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SOLID STATE BEHAVIOUR OF "DYNAMIC COMPOUNDS" : A ^{13}C CP/MAS NMR SPECTROSCOPY STUDY

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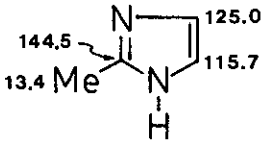
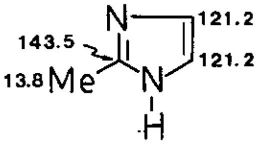
Abstract - The ^{13}C CP/MAS NMR spectra of 2-methylimidazole, antipyrine, 1-phenyl-3-hydroxy-5-methylpyrazole, 1-*p*-bromophenyl-3-methyl-pyrazolin-5-one, tetrazolo[5,1-*b*]benzothiazole, and 9-acetylcarbazole have been recorded and the signals assigned. Problems such as annular prototropic tautomerism, functional tautomerism, azido/tetrazole isomerism, and rotational isomerism have been studied and, in most cases, solved.

Continuing with our work on the study of heterocyclic compounds in the solid state by ^{13}C CP/MAS NMR spectroscopy,[1] we now wish to report the behaviour of six compounds, 1 to 6, all of them capable of showing some kind of dynamic phenomena.

2-Methylimidazole 1 shows four well-resolved lines, that can be assigned by analogy with imidazole.[2]



1 (solid state)

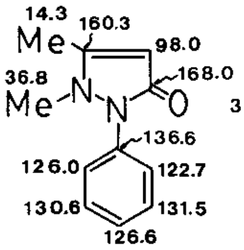


1 (DMSO-d_6)[3]

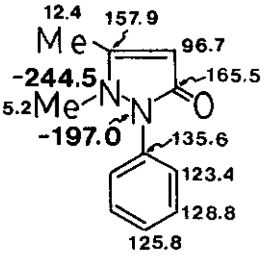
The values are comparable with those observed in solution, where rapid tautomerism occurs. The mean value for the signals of carbons C_4 and C_5 (120.35 ppm) is close to the value in solution, showing that solid state chemical shifts can be used, instead of methylated derivatives[4] for tautomeric studies.

Another case of prototropic tautomerism, functional instead of annular,[4] occurs in pyrazolones. Antipyrine 2 has been studied as a model compound, since its structure is unambiguously known (for the X-ray determination, see[5]). Here also, the chemical shifts in the solid state are closely related to those in solution. Even if line multiplicities in solid state ^{13}C NMR can have different origins,[6] the fact that five resolved resonances of protonated aromatic carbons are observed is probably due to the twisted conformation of antipyrine (X-ray dihedral angle = 52.1°).[5]

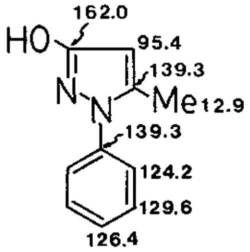
1-Phenyl-3-hydroxy-5-methylpyrazole 3 exists as such in the solid state, as it has been proved by X-ray crystallography.[7]



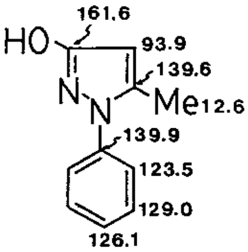
2 (solid state)



2 (DMSO-d_6)



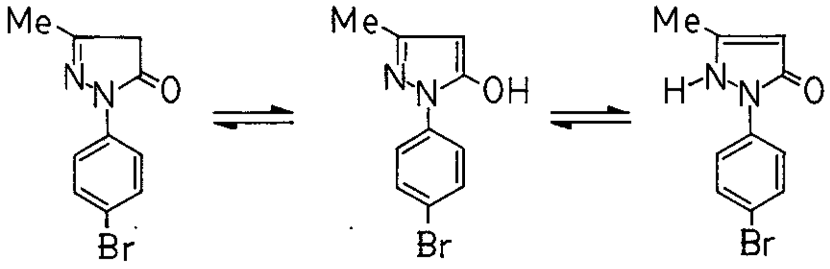
3 (solid state)



3 (DMSO-d_6)

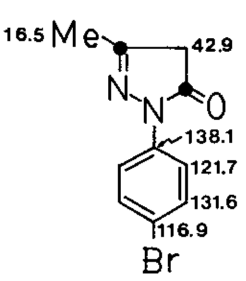
The strong hydrogen-bonds existing in the solid state (3: cyclic dimer -O-H···N_2)[7] do not affect the chemical shifts.

1-p-Bromophenyl-3-methyl-pyrazolin-5-one 4 presents a more complicated problem. This class of compounds exist in solution as a mixture of three tautomers:[4,8]

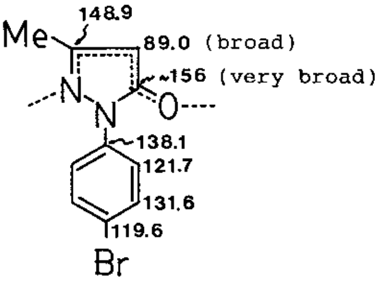


4a 4b 4c

In the solid state[9,10] only tautomers 4b and 4c are present in the form of long chains of proton-bound ···4b···4c···4b···4c··· . The spectra in DMSO-d_6 corresponds to a mixture of 10% of CH-tautomer 4a (which gives separate signals) and 90% of OH- and NH-tautomers, 4b and 4c (which give averaged signals). Black dots correspond to not observed signals.

