

Hydrogen Bonding in Dileucine Hydrochloride (with Reference to Triglycine Sulphate)

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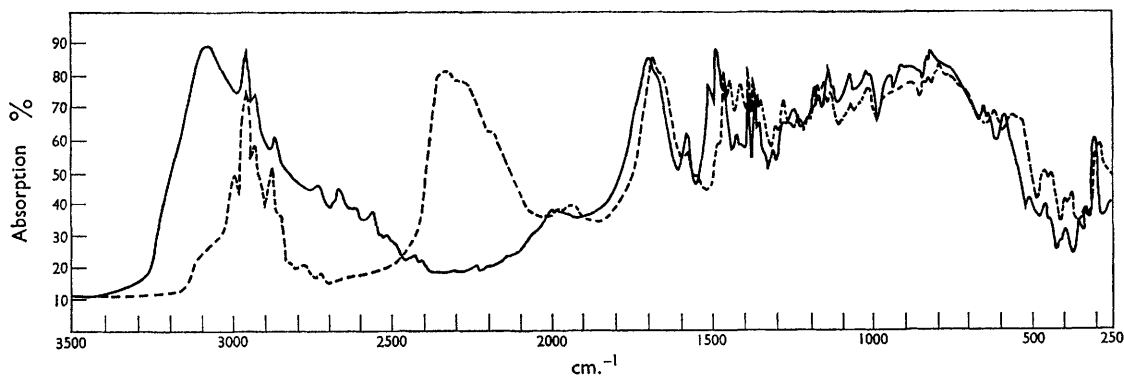
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THE hydrogen bonding in glycine adducts of the type $(\text{Gly})_2\text{HX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$) and $(\text{Gly})_3\text{H}_2\text{Y}$ ($\text{Y} = \text{SO}_4, \text{SeO}_4$) has been investigated by infrared spectroscopy and other physical methods.¹⁻⁸ There is general agreement about the existence of asymmetrical bonding in the first group, *i.e.*, that it is possible to observe separately the glycinate and the zwitterion on a time base of molecular vibrations.^{1,3} There is a discrepancy concerning the second type³⁻⁶ which is particularly interesting because triglycine sulphate is an important ferroelectric. The shortness of the hydrogen bond (2.44 Å) connecting a glycine and a glycinate residue⁷ is indeed in the range where symmetrical hydrogen bonds are possible. The spectroscopic differentiation between such a bond and a similarly short,

but double-minimum type of hydrogen bond as, for example, in $(\text{Gly})_2\text{HBr}$ would be assisted by having an amino-acid adduct with a symmetrical hydrogen bond for comparison. Dileucine hydrochloride⁹ $[(\text{Leu})_2\text{HCl}]$ shows an infrared spectrum (Figure) which is very similar to those of acid salts of carboxylic acids containing symmetrical or nearly symmetrical hydrogen bonds.^{10,11} The carbonyl band near 1680 cm^{-1} has two components one of which shifts by 20 cm^{-1} to lower frequencies on deuteration. There is no obvious band attributable to the asymmetrical stretching of a carboxylate group; the bands of the coupled C-OH stretching and CO-H deformation which are readily detectable in the spectra of *e.g.*, $(\text{Gly})_2\text{HCl}$ cannot be identified in that of $(\text{Leu})_2\text{HCl}$. But the very broad and



FIGURE

Infrared spectra of dileucine hydrochloride. Full line: normal; dashed: partly deuterated (mulls in Nujol and hexachlorobutadiene).

strong absorption in the region between 1300 and 400 cm^{-1} , interrupted with transmission "windows" appears as clearly as in the spectra of other substances which may contain symmetrical hydrogen bonds. We conclude that the structure* of $(\text{Leu})_2\text{HCl}$ can schematically be given as $(\text{H}_3\text{N}^+\cdot\text{C}_5\text{H}_{10}\cdot\text{CO}_2^-\cdots\text{H}\cdots-\text{O}_2\text{C}\cdot\text{C}_5\text{H}_{10}\cdot\text{N}^+\text{H}_3)^+\cdot\text{Cl}^-$ and that the hydrogen bond connecting the two

zwitterions is close to the symmetric type. It is obvious even without detailed assignments that the spectrum of triglycine sulphate is not showing the characteristic features of such hydrogen bonds neither in the ferroelectric nor in the paraelectric phase^{3,5,8} and therefore its short hydrogen bond is not of the symmetrical type.

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* Under investigation by X-ray diffraction.

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