Linear Relationships Between Carbon-13 and Proton Chemical Shifts and Hückel π-Electron Densities in Diazoles and Triazoles

By BRIAN M. LYNCH

(*Department of Medical Chemistry, John Curtin School of Medical Research, Australian National University, Canberra, Australia*)

REES and GREEN[1] have reported that they were unable to find any correlation between theoretically calculated π-electron densities and ^{13}C chemical shifts in pyrazoles. In view of our success[2] in relating calculated π-electron densities for the diazoles with the proton chemical shifts, and the correlations noted by Weigert and Roberts[3] between the $2p_z$ atomic populations from extended Huckel calculations (which reflect π-electron distributions) and the ^{13}C chemical shifts, these results appear surprising. This discrepancy may arise if the calculations cited by Rees and Green employed parameters for two types of nitrogen atom, while I only considered a single heteroatom, as exchange renders all the nitrogens equivalent on the n.m.r. time scale.

Carbon-13 *and proton chemical shifts of diazoles, triazoles, and tetrazole and MO π-electron densities*

Position on nucleus	Species	Carbon-13 shift (p.p.m. upfield from CS$_2$)[3,a] δ_C	Proton shift (p.p.m. downfield from tetramethylsilane, for CF$_3$CO$_2$H solutions) δ_H	MO π-electron density q_π
4	Pyrazole	88·1	6·95[b]	1·137
4	Imidazole	71·0	7·53[b]	1·067
4	1,2,3-Triazole	62·4	7·90	0·980
3	Pyrazole	59·5	8·25[b]	0·973
2	Imidazole	57·1	8·67[b]	0·907
3	1,2,4-Triazole	45·2	8·80	0·835
5	Tetrazole	48·8[c]	9·12	0·813

[a] Solvent, acetone except where noted. [b] Ref. 2.
[c] In dimethyl sulphoxide, therefore excluded from correlations as not comparable.
$\delta_C = -64{\cdot}88 + 131{\cdot}0\, q_\pi$ ($r = 0{\cdot}974$, 6 points).
$\delta_H = 14{\cdot}32 - 6{\cdot}41\, q_\pi$ ($r = 0{\cdot}984$, 7 points).

A good linear relationship (correlation coefficient: 0·974) is found between the π-electron densities calculated for the diazoles and triazoles by the simple MO method[4] (with the nitrogen electronegativity parameter set at +1 for all nitrogen atoms) and the ^{13}C chemical shifts of Weigert and Roberts (see the Table). The slope of the relationship (*ca.* 130 p.p.m./electron) is comparable to that noted for some charged carbocyclic aromatic species.[5] The proton shifts for these compounds in trifluoroacetic acid also show linear correlations with the MO π-electron densities; furthermore, tetrazole, which exhibits abnormal carbon shielding in terms of correlations with extended Huckel calculations or with MO results, shows a proton shift in agreement with the calculated MO π-electron densities.

The results suggest very strongly that the ^{13}C and proton chemical shifts in these five-membered azoles are determined by the same factors: namely, the π-electron densities. Further, the simple MO method seems as valid a predictor of the order of chemical shifts as the extended Huckel technique.

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