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ON THE OCCURRENCE OF HYDROGEN BONDING IN C-ALKYL- AND C-HALOGEN- FORMAZANS

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MUCH effort was directed also recently[1,4] towards the location of azo-group stretching vibration in different types of molecules, but the problem is still unsolved; the situation is somewhat complicated by the fact that the position and intensity of the band seem to be highly dependent of structural factors, and that it is often likely to be partially covered by strong, nearly located phenyl-ring vibrations; it is generally located in the range 1400-1600 cm^{-1}.

Particular interest is connected with the azo-group vibration in formazans, because there is good evidence, both from ultra-violet spectroscopic[2] and kinetic[3] data, as to the presence of a N-H...N

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[1] R. J. W. Le Fèvre *et al.*, *Aust. J. Chem.* **6**, 341 (1953); **10**, 26 (1957); **11**, 92 (1958); G. Costa, *Ann. Chim.* **46**, 649 (1956); D. Hadzi, *J. Chem. Soc.* 2143 (1956); R. Mecke and E. Greinacher, *Z. Elektrochem.* **61**, 530 (1957); K. Ueno, *J. Amer. Chem. Soc.* **79**, 3205 (1957).

[2] I. Hausser, D. Jerchel and R. Kuhn, *Ber.* **82**, 195, 515 (1949); **84**, 651 (1951); K. H. Hausser, *Naturwissenschaften* **36**, 313, 314 (1949); *Z. Naturf.* **5a**, 41 (1950); R. Kuhn and H. Zahn, *Ber.* **84**, 566 (1951); A. Foffani and A. Stuparich, *Gazz. Chim. Ital.* **83**, 508 (1953).

[3] R. Kuhn and H. M. Weitz, *Ber.* **86**, 1199 (1953); A. Foffani, A. Stuparich and L. Salvagnini, *Gazz. Chim. Ital.* **85**, 175 (1955); **89**, 922 (1959).

intramolecular hydrogen bond in the "red" forms of these molecules. The bond involves one nitrogen atom of the azo-group, and its occurrence is likely therefore to cause a noticeable frequency lowering of the azo-band, giving for this very fact an additional criterion for its location.

In the recent infra-red work on formazans[4] there was not taken advantage of this situation, because only triphenyl-derivatives were examined, and these are known to exist almost completely in their red form in all physical conditions, except under ultra-violet irradiation.

We have extended the infra-red study to C-hydrogen-N,N"-diphenylformazan and to the corresponding C-chloro, C-iodo, C-methyl- and C-ethyl-derivatives, which are particularly suitable for the present purpose, since the first three compounds appeared, from previous evidence,[2] to be stable only in the "yellow" form, while the last two give rise to equilibria between the two forms in convenient media, and the equilibrium position is quite sensitive to ultra-violet irradiation.

For the recording of the spectra two Perkin Elmer instruments were used, a double beam Model 21 and a single-beam double-pass Model 112, with NaCl and CaF_2 and, for the N-H stretching region, also with LiF optics. The compounds were examined in a series of polar and non-polar solvents of widely different character, as well as in the solid state (as KBr pellets and, where feasible, also as Nujol or hexachlorobutadiene mulls).

The analysis of the spectra (for details see ref. 5) gives results

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[4] R. J. W. Le Fèvre *et al., Aust. J. Chem.* **9**, 151 (1956); see also **10**, 32 (1957).

[5] A paper by the same authors, to be presented before the Meeting of European Molecular Spectroscopists, Bologna, Italy, 7-12 Sept. (1959).

of particular interest in connection with the present discussion in the N-H stretching region and in the 1400-1600 cm^{-1} range.

In the N-H stretching region there is observed that, in the cases where previous evidence[2] indicated the system as being prevailingly in its yellow form, a well developed band of mean intensity is present indeed in the range 3300-3350 cm^{-1} in solution, while strongly shifted (by about 100 cm^{-1}) to lower frequencies on going to the solid state. This is the case of the C-hydrogen-, C-chloro- and C-iodo-derivatives in all physical conditions, and of the corresponding C-methyl- and C-ethyl- as yellow solids and as benzene solutions of these solid forms when examined just after dissolution. No band is observed in this region in the red forms.

