# An I.r.-spectroscopic Study of a Postulated C–H···N Hydrogen Bond Suggested by the *X*-Ray Structure of a Novel Heterocycle

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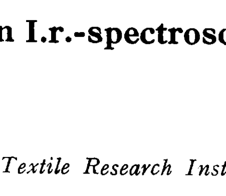
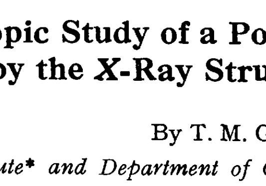
*Summary* I.r.-spectroscopic methods indicate that the short C–H··· N distance found in the *X*-ray structure of *Z*-1-(*p*-bromophenylphenylmethylene)-3-oxo-1,2-diazetidinium inner salt (I) is probably not due to *strong* hydrogen bonding.

In special cases, C–H groups can function as proton donors in hydrogen bonding.[1] The strength of such a bond is dependent upon carbon hybridization: $C(sp)$–H > $C(sp^2)$–H > $C(sp^3)$–H, and, in addition, increases with the number of effectively positioned electron-withdrawing groups.[2] Intermolecular C–H hydrogen bonding can be detected by the sensitive i.r.-spectroscopic method only when the aromatic ring is substituted with three electron-withdrawing groups, and even then strong proton acceptors had to be employed.[2] However, the *X*-ray structure of the *Z*-1-(*p*-bromophenylphenylmethylene)-3-oxo-1,2-diazetidinium inner salt (I), with only the *p*-bromophenyl and diazetidinium rings nearly coplanar, has been interpreted by Fritchie and Wells to indicate the presence of intramolecular C–H··· N hydrogen bond,[3]† despite the presence of only two electronegative groups on the proton donating benzene ring.



(I) R = H
(Ia) R = D



(II) R = H, X = Cl
(IIa) R = D, X = Br

This conclusion was based primarily on the *X*-ray criterion for hydrogen bonding.[4]† The reported H··· N distance in (I), 2·15 Å, is shorter than the van der Waals radii sum of 2·7 Å.[5] However, the use of such shortened contact distances *per se* as criteria for hydrogen bonding in *X*-ray determined structures has been criticized by Donohue, since crystal packing forces might be responsible.[6] For example, the attribution of the short distance between a methyl group and an oxygen atom in 1,3,5,7-tetramethyluric acid to hydrogen bonding[7] seems questionable, since methyl groups are highly improbable proton donors.[2]

We have now investigated this problem using i.r. techniques. Solid (KBr) and solution ($CCl_4$) i.r. spectra of (I) and its uncyclized precursor, *Z*-α-chloroacetyl-4-bromobenzophenone hydrazone (II),[8] were studied; *p*-bromobenzophenone (III) was also used as a model for comparison.

The CH stretching region of these compounds proved to be complex; even the spectra of the deuteriated methylene compounds, (Ia) and (IIa),[8] were not simplified appreciably.

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† In support of the postulated C–H hydrogen bond in (I), Fritchie and Wells[3] cited the n.m.r. deshielding of the *ortho*-hydrogens of the analogue of (I) *lacking the bromine* atom. However, several analogues of (I) have been synthesized, and all show this deshielding effect for groups (including methyl) *cis* to the amide nitrogen.[8] Magnetic anisotropy, rather than hydrogen bonding, would thus appear to be responsible.

However, the band envelopes of all the compounds studied could be decomposed by means of a curve resolver into components taken to be due to aryl C–H stretching vibrations[9] at about 3082, 3058, and 3030 cm$^{-1}$ (± 5 cm$^{-1}$). These bands were observed at essentially unchanged positions for (I), (II), and (III) both in solution and in the solid phase (KBr). Thus, no *frequency shift* evidence for intramolecular hydrogen bonding could be found for (I).

In the case of weak hydrogen bonds not exhibiting shifts in peak positions, an increase in *band intensity* has been used as an additional criterion.[10] In $CCl_4$ solution, the relative band areas‡ (Table) of (I) and (Ia), (II) and (IIa), and (III) are the same within experimental error (±4%). This is also true for the KBr spectrum of (III), but significant area changes are observed in the KBr spectra of (I) and (Ia) and of (II) and (IIa). The high-frequency (3082 cm$^{-1}$) band is intensified in the KBr spectrum of (II), but its relative area is lower in (I). In the latter, it is the low-frequency (3030 cm$^{-1}$) band which shows intensification. It is this band which might reasonably be expected to be the one associated with hydrogen bonding, but this assignment cannot be made with certainty.

TABLE

*Areas*[a] (±4%) *of characteristic phenyl C–H stretching bands*

| | Compounds | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ν(cm$^{-1}$) | (I) | | (Ia) | | (II) | | (IIa) | | (III) | |
| | $CCl_4$ % | KBr % | $CCl_4$ % | KBr % | $CCl_4$ % | KBr % | $CCl_4$ % | KBr % | $CCl_4$ % | KBr % |
| 3082 ± 5 .. | 24 | 13 | 28 | 14 | 23 | 40 | 24 | 40 | 19 | 20 |
| 3058 ± 5 .. | 39 | 47 | 38 | 46 | 45 | 41 | 40 | 43 | 53 | 55 |
| 3030 ± 5 .. | 37 | 40 | 34 | 40 | 32 | 19 | 36 | 17 | 28 | 25 |

[a] A du Pont 310 Curve Analyzer was used to obtain % areas (based on percent transmission). This method of spectral analysis is found in the Ph.D. Thesis of T. M. Gorrie, Princeton University, 1972.

Although the approach we have used is unsophisticated, *strong* C–H hydrogen bonding in (I) can definitely be excluded both in solution and in the solid phase, because of the absence of a pronounced frequency shift. If the reference compounds (II) and (III) are conceded to be reasonable models, no i.r. evidence at all for intramolecular hydrogen bonding of (I) in $CCl_4$ solution was found, and, at best, only a slight band intensification for (I) in the *solid phase* was observed. The short C–H · · · N distance in the crystal structure of (I) is evidently due to factors other than hydrogen bonding, *e.g.*, crystal packing forces.

T.M.G. (Textile Research Institute Fellow, 1967—71) and N.F.H. (National Science Foundation Trainee, 1970—71) thank Professors P. v. R. Schleyer and E. C. Taylor for useful comments and the Whitehall Foundation for use of the Perkin-Elmer 421 Grating Spectrometer.

(*Received*, 18*th May*, 1971; *Com.* 863.)

‡ Because of the low solubility of (I), and the attendant need for tenfold spectra band amplification despite the use of 4 cm cells, *absolute* band areas could not be determined accurately.

[1] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco, 1960.
[2] A. Allerhand and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 1715.
[3] C. J. Fritchie, jun., and J. L. Wells, *Chem. Comm.*, 1968, 917.
[4] W. H. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solid," Benjamin, New York, 1968.
[5] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 1960.
[6] J. Donohue, "Structural Chemistry and Molecular Biology," eds. A. Rich and N. Davidson, Freeman, San Francisco, 1968, p. 443.
[7] D. J. Sutor, *J. Chem. Soc.*, 1963, 1105.
[8] N. F. Haley, Ph.D. Thesis, Princeton University, 1971; see also R. B. Greenwald and E. C. Taylor, *J. Amer. Chem. Soc.*, 1968, **90**, 5727.
[9] M. L. Josien and J. M. Lebas, *Bull. Soc. chim. France*, 1956, 53.
[10] C. M. Huggins and G. C. Pimentel, *J. Chem. Phys.*, 1955, **23**, 896.