**Tetrahedron Letters No.35, pp. 3163-3167, 1965. Pergamon Press Ltd.
Printed in Great Britain.**

C^{13} N.M.R. STUDIES OF THE DIAZINES AND THEIR CATIONS

A.Mathias* and V.M.S.Gil†

* I.C.I.Ltd., Dyestuffs Division, Blackley, Manchester 9

† Department of Chemistry, The University, Sheffield 10
and on leave from the University of Coimbra, Portugal

(Received 15 July 1965)

C^{13} chemical shifts can be measured in two main ways (a) by direct observation at the C^{13} resonant frequency and (b) by indirect observation using heteronuclear double resonance techniques on the C^{13} satellites which are present in the proton spectra of organic molecules. Lauterbur (1) has examined some azines directly. In this work a modified Varian HA.100 spectrometer has been used to obtain the chemical shifts of C^{13} nuclei in natural abundance in the diazines and their cations by the indirect method. Details of the apparatus and experimental procedures have already been given (2). Table 1 shows the C^{13} chemical shift values obtained. These are in p.p.m. relative to benzene and are accurate to ± 0.08 p.p.m. For comparison Lauterbur's results for the neutral diazines are also shown. These latter results were obtained relative to an external reference of CS_2 and are judged to be accurate to ± 0.5 p.p.m. The value of - 65.0 p.p.m. for the C^{13} chemical shift of CS_2 relative to benzene (3) has been used to convert all the results to the benzene scale.

The three blank spaces in Table 1 indicate cases where the C^{13} satellites could not be located accurately due to the superposition of small impurity peaks in the samples. It is hoped to obtain these shifts shortly. It can be seen from Table 1 that there is good agreement between the two sets of results for the C^{13} chemical shifts of the neutral species.

TABLE 1.

	δ C^{13}	δ C^{13} ref. 1	δ C^{13} Cation
Pyrazine (sat. soln. H_2O)			
$C_{2,3,5,6}$	- 16.77	- 17.4	- 14.72
Pyridazine (neat)			
$C_{3,6}$	- 24.07	- 23.9	- 22.57
$C_{4,5}$	+ 1.29	+ 1.0	-
Pyrimidine (neat)			
C_2	- 31.34	- 30.5	- 23.57
$C_{4,6}$	- 28.91	- 28.9	- 29.21
C_5	-	+ 6.1	-

Karplus and Pople (4) have discussed theoretically the factors which control the carbon shieldings in aromatic ring systems. They stated that the main contribution to the C^{13} chemical shifts relative to benzene must originate in changes in the paramagnetic term ($\Delta\sigma^p_c$) and worked out an expression whereby the shieldings of ring carbon atoms could be calculated from the changes in the local π electron density, ρ^π_c and the free valence parameter of the atom in question, F_c .

Using a mean excitation energy $\Delta E \approx 8eV$ (1, 5) for the excited states involving ($\sigma \longleftrightarrow \pi$) and ($\sigma \rightarrow \sigma$) transitions, the Karplus-Pople equation can be rewritten

$$\Delta\sigma^p_c \approx [108 + 58\ (\lambda_x + \lambda_y + \lambda_z)](\rho^\pi_c - 1) + 58(F_c - 0.399) \qquad [1]$$

where λ_x is a polarity parameter for the CX σ bond. The effect of the polarity of the σ bonds on the coefficient of (ρ^π_c - 1) is only a few per cent, the main dependence on the local π charge coming from changes in the quantity $\langle r^{-3}\rangle_{2p}$ through the Slater screening effect. The charge dependence predicted by equation [1] agrees in sign and order of magnitude with the empirical correlation $\Delta\sigma_c \approx 160(\rho^\pi_c - 1)$ (3, 6). However, when changes in the local charge contributed by the σ bonds are not negligible, a new term - $108(\rho_C^\sigma - 3)$ - should be added to [1], as $\langle r^{-3}\rangle_{2p}$ is affected both by π and σ charges. This extension of the Karplus-Pople equation was first done by Lauterbur (1) who obtained good agreement between experimental and calculated C^{13} chemical shifts for the azines by introducing a reasonable amount of ionic character in the NC bonds and using theoretical π electron densities.

