

## SHORT COMMUNICATIONS

### PROTON MAGNETIC RESONANCE SPECTRA OF $A_2B_2$ SYSTEMS\*

By P. J. BLACK† and M. L. HEFFERNAN†

In the course of investigations on the proton magnetic resonance spectra of *N*-substituted heterocyclic systems, we have recently examined the resonances from the aromatic protons in benzimidazole and benzotriazole. The spectra were recorded for solutions of these compounds in acetone. Because of the rapid proton exchange that takes place in the heterocyclic ring under these conditions, there is an effective plane of symmetry and hence both spectra are classified as  $A_2B_2$  systems.

#### *Experimental*

The spectra were measured on a Varian DP 60 high resolution spectrometer equipped with a flux stabilizer and operating at a resonance frequency of 56.4 Mc/s. The samples were saturated solutions in acetone and were contained in precision-walled tubes of 5 mm o.d. The spectra were calibrated with respect to an internal tetramethylsilane reference using the usual side-band modulation technique. In each case several spectra were measured and mean line positions and intensities were obtained.

#### *Results and Discussion*

The  $A_2B_2$  spectra were conveniently analysed using the expressions derived by Dischler and Maier (1961) rather than by the earlier scheme of analysis due to Pople, Schneider, and Bernstein (1957). In this latter scheme the *para* spin-coupling constant,  $J_{12}$ , is assumed to have a value of zero. In the more recent work this assumption is found to be incorrect and a small *para* coupling constant of the order of 1 c/s is obtained directly from the analysis.

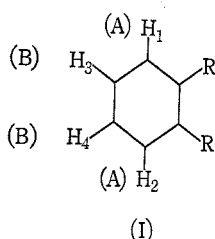
Since there is inevitably some experimental error in the line positions, we found that the line spacing rules used as internal checks on the validity of our parameters were not obeyed exactly. However, by assuming small deviations in the observed line positions (*c.* 0.1–0.2 c/s) it was possible to obtain unambiguous values for the parameters.

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† Department of Chemistry, Monash University, Clayton, Victoria.

TABLE 1  
SPIN-SPIN COUPLING CONSTANTS AND  $\tau$ -VALUES FOR BENZIMIDAZOLE AND BENZOTRIAZOLE

	$J_{12}$ (c/s) (para)	$J_{34}$ (c/s) (ortho)	$J_{13}=J_{24}$ (c/s) (ortho)	$J_{14}=J_{23}$ (c/s) (meta)	$\tau$	$\tau_{12}$	$\tau_{34}$
Benzimidazole ..	0.7	7.1	8.2	1.4	2.52	2.30	2.74
Benzotriazole ..	1.0	7.2	8.6	0.8	2.29	2.03	2.55



The numbering system used in these compounds is shown in (I). The parameters are the four coupling constants  $J_{12}$  (*para*),  $J_{34}$  (*ortho*),  $J_{13}=J_{24}$  (*ortho*),  $J_{14}=J_{23}$  (*meta*), and the dimensionless  $\tau$  values  $\tau_{12}$ ,  $\tau_{34}$ . The  $\tau$ -value of the position corresponding to the centre of symmetry is denoted by  $\tau$ . The values obtained are shown in Table 1.

The estimated precision is within  $\pm 0.1$  c/s for the coupling constants and  $\pm 0.01$  for the  $\tau$ -values. The experimental spectra together with the values calculated using the above parameters are shown in Figure 1.

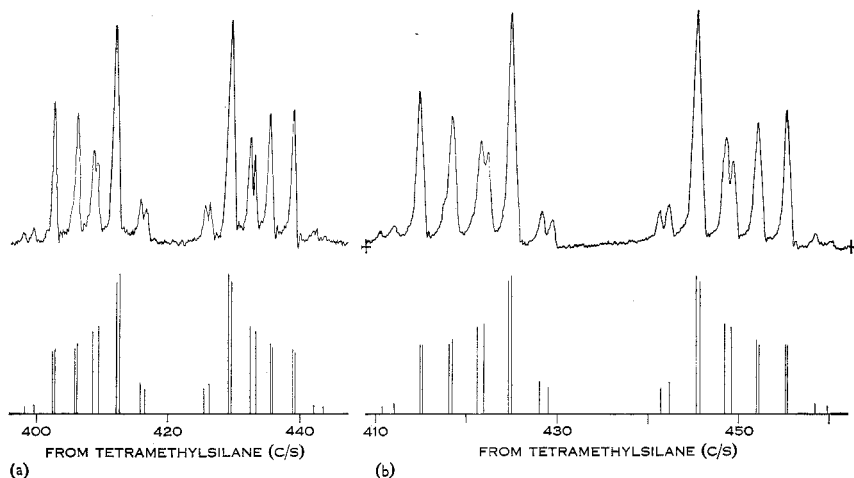


Fig. 1.—Experimental and calculated spectra of (a) benzimidazole and (b) benzotriazole.

The ordering of the nuclei, i.e. whether  $H_1$  and  $H_2$  are  $A_2$  or  $B_2$ , is not implicit in an  $A_2B_2$  spectrum. However, from earlier work on similar systems it seems certain that the above numbering is the correct one.

The coupling constants are similar in magnitude to those obtained for related systems by Dischler and Englert (1961).

We hope to use these results as a starting point for the analysis of more complicated spectra derived from unsymmetrical four spin systems.

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### *References*

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