Molar Kerr Constants and Conformations of 2- and 4-Phenylpyridine

By H. H. HUANG
(*Chemistry Department, University of Singapore, Singapore,* 10)

Summary The molar Kerr constants of 2- and 4-phenylpyridine (105 and 778 $\times 10^{-12}$, respectively, in carbon tetrachloride at 25°) indicate a nonplanar structure for the former compound and may be reconciled with a flat configuration for the latter, in which conjugation produces a strong polarisability exaltation along the 1,1′-bond.

CONSIDERABLE interest[1] has recently been shown in the relative steric requirements of the lone electron pair on a ring nitrogen atom, a covalently bound hydrogen atom (N–H) and an *N*-methyl group as deduced from conformational analysis of piperidines. I report molar Kerr constants of two heterocyclic molecules, namely 2- and 4-phenylpyridine, which throw new light on the steric requirements of the nitrogen lone pair compared with covalently bound hydrogen, through the determination of their configurations as solutes in carbon tetrachloride at 25°.

For 4-phenylpyridine, molar Kerr constants calculated from the group polarisabilities of pyridine[2] and benzene[3] by tensor addition are 403 $\times 10^{-12}$ for the configuration in which the two rings are coplanar, and 383 $\times 10^{-12}$ for the orthogonal configuration. The measured value however, is 778 $\pm$ 30 $\times 10^{-12}$. This striking discrepancy between calculated and observed values is similar in pattern and magnitude to those previously observed[4] for the 4-derivatives of biphenyl and by analogy with those compounds, may be attributed to a pronounced polarisability exaltation effect along the 1,1′-bond due to ring–ring conjugation Such an effect is understandable if the 4-phenylpyridine molecule has an effectively flat configuration in solution.

For 2-phenylpyridine, the calculated molar Kerr constants for the coplanar and orthogonal configurations, after allowing for moments induced in the phenyl ring by the primary dipole at the heteroatom, are $+179$ and -68×10^{-12}, respectively. The observed value however, is 105 $\pm$ 5 $\times 10^{-12}$. The absence of a polarisability exaltation effect here is unambiguous, and certainly in striking contrast to that observed for 4-phenylpyridine, thus providing strong support for the view that 2-phenylpyridine, unlike 4-phenylpyridine, is nonplanar although opportunities for conjugation in the 2-derivatives are not lacking. Further, the observed molar Kerr constant for 2-phenylpyridine suggests that the dihedral angle between the two rings is *ca.* 30°. Scale drawings of 2-phenylpyridine with van der Waals' radii show that the overlap between the nitrogen atom and the hydrogen atom nearest to it in the adjacent ring is less than that between 2,2′ hydrogen atoms; it is also less than that between 2,2′ and 6′6′ hydrogen atoms in 4-phenylpyridine. The foregoing results can be explained if the steric requirements of a pyridine nitrogen lone pair are greater than those of a hydrogen atom covalently bound to a phenyl carbon atom.

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