The C^{13} chemical shifts of the diazine cations were obtained using solutions in trifluoroacetic acid. Since protonation of the azines leads to increased positive charge at the C atoms, low field shifts might be expected. However, Grant and Pugmire (7) found that the α-C^{13} in pyridinium ion (PyH^+) are more shielded by 8.5 p.p.m. than in pyridine (Py). The C^{13} chemical shift values in p.p.m. relative to benzene were:

TABLE 2.

	$C_{2,6}$	$C_{3,5}$	C_4
Pyridine	- 21.7	+ 4.6	- 7.4
Pyridinium ion	- 13.2	+ 0.4	- 19.2

The results in Table 1 show that for the diazine cations also most of the ring carbon atoms are more shielded than in the neutral species. It is interesting to note that the changes in the C^{13} chemical shifts of the diazines on protonation can be calculated to within ± 1.3 p.p.m. by taking the average of the corresponding shifts for pyridine. (It is assumed that no significant concentration of di-protonated species is present). For example, the shift for pyrazine on protonation, + 2.05 p.p.m., is to be compared with the average of the α- and β-C^{13} shifts of pyridine, i.e. $\frac{1}{2}(8.5 - 4.2) = + 2.15$ p.p.m.

Two possible explanations can be offered for the observed high field shifts on protonation:

(a) It is interesting that the α-C^{13} and the N^{14} shifts observed on protonating Py have the same direction. The N^{14} screening constant is known to increase by ca. + 120 p.p.m. on protonation (8), although the total electron density at the N atom probably decreases. This has been shown to be mainly due to the low-lying $n \rightarrow \pi^*$ state of Py (absent in PyH^+) which is responsible for a larger paramagnetic term in the case of pyridine (9). It is conceivable that due to delocalisation of the σ orbitals, the $n \rightarrow \pi^*$ transition is not entirely localised on the N atom; therefore a smaller value for the mean excitation energy for the C^{13} nuclei adjacent to N atoms in the neutral azines might be more appropriate (contrary to what has been assumed by Lauterbur (1)), hence contributing to the large low-field shifts of these nuclei. The absence of the $n \rightarrow \pi^*$ state in the protonated species would therefore partially account for the observed high-field shifts.

(b) The calculations of Mataga and Mataga (10) and of Brown and Heffernan (11) show that the N-C π bond order in Py is decreased considerably by protonation, whereas the C_α-C_β bond order may slightly increase. The overall effect is an increase in the free valence index of the α-C of the order of 0.1 on going from Py to PyH^+. This change corresponds in equation [1] to a shielding effect of ca. 6 p.p.m.

Finally, we note that protonation of the diazines leads to increase of CH coupling constants involving C^{13} nuclei adjacent to N atoms of the order of 10-15 c.p.s. These changes reflect the increase of the effective electro-negativity of the N atoms on protonation and are in agreement with theoretical calculations of the hetero-atom effect on the CH coupling constants of azines (12). A more complete study of CH and HH coupling constants in protonated azines and substituted azines is now in progress.

Acknowledgements

Thanks are due to Professor J.N.Murrell for helpful discussions, Mr.P.Hampson for experimental assistance, and the Comissão Coordenadora da Investigação para a NATO (Portugal) for the award of a fellowship to one of us (V.M.S.G.)

References

(1) P.C.Lauterbur, *J. Chem. Phys.* in press.
(2) J.H.Allen, J.K.Becconsall and D.W.Turner, *J. Sci. Inst.* **41**, 673,(1964)
(3) P.C.Lauterbur, *J. Amer. Chem. Soc.* **83**, 1838,(1961.)
(4) M.Karplus and J.A.Pople, *J. Chem. Phys.* **38**, 2803,(1963)
(5) J.A.Pople, *Mol. Phys.* **7**, 301,(1964)
(6) H.Spiesecke and W.G.Schneider, *Tetrahedron Letters*, 468,(1961)
(7) D.M.Grant and R.J.Pugmire, private communication.
(8) J.D.Baldeschwieler and E.W.Randall, *Proc. Chem. Soc.*, 303,(1961.)
(9) V.M.S.Gil and J.N.Murrell, *Trans. Faraday Soc.* **60**, 248,(1964.)
(10) S.Mataga and N.Mataga, *Z. Physik. Chem.*,**19**, 231,(1959.)
(11) R.D.Brown and K.L.Heffernan, *Aust. J. Chem.*, **12**, 554,(1959.)
(12) J.N.Murrell, F.B. van Duijneveldt and V.M.S.Gil, to be published.