Annular Tautomerism in the Solid State: a High Resolution N.M.R. Study

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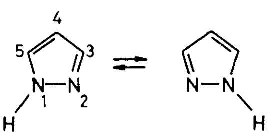
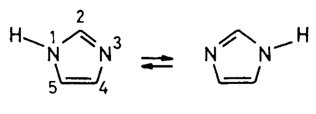
Summary ^{13}C N.m.r. spectra of solid samples of pyrazole and imidazole were obtained using the 'magic angle' spinning technique; both compounds show three separate signals corresponding to C_s structures (no proton exchange).

AMONGST the examples of tautomerism of heteroaromatic compounds, annular tautomerism[1a] is one of the most widely studied, even though strong hydrogen bonds and low activation energies complicate the study. In the case of pyrazole (**1**) and of imidazole (**2**), there is a degenerate equilibrium (autotropic rearrangement[2]) and, by simple symmetry considerations, it is possible to obtain information about their structures.



(1a) (1b)

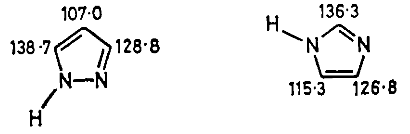


(2a) (2b)

In the vapour phase and in solution there is no doubt that both diazoles exist in equal tautomeric equilibria brought about by proton exchange.[1b,c] It is worthy of notice that, in contrast with the pyrazole,[3–5] no-one has succeeded in slowing down the proton exchange rate for imidazole sufficiently to observe separate signals (protons 4-H and 5-H, carbons C-4 and C-5, nitrogens N-1 and N-3), even in ^{15}N n.m.r. spectroscopy.[6]

In the solid state, there has been some controversy about the structure of diazoles. For pyrazole (**1**) an incorrect geometry was proposed from *X*-ray studies[7] that was later corrected, after both *X*-ray[8] and neutron diffraction[9] examinations. Zimmermann, from i.r.[10] and wide-line ^{1}H n.m.r.[11] spectral studies of polycrystalline samples of imidazole (**2**), concluded that there is intermolecular N–H · · · N hydrogen bonding with rapid transposition of the hydrogen atom between two potential wells (tunnel effect). Those experiments led Zimmermann[12] to introduce the controversial theory of 'protomerism' (A–H · · · B $\longleftrightarrow$ A · · · H–B). The Zimmermann interpretation of the i.r. spectrum of imidazole has been criticised,[13] the French authors discussing the spectrum with regard to C_s symmetry; however, Cordes and Walter[14] later published an i.r. spectral study of imidazole in the solid state based on C_{2v} symmetry for the molecule. An *X*-ray study of compound (**2**) at −150 °C shows that the geometry is clearly of the C_s-type with a localized tautomeric proton.[15] A more recent publication by Omel'chenko and Kondrasev[16] concluded tentatively that the *X*-ray spectrum of imidazole at room temperature has a *quasi*-C_{2v} structure with rapid proton transfer along the hydrogen bond, but since the model converged only to an *R* factor of 0·10, these conclusions must be taken with caution (see, for instance ref. 17).

High-resolution solid state ^{13}C n.m.r. spectroscopy† (combining cross-polarization and high power decoupling with 'magic angle' spinning[18]) was used to obtain the spectra of pyrazole (**1**) and imidazole (**2**); the results are shown in the Figure.



(**1**) (**2**)

FIGURE. ^{13}C N.m.r. chemical shifts for pyrazole and imidazole in p.p.m. from Me$_4$Si.

The chemical shifts of pyrazole are similar to those obtained by Litchman[4c] in Me$_2$SO at 10 °C (138·9, 105·8, and 128·5 p.p.m.) and by Chenon *et al.*[4b] in hexamethylphosphoric triamide at −17 °C (138·1, 103·9, and 127·8 p.p.m.). For imidazole, as indicated before, the activation energy in solution is lower than for pyrazole, and there are no reports in the literature of the n.m.r. spectrum of a blocked-exchange imidazole; thus, the comparison ought to be made with *N*-methylimidazole: C-2 137·6, C-4 129·3, and C-5 119·7 p.p.m. (CDCl$_3$).[19] The result obtained in the case of imidazole (**2**) shows that spectroscopic interpretations based on a C_{2v} structure (i.r.[14] and *X*-ray[16]) are erroneous and that the concept of 'protomerism'[12] does not have an experimental basis.

In conclusion, high-resolution ^{13}C n.m.r. spectroscopy constitutes a very powerful tool for the study of tautomerism in the solid state, without the necessity of obtaining single crystals and without the complexities of solid i.r. spectral studies (strong hydrogen-bonds; isotopic labelling).

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† The spectra were recorded on a Bruker CXP-300 spectrometer working at 75·46 MHz by Drs. D. Müller and G. Hermann (Bruker Analytische Messtechnik GmbH, Karlsruhe, and Bruker Spectrospin, Wissembourg) to whom we are greatly indebted: spinning rate, 4·07 kHz; spectral width, 31·25 kHz.

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