Letters to the Editor

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HYDROGEN BONDING IN N-METHYL FORMAMIDE

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In our earlier work (1952), we have calculated the shifts in the OH and NH stretching frequencies of alcohols and amides, treating hydrogen bonding as an electrostatic interaction. In these calculations it is assumed that the ionic character of the NH bond diminishes due to intermolecular associations. In this communication, the shift in the NH stretching frequency of N-methyl formamide due to intermolecular associations of the type N-H...O = C is calculated and compared with the experimentally observed value.

The infrared spectra of N–methyl formamide have been recorded with Perkin-Elmer IR Double beam Spectrophotometer Model 21, with NaCl optics. The bonded NH stretching absorption has been recorded by pressing a drop of the liquid between two plates of NaCl so as to form a microfilm of unknown thickness. The free NH stretching frequency of the amide was recorded in dilute solutions of CCl_4 with matched cells of 0.94 mm thickness. The bonded and free NH stretching frequencies, thus recorded are 3290 cm^{-1} and 3484 cm^{-1}.

The bond lengths used in these calculations are (Katz, 1957) $d(N–H) = 0.995$ Å, $d(N–CH_3) = 1.47$ Å, $d(C–N) = 1.29$ Å, $d(C–H) = 1.094$ Å, $d(C = O) = 1.23$ Å and $d(N–H...O) = 2.83$ Å. The bond moments of the various linkages are the same as reported earlier (1962).

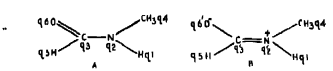

Fig. 1

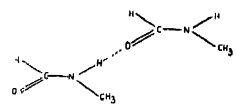

Fig. 2

In N-methyl formamide there are two possible resonance structures as shown in Fig. 1.

The unbalanced charges in e.s.u. on various atoms in these two structures are also indicated in Fig. 1 and are calculated as earlier (1962). They are

$$q_1 = 1.3\times10^{-10}, \quad q_2 = -0.46\times10^{-10}, \quad q_3 = -0.13\times10^{-10}.$$
$$q_4 = 0.88\times10^{-10}, \quad q_5 = 0.36\times10^{-10} \quad q_6 = -1.95\times10^{-10}$$
$$q'_2 = -1.2\times10^{-10} \quad q_3' = -0.69\times10^{-10}, \quad q_6' = -0.65\times10^{-10}.$$

The percentage of double bond character of C = O and C–N bonds in this amide are 88 per cent and 70 per cent respectively. The unbalanced charge on the oxygen atom is therefore -1.79×10^{-10} e.s.u. and that on the nitrogen atom is -0.99×10^{-10} e.s.u.

The intermolecular associations in N-methyl formamide are as shown in Fig. 2. The ratio of the electrostatic force F_1 on the hydrogen atom due to hydrogen bonding to F_2 due to charge inequality in the NH groups is given as

$$F_1/F_2 = 1.79\times(0.995)^2/(1.853)^2\times0.99 = 0.537 \tag{1}$$

The fractional reduction ionic character of the *NH* bond, due to intermolecular associations is $22.1\times(F_1/F_2)$. The dissociation energy D' of the bonded NH linkage is then given by

$$D' = 93.4-22.1\times(F_1/F_2) \tag{2}$$

where 93.4 Kcal/mole is the dissociation energy of the free NH linkage. D' thus obtained is 81.7 Kcal/mole. The dissociation energy of the free NH linkage, the reduced mass of the NH group and the free NH stretching frequency of *N*-methyl formamide are used in

$$\nu = a/\pi c(D/2M)^{\frac{1}{2}}-a^2h/4\pi^2Mc \tag{3}$$

to obtain the constant 'a'. Its value is 2.43×10^8 in cm^{-1}. Using the value of D' and 'a' in equation (3) the bonded NH stretching frequency of *N*-methyl formamide is obtained as 3200 cm^{-1}. It is seen the calculated and the observed values agree very well.

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