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PROTON RELAXATION AND THE SYMMETRY OF SPIN FUNCTIONS IN THE AB_2 SYSTEM

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Proton relaxation for nine aromatic AB_2 systems were studied by saturation method. It has been concluded that singlet-triplet transition exists in all the systems examined. Possible mechanisms for this phenomenon were discussed briefly.

In this note, we report an nmr relaxation study of a variety of AB_2 systems using saturation method. The results will be discussed in terms of the symmetry property of spin functions.

Proton nmr spectra were recorded on a JEOL C-60H or a JEOL PS-100 spectrometer operating at 60 MHz and 100 MHz, respectively. 2,6-Lutidine of analytical reagent grade was used after distillation. 1,2,3-Tribromobenzene was synthesized and purified by zone melting method(1). All the other compounds and solvents used are of analytical reagent grade and were used without further purification. Samples were vacuum degassed by repeated freeze-pump cycles, if necessary. All measurements were carried out at room temperature(22° C).

The ring protons of 2,6-lutidine exhibit an AB_2 type spectrum(2). In this system there are six symmetric(triplet) and two antisymmetric(singlet) spin functions giving rise to a total of eight transitions. A proton spectrum of the system is shown in Fig. 1, where line 3(marked by an arrow) is due to transition between the antisymmetric states. Under partial-saturation conditions, all peaks in the A quartet including line 3 change in intensity upon inverting the sweep direction. As shown in Fig. 2, whatever peaks swept through, later gives lower intensity regardless of the sweep direction. This phenomenon is strongly dependent on the

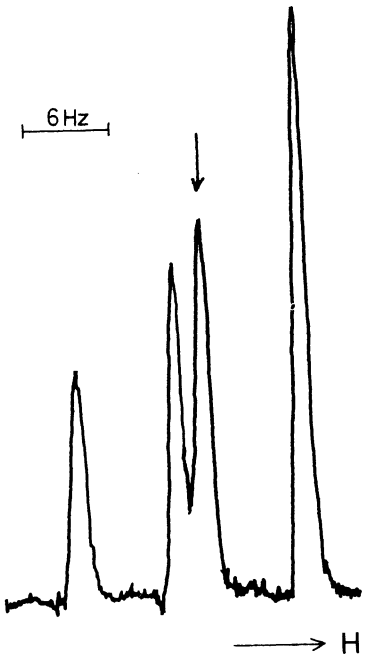

Fig. 1 Ordinary 60 MHz spectrum of the A quartet of AB_2 system for 20 %(v/v) 2,6-lutidine in CCl_4. Degassed by N_2 bubbling. Transition between antisymmetric states is indicated by an arrow.

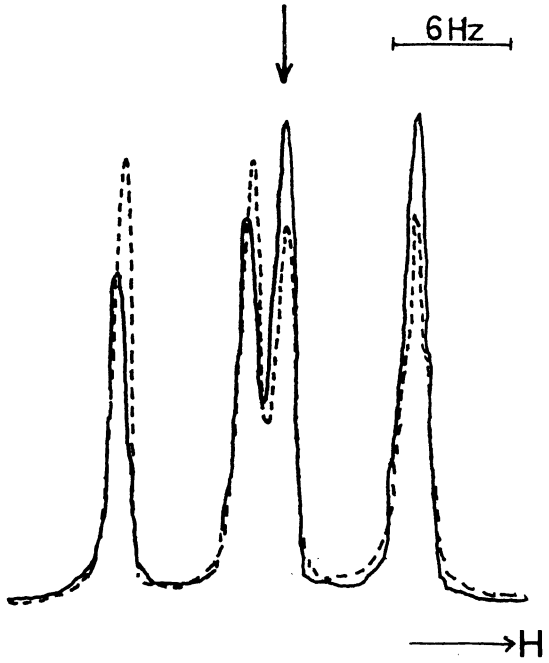

Fig. 2 Change in intensity of the A quartet upon inverting the sweep direction under partial saturation conditions. Solid line: backward-sweep(sweep to lower field), Dotted line: forward-sweep, Sweep rate: 0.72 Hz/sec. Chemical system: the same as that of Fig. 1. Arrow: transition between antisymmetric states.

magnitude of RF power and the sweep rate. As Fig. 3 shows, the magnitude of Δ_R, where Δ_R = (Intensity observed with backward-sweep)/(Intensity observed with forward-sweep), for line 3 of 2,6-lutidine increases with increasing RF power, whereas Δ_R for line 2 decreases with increasing RF power. These results suggest that cross-relaxation exists among the lines of the A quartet in the 2,6-lutidine system(3). It should be noted that the line 3 in the A quartet which corresponds to the transition between two antisymmetric(singlet) states also shows a large change in intensity upon inverting the sweep direction. Similar behaviors were also observed in a variety of aromatic AB_2 systems such as 1,2,3-tribromobenzene, 2,6-dimethylnitrobenzene, 2,6-dibromoaniline, 2,6-dimethylpyridine N-oxide, 1,2,3-trichlorobenzene, 2,6-dimethylphenol, 2,6-xylidine, and hemimellitic acid(Fig. 4). In view of all the above results, it may be concluded that the random perturbation which is responsible for the relaxation in the aromatic AB_2 systems examined in the present work does connect the symmetric and antisymmetric states. Singlet-triplet transitions cannot be induced by symmetrical perturbations such as ordinary intramolecular dipole-dipole interactions(4, 5). Singlet-triplet interactions of this kind have been discussed in detail in the case of the molecule CH_2CF_2(6), where it has been concluded that spin-rotation interaction is primarily responsible for the fluorine relaxation. For ordinary proton systems such as 2,6-lutidine, however, it is unlikely that spin-rotation interaction is a dominant relaxation mechanism. A sample of liquid 2,6-lutidine was degassed down to 5×10^{-6} mmHg to examine a possible role of oxygen on the observed phenomenon. It was found that in the 2,6-lutidine system the effect of oxygen on the magnitude of probability for the singlet-triplet transition is negligible, indicating that complex formation with oxygen can be eliminated as a source of the relaxation. A possibility of aggregation of sample molecules can also be denied because very little concentration dependence is observed upon diluting the liquid 2,6-lutidine with $CDCl_3$, CCl_4, or deuteroacetone. Further study is in progress to make more quantitative discussion about the symmetry properties of interactions responsible for proton relaxation.

