

10 Aromatic Compounds

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1 General

The plenary lectures, presented at the fourth international symposium on the chemistry of novel aromatic compounds, have been published.¹ It is now apparent that the transition from bond equalization, an accepted criterion for an aromatic structure, to bond alternation will be gradual.² In borderline cases the degree of distortion will be small. Substitution by methyl groups does not appear to affect the magnetic anisotropy of the benzene nucleus. Despite some criticism large anisotropies in the molar susceptibilities are still used as a test for aromaticity.³

The possibility of cycloheptatriene-norcaradiene isomerization in the presence of an annelated cyclobutadiene has been investigated as a probe for the anti-aromaticity of the latter sub-unit. The n.m.r. spectroscopic results are in favour of a significant negative resonance energy.⁴ The extent and pattern of π -electron delocalization in aromatic (and olefinic) aldehydes have been investigated using lanthanum-induced diamagnetic shifts in ¹³C n.m.r. spectra.⁵ The free-radical 2,2,6,6-tetramethylpiperidin-1-oxyl has been used as a shift reagent and paramagnetic effects have been reported for a number of arenes.⁶

The temperature dependence of ¹H spin-lattice relaxation times has been used to determine the size of the rotational barriers in methyl-substituted triptycenes.⁷ Barriers involving bridgehead methyls are significantly increased by a peri-methyl group. This suggests that a gear effect is probably absent. The ground-state energy in, for example, 1-fluoro-9-(1-naphthyl)fluorene is higher than in the parent hydrocarbon and results in a lowering of the rotational energy barrier.⁸ Restricted rotation at the 1,8-positions has been observed by differential scanning calorimetry in 1,8-di(1-naphthyl)naphthalene.⁹

A series of papers report the results of further investigations on the conformational behaviour of benzo-derivatives of medium-sized ring systems by dynamic

¹ *Pure Appl. Chem.*, 1982, **54**, 927-1155.

² R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.*, 1982, **104**, 3517.

³ M. M. Abdel-Kader, *Chem. Phys. Lett.*, 1982, **93**, 297.

⁴ F.-G. Klärner, E. K. G. Schmidt, and M. A. Abdel Rahman, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 138; F.-G. Klärner, E. K. G. Schmidt, M. A. Abdel Rahman, and H. Kollmar, *ibid.*, p. 139.

⁵ R. J. Abraham, H. A. Bergen, D. J. Chadwick, and F. Sancassan, *J. Chem. Soc., Chem. Commun.*, 1982, 998.

⁶ Z. W. Qui, D. M. Grant, and R. J. Pugmire, *J. Am. Chem. Soc.*, 1982, **104**, 2747.

⁷ F. Imashiro, K. Takegoshi, T. Terao, and A. Saika, *J. Am. Chem. Soc.*, 1982, **104**, 2247.

⁸ E. Ibuki, S. Ozasa, Y. Fujioka, and H. Mizutani, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 845.

⁹ S. Murata, T. Mori, and M. Oki, *Chem. Lett.*, 1982, 271.

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