We have extended the study to a wide range of solvents, observing typical solvent effects: (a) in such non-polar solvents as CCl_4,C_2Cl_4 or C_6H_6 the band is sharp and has its highest frequency value, but in the case of the C-methyl- and C-ethyl-compounds it disappears more or less rapidly with time; (b) in such polar media as acetonitrile, pyridine, dioxane or ethyl ether the band, fairly stable with time, is much broader and at much lower frequencies, often comparable to those observed in the solids. Some actual approximate values for the typical case of the C-methyl-derivative are: CCl_4 and C_2Cl_4 3357; CH_2Cl_2 3352; CS_2 3347; C_6H_6 3345; CH_3CN and C_6H_5CN 3305; dioxane 3287; ethyl ether 3284; pyridine 3225 cm^{-1}.

Such a behaviour is readily explained on admitting the red forms of our molecules actually being intramolecularly bonded (with the yellow-red equilibrium position being reached more or less rapidly according to the type and purity of the non-polar solvent), and the yellow forms being partially linked through solute-solvent interaction in polar solutes and in the solid state. In this respect, it is remarkable that the yellow form is stable not only in hydroxylic solvents, as previously verified,[2] but also in typical proton-accepting media such as ether and dioxane, and in solvents such as nitriles which are known[6] to act mainly through dipole-dipole associations. In the red forms the N-H stretching vibration, strongly lowered in frequency, has been presumably covered by the C-H stretching band around 3000 cm^{-1} or drastically weakened.

Going now to the region (1400-1600 cm^{-1}) where the -N=N- stretching mode should presumably be observed, the examination of the spectra (see ref. 5) shows that only one intense band is present indeed which cannot reasonably be interpreted as a ring vibration; its dependence on structural factors and on the solvent is in quite a good agreement with its being assigned to such a stretching mode. The band, lying in the somewhat restricted range 1530-1590 cm^{-1}, is fairly stable in position, in all conditions, in the C-hydrogen-, C-chloro- and C-iodo-derivatives; correspondingly it shifts to lower frequencies by about 23 cm^{-1} both in the C-methyl- and the C-ethyl-derivative on going from the yellow to the red, hydrogen-bridged, form. The positions in C_2Cl_4 are as follows: C-hydrogen- 1547; C-chloro- 1552; C-iodo- 1550; C-methyl-(yellow) 1581; C-methyl-(red) 1558; C-ethyl-(yellow) 1576; C-ethyl-(red) 1553 cm^{-1}.

The parallelism with the behaviour of the N-H stretching vibration is even more remarkable on looking to the variations of our band with time for the C-alkyl-derivatives: in the conditions where, as mentioned before, the

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[6] A. Foffani, C. Pecile and F. Pietra, *Nuovo Cim.* In press (1959); L. J. Bellamy, R. L. Williams and H. E. Hallm, *Trans. Faraday Soc.* **54**, 1120 (1958); **55**, 14 (1959); E. L. Zhukova, *Optika i Spek.* **4**, 750 (1958).

N-H stretching is disappearing, the intensity of the peak at 1581, respectively 1576 cm^{-1} is decreasing, while correspondingly that of the low-frequency one, initially absent, is increasing.

The possibility of the assignment of the band to a N-H bending mode seems to be ruled out, taking also into account the fact that, apart from the relatively small frequency shift, the intensity of the band is almost unaffected on passing from the yellow to the red form; this should be difficult to understand for a bending mode of the N-H bond, which is directly involved in the N-H...N hydrogen bond. It is however to be pointed out that our assignment, although in general agreement with the present experimental evidence, is only tentative and clearly requires further confirmation.

Work is in progress on the effect of ligands capable of giving intermolecular N-H...N bonds with the -N=N-, respectively with the N-H group of the formazan molecule, in competition with the intramolecular hydrogen bond active in the red forms; we are also planning the study of formazans deuterated and alkylated in their N-H group.