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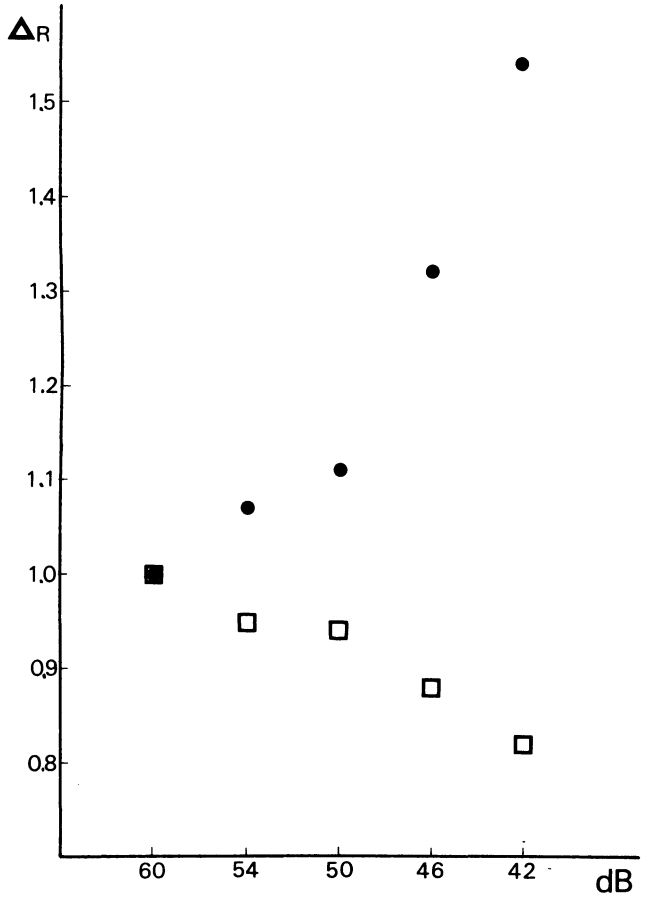

Fig. 3 Effect of the strength of RF power on Δ_R (see Text).
System: liquid 2,6-lutidine, Abscissa: attenuation of RF power, Ordinate: accurate to ± 0.02, □: line 2 in A quartet, ●: line 3 in A quartet.
RF power increases with decreasing the magnitude of dB.

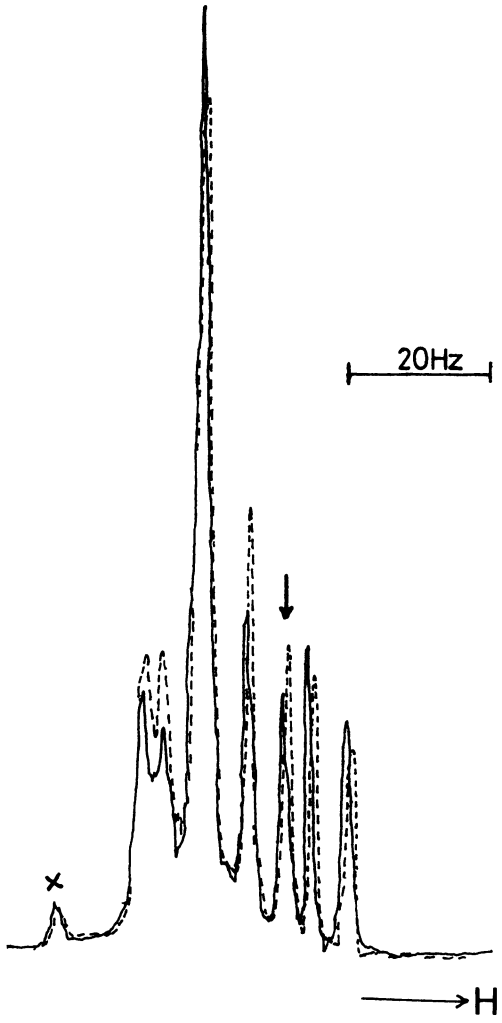

Fig. 4 Change in intensity for 2 M/ℓ 2,6-dimethylphenol in C_6D_6 under partial saturation conditions.
Solid line: backward-sweep, Dotted line: forward-sweep, Recorded at 100 MHz with a sweep rate 1.08 Hz/sec.
Arrow: transition between antisymmetric states.

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