Stereospecificity of Benzene–Nitrosamine Complexes by Nuclear Magnetic Resonance Studies

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NUCLEAR MAGNETIC RESONANCE solvent-shift studies on the diamagnetic shielding of specifically oriented aromatic molecules in collision complexes can provide valuable information on the stereochemistry and structure of these complexes.[1] Although a general description of a benzene–nitrosamine complexation has been given on the basis of n.m.r. studies,[2] an investigation on the geometry of such complexes becomes possible now that decoupling experiments have furnished unequivocal assignments of the α-protons of conformationally frozen 4-alkyl-1-nitrosopiperidines. These nitrosamines show four distinct signals for the four magnetically nonequivalent α-protons in a rigid chair conformation.

The chemical shifts (3M-solution in CCl_4 from internal Me_4Si at 60 Mc./sec.) of four α-protons of 4-t-butyl-1-nitrosopiperidine are $H_a = 140$, $H'_a = 213$, $H'_e = 284$ and $H_e = 279$ c./sec. respectively. The chemical shift differences [$\Delta\delta = \delta(CCl_4) - \delta(CCl_4 - C_6H_6)$ in c./sec.] of these protons on dilution with increasing amounts of benzene at 33° were plotted against mole fraction of benzene as shown in the Figure. A similar plot for t-butyl protons was included to indicate the general diamagnetic shielding of benzene since the protons were located sufficiently far from the nitrosamino-moiety to isolate the protons from specific shielding effects. Other 4-alkyl-1-nitrosopiperidines showed the same solvent shift trends in benzene.

The rates of specific benzene shift in the vicinity of nitrosamine groups arising from a collision complex are greater for *trans*-protons (H'_a and H'_e) and for α-axial protons and almost nil at *cis*-α-equatorial (H_e). The nearly straight lines of the plots below a benzene mole-fraction of 0·8 suggest a 1 : 1 complex formation up to this concentration. The deviations shown by H_a, H'_a, and H'_e beyond this concentration in comparison to t-butyl protons are indicative of multiple complexation. If the extrapolation of the straight lines at infinite dilution $\Delta\delta_\infty$ are taken as the shift differences for the "pure" 1 : 1 complex, the association constant is calculated to be 0·210 ± 0·002.

These results provide an empirical correlation with the stereochemistry of nitrosamines. Further assuming the nonbonding orbitals and the polar form contribution in the nitrosamine resonance do not interfere with the above induced diamagnetic shifts, the Johnson–Bavey plots[3] of "isoshielding" curves around a benzene magnetic field can be used to estimate the approximate geometry of the complex. One of the best approximations defined by the four parameters is that the plane of benzene ring approaches from H_a and H'_a side at the distances of 2·5 and 2·8 Å respectively and the in-plane benzene axes is parallel to the N–N bond but shifted 0·5 Å toward *trans*-side.

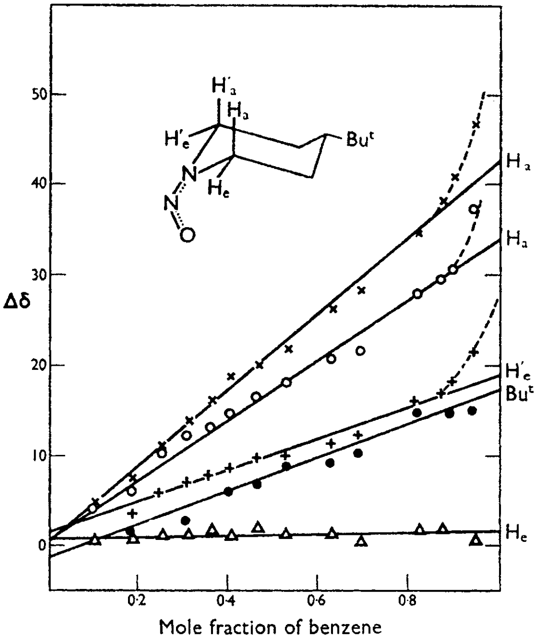

FIGURE.

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[3] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.