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NMR STUDIES OF TAUTOMERISM OF BENZOTRIAZOLE

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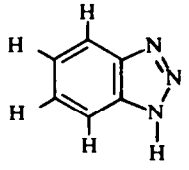
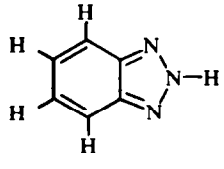
Abstract—The PMR spectrum of benzotriazole at different temperatures has been studied. At very low temperature (−100°) benzotriazole actually exists only in asymmetrical form I.

IN ORDER to investigate the heterocyclic derivatives of transition metals,[1-3] the PMR spectra of different substituted 1,2,3-triazoles, were studied. The PMR spectrum of benzotriazole at room temperature in different solvents has been reported,[4-8] and it was found[4,5,8] that NH protons take part in a rapid exchange, so that the NH and CH proton spin-spin coupling constant is equal to zero. Consequently, it is possible to assign the protons of the carbocyclic part of benzotriazole to an AA'BB' system, as in the case of naphthalene. However, on account of the rapid proton exchange, the spectra of distinct tautomeric forms cannot be obtained, and therefore the spectrum of benzotriazole was taken at different temperatures. Absolute tetrahydrofurane (THF) was selected as solvent since it dissolves benzotriazole at a very low temperature (−100°).



I



II

At room temperature, the PMR spectrum of benzotriazole in THF and other solvents (see Table) consists of a wide resonance of NH protons and two symmetric multiplets which should be assigned to carbocyclic protons. These multiplets are typical of a four-spin systems AA'BB' (Fig. 1a).

We assign the downfield part of the multiplet to A protons which are near the heterocyclic part of the molecule because these protons are influenced by anisotropy of the ring current of two aromatic cycles.[4,5,8] The upfield part of the multiplet is assigned to B protons. Recent careful analysis of this spectrum taken at room temperature[8] obviates the necessity of this spectrum consideration. The parameters of the benzotriazole spectrum in acetone solution coincide with the data of other authors.[4-7]

The spectrum of benzotriazole in THF solution changes considerably as the temperature is lowered. The spectrum of carbocyclic protons loses its fine structure at about

TABLE. DATA OF BENZOTRIAZOLE PMR SPECTRA TAKEN IN DIFFERENT SOLVENTS AT ROOM TEMPERATURE[a]

Solvent	NH	H (A)	H (B)
DMSO		7·93	7·45
Aceton	12·86	7·96	7·37
THF	12·23	7·75	7·23

[a] The measurement of chemical shifts value is done using the centre of multiplets.

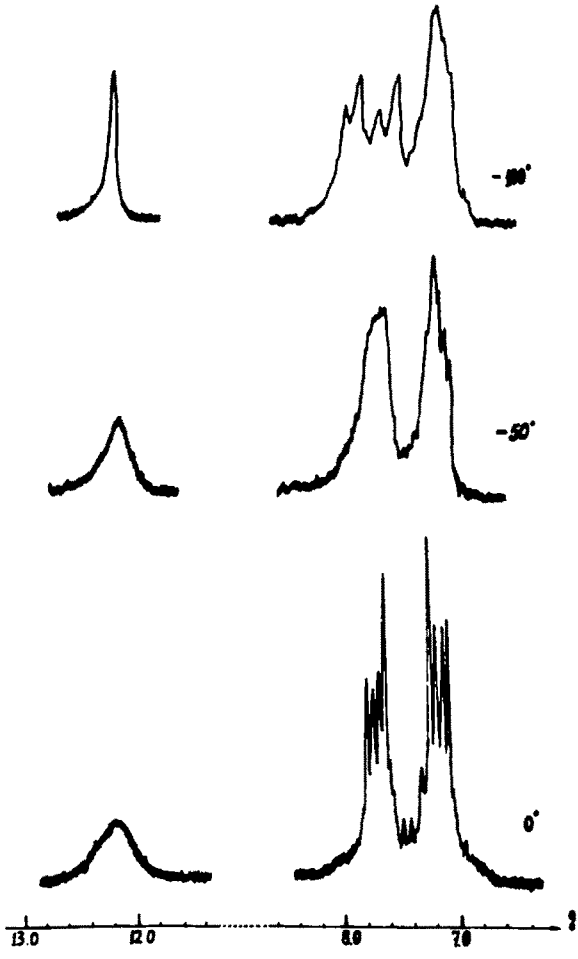


FIG. 1. PMR spectra of benzotriazole in THF solution taken at different temperature*

* The chemical shifts of centers of the multiplets remain constant with a lowering of temperature.

$-20°$ and consists of two wide asymmetrical resonance signals at about $-50°$ (Fig. 1b). The narrowing of the NH proton signal from 56 c/s at $+56°$ to a rather sharp singlet with the width of 2 c/s at $-100°$ was observed simultaneously with the change of the A and B proton spectrum. The line width temperature dependence of the NH-signal provides an estimation of the proton transition barrier ΔH in the Arrhenius equation.

$$\nu = \nu_0 \exp(-\Delta H/RT)$$

We evaluate $\nu_0 = 1{\cdot}5 \cdot 10^3$ c/s and $\Delta H = 2 \cdot 10^3$ cal/mol. The very small value of the frequency factor, shows a low rigidity of the NH bond.

The observed transformation of the spectrum may be explained as follows: intensive inter- and intramolecular NH proton exchange slackens as the temperature is decreased to $-50°$, which results in the change of magnetic interaction of the ring protons and consequently the fine structure of CH proton in the PMR is destroyed (Fig. 1b). A further temperature decrease ($-100°$) again reduces the rate of NH exchange (the period being at a certain position increases up to 0·1 sec), and one of the tautomeric forms is fixed (Fig. 1c). We suggest that the fixed form is tautomeric with an asymmetrical position of NH protons, i.e. form I. Indeed, the symmetry of spectrum of carbocyclic protons may be destroyed only in the case of structure I, because they are very sensitive to the asymmetry in a triazole ring.[7] The shape of the downfield part of the spectrum at $-100°$ favours form I (Fig. 1c). The appearence of two doublets shows that protons responsible for these signals have different shielding and take part in only one strong interaction. This consideration singles out only protons A which are in form I (generally speaking the system of carbocyclic protons of fixed form I is to be assigned to ABXY type).

Thus the data obtained makes it possible to conclude that benzotriazole actually exists only in the asymmetrical form I at $-100°$.*

This conclusion that benzotriazole exists mainly in the asymmetrical form I, where the NH proton quickly migrates between positions 1 and 3 at room temperatures, is supported by the comparison of UV and PMR spectra of benzotriazole and its 1- and 2-methyl derivatives.[5]

EXPERIMENTAL

The parent benzotriazole was prepared according the technique.[9] THF used as solvent was purified by distillation in an anhydrous argon atmosphere. The PMR spectra were taken with a Perkin–Elmer R-12 spectrometer. Low temperature measurements were taken with a NMR-2305 spectrometer. Temps were given accurately to $\pm 1°$. The operating frequency of both spectrometers was 60 Mc/s. Values of chemical shifts are in the δ-scale.

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* Naturally, this conclusion is connected with the sensitivity of a PMR method.

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