SHORT COMMUNICATIONS

PROTON MAGNETIC RESONANCE SPECTRA OF $A_4B_2$ SYSTEMS*

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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 $A_4B_2$ 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 $A_4B_2$ 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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The numbering system used in these compounds is shown in (I). The parameters are the four coupling constants $J_{12}$ (para), $J_{94}$ (ortho), $J_{13}=J_{24}$ (ortho), $J_{14}=J_{23}$ (meta), and the dimensionless $\tau$ values $\tau_{13}$, $\tau_{34}$. 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 ±0.1 c/s for the coupling constants and ±0.01 for the $\tau$-values. The experimental spectra together with the values calculated using the above parameters are shown in Figure 1.

The ordering of the nuclei, i.e. whether $H_1$ and $H_2$ are $A_2$ or $B_2$, is not implicit in an $A_2E_2$ 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

INFRARED SPECTRA OF SUBSTITUTED PHENANTHROLINES IN THE OUT-OF-PLANE $\text{CH}$ DEFORMATION REGION

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Detailed interpretation of vibrational spectra is impossible for complex molecules but information of value may be obtained from an empirical study of the spectra of series of related substances. The dependence of band pattern on molecular substitution has been demonstrated for several regions in the infrared spectra of aromatic compounds, for example, the out-of-plane $\text{CH}$ deformation region, $900-650 \text{ cm}^{-1}$.

The correlation between the number of adjacent hydrogen atoms and the frequency of the corresponding absorption band for in-phase out-of-plane $\text{CH}$ deformation is well established for benzene variously substituted (Bellamy 1958) and fused ring aromatic compounds (Wiberley and Gonzalez 1961). The infrared spectra of heteroaromatics, e.g. pyridine, quinoline, and their derivatives, likewise show the above correlation (Karr, Estep, and Papa 1959; Godar and Mariella 1961). The study is now extended to 1,10-phenanthroline and a number of its derivatives. Only one report of a systematic study of the infrared spectra of substituted phenanthrolines seems to have been made (Smith and Diehl 1961). Few details were published.

Results and Discussion

Table 1 lists the frequencies of the absorption bands observed between 900 and 650 cm$^{-1}$ in the various spectra. The data for 1,10-phenanthroline are taken from the work of Schilt and Taylor (1959). Possibilities of one hydrogen, two and three adjacent hydrogen atoms arise. The corresponding regions of absorption (Bellamy 1958) are inserted in the column headings of Table 1. Frequencies of absorption observed below 750 cm$^{-1}$ are entered in the final column. Band intensities are enclosed in parentheses. Some of the substances

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