as follows:

$$R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$
 where *F* is the structure factor.
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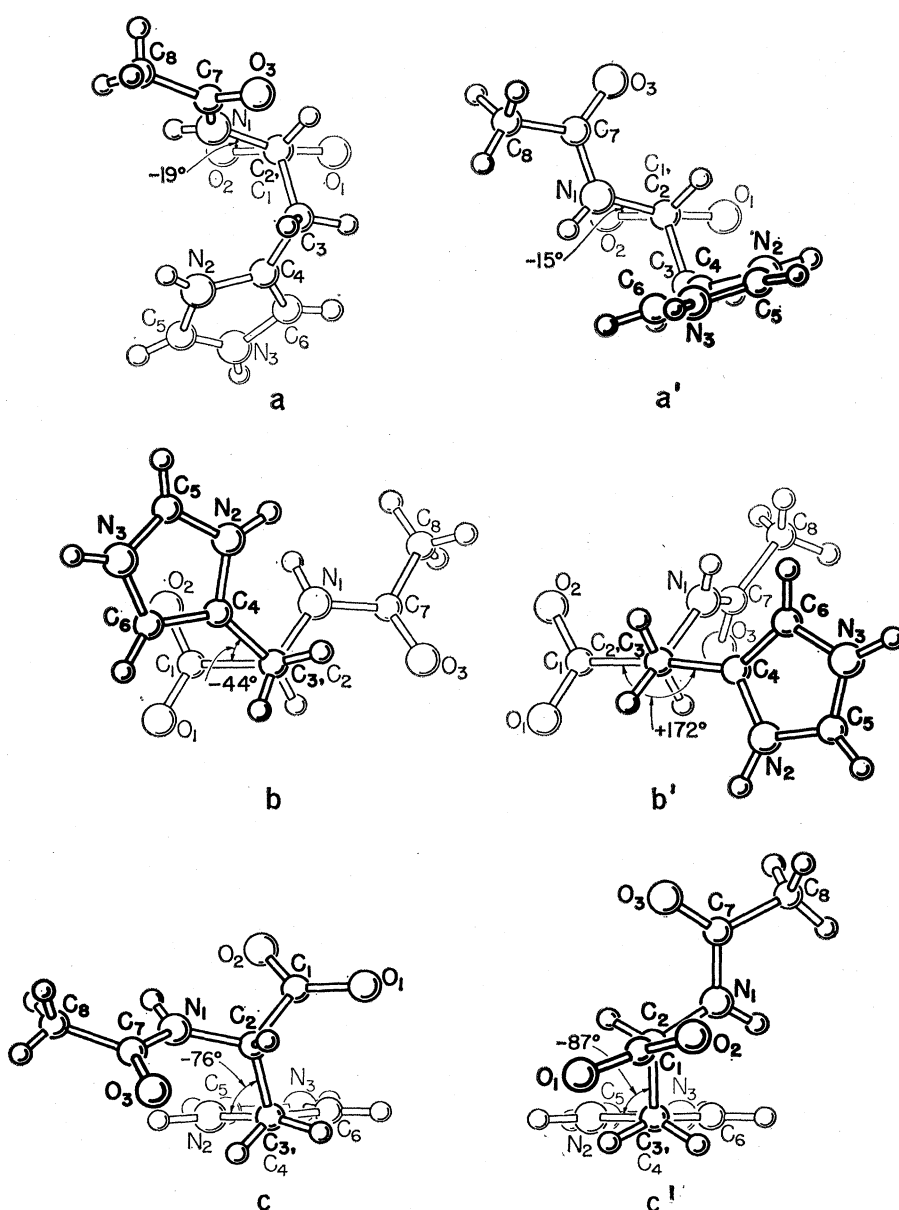


Fig. 1. An illustration of various conformation angles in N-acetylhistidine. Molecule A is represented in the left column and molecule B in the right column. The various views are: views a and a', down C₂–C₁; views b and b', down C₃–C₂; and views c and c', down C₄–C₃. The signs of the torsion angles are as described by Brown and Levy (7).