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Edge Association and Nuclear Magnetic Resonance Solvent Effects in Cyclopropane

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Cyclopropane, unlike other cycloalkanes, is distinctly basic[1,2] and strongly anisotropic in both its magnetic susceptibility[3] and its basicity.[1] The magnetic anisotropy of cyclopropane derivatives is observed frequently in NMR spectra as the strong shielding of protons located above the face of a cyclopropane ring.[4,5] In this respect cyclopropane is quite similar to benzene.[5] The anisotropy of the cyclopropane basicity appears in the observation that intramolecular hydrogen bonds between hydroxyl and cyclopropyl groups are formed only when a cyclopropane edge is accessible to the hydroxyl proton.[1] Here cyclopropane, apparently most basic at its periphery, differs from benzene, which has a high π-electron density above the plane of the ring. Dipolar solutes such as acetonitrile, dichloromethane, 1,1,1-trichloroethane etc. are therefore expected to associate with cyclopropane mainly in its deshielding region, in contrast to the benzene case, where predominant association above the face of the ring gives rise to the well-known aromatic solvent-induced