^{13}C–H Coupling Constants as a Tool in Studies of Azole Tautomers

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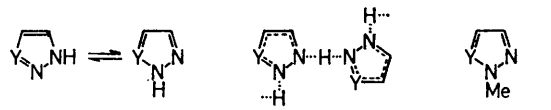
Summary One bond ^{13}C–H coupling constants [$^1J(^{13}C$–H)] provide a useful tool for assessing the equilibria of *N*-prototropic species in solutions of azoles, *e.g.* 1,2,3-triazole.

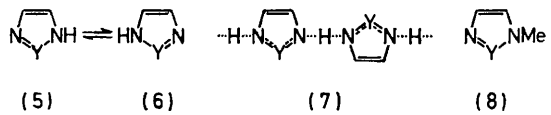
REPORTED spectroscopic data[1,2] do not provide precise information on the tautomeric composition of solutions of 1,2,3-triazole at room temperature. We report that $^1J(^{13}C$–H) values, known,[3a] in contrast to ^{13}C chemical shifts,[3b] to be only slightly influenced by *N*-methylation, are useful for the above purpose.

In pyrazole, existing in solution as rapidly interconverting monomers (**1a**) $\rightleftharpoons$ (**2a**), cyclic dimers, or linear associates (**3a**),[4] the observed $^1J(^{13}C$–H) constant (185·5 Hz) for C-3 (≡C-5) can be considered as an average value of the C-3 and C-5 methine groups of (**1a**). Significantly, it equals the

mean of the $^1J(^{13}C–H)$ values for C-3 (184·4 Hz) and C-5 (186·6 Hz) in 1-methylpyrazole (**4a**), suggesting that virtually the same coupling constants obtain for the non-methylated species (**1a**). Similarly, in imidazole, existing in solution as rapidly interconverting monomers (**5a**) ⇌ (**6a**)



(1) (2) (3) (4)



(5) (6) (7) (8)

a; Y = CH
b; Y = N

or linear associates (**7a**),[5] the observed $^1J(^{13}C–H)$ value (188·6 Hz) for C-4 (≡C-5) is equal to the mean of the coupling constants (188·1 and 189·5 Hz) determined for 1-methylimidazole (**8a**).

Similar reasoning was applied to the 1,2,3-triazole system: the coupling constant (194·3 Hz) for C-4 (≡C-5) in non-substituted triazole falls within the range of that for C-4 in 2-methyltriazole (**4b**) (192·5 Hz) and the averaged value for the C-4 (194·3 Hz) and C-5 (196·6 Hz) methine groups in 1-methyltriazole (**8b**) implying that in $CDCl_3$ solution at 32° 1,2,3-triazole exists as a 2 : 3 equilibrium of the 2*H*- and the 1*H*-tautomer. The intermediacy of (**3b**), or a cyclic dimer, in the interconversion of the tautomers seems likely. The calculated $^1J(^{13}C–H)$ value for the latter species (196·5 + 192·5 + 194·3 + 192·5/4 = 194·0 Hz) is in good agreement with the observed constant.

Undecoupled ^{13}C n.m.r. spectra were recorded on 33% w/v solutions in $CDCl_3$ at 32°, as previously described.[6] The resolution in the present work corresponds to an accuracy of ±0·2 Hz in the coupling constant values, obtained by first-order analysis.

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