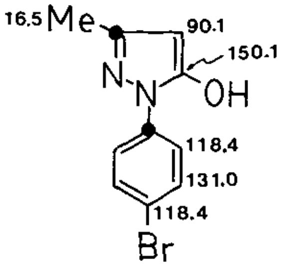


4a

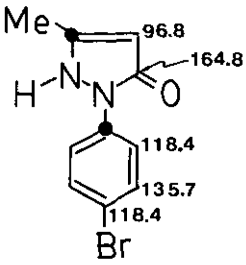


4b + 4c

The fact that C_4 and mainly C_5 are broad signals proves that there is a dynamic equilibrium 4b $\rightleftharpoons$ 4c. The ^{13}C CP/MAS NMR spectrum of 4 shows the absence of 4a tautomer and the presence of a mixture of tautomers 4b and 4c, the equilibrium 4b $\rightleftharpoons$ 4c being frozen:



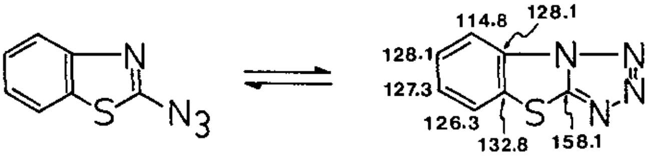
4b



4c

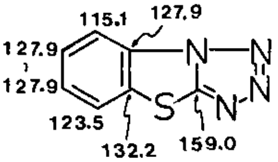
Taking into account the results of the X-ray analysis[9,10] it is reasonable to assume that in the solid state there is a 50:50 mixture of **4b** and **4c**. The spectrum of **4c** is comparable to that of antipyrine 2. In solution, the value observed for C_4 (89.0 ppm) is close to the value for tautomer **4b** (90.1 ppm), but the C_5 signal, more sensitive to tautomerism (~156 ppm), corresponds to the mean value for tautomers **4b** (150.1 ppm) and **4c** (164.8 ppm).

2-Azidobenzothiazole 5 presents another kind of tautomerism:[11] the ring-chain isomerism of heterocyclic azides.



5a 5b

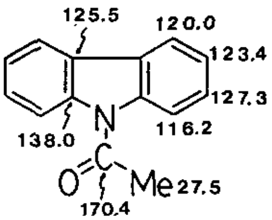
In DMSO-d_6, the compound exists mainly in the tetrazole form 5b, and in the solid state (X-ray structure),[12] the tetrazolo[5,1-b]benzothiazole 5b is the only form present. The ^{13}C chemical shifts of 5b in DMSO-d_6 have already been published.[13] The spectrum obtained in the solid state is very similar to the above reported result:

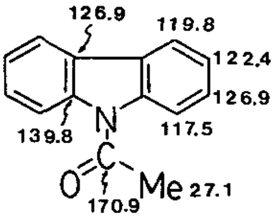


5b (solid state)

The last example concerns the rotational isomerism of N-acetylcarbazole 6. It is known[14] that at about -100°C the rotation is frozen and non equivalence is observed for all aromatic carbons, the most sensitive being $C_{1,8}$ ($\Delta\delta$ = 2-3 ppm, depending on the solvent) and $C_{8a,9a}$ ($\Delta\delta \sim 1.5$ ppm). The equivalence of all aromatic carbon-pairs in the solid state cannot be due to a free rotation, but to a lack of resolution (there is an overlapping of the signals appearing at 119.8 and 117.5 ppm).

6 (DMSO-d_6)[15]





6 (solid state)

In order to check the validity of the ^{13}C CP/MAS NMR approach to structural problems, most of the preceding compounds were selected because their X-ray structures had been determined. Only in the last example, 6, it was not possible to reach the expected goal. In general, ^{13}C CP/MAS NMR is a powerful and exciting tool for the study of a large variety of structural problems.[16]

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16. All the compounds here studied are known and described in the references corresponding to NMR studies in solution. Spectra were obtained with a Bruker CXP-200 FT NMR spectrometer (C.E.N.G.), operating at an applied field strength of 4.5 T or a ^{13}C resonance frequency of 50.31 MHz. A typical cross-polarization time was 5 ms with a recycle time of 10 to 15 s. Spectral width, 20 kHz. Spinning rate (estimated from the location of spinning sidebans), 3.2 to 3.5 kHz. Proton decoupling field $\geqslant$ 1.2 mT. Crystalline linear polyethylene (33.63 ppm downfield from tetramethylsilane)[17] or powdered hexamethylbenzene were used as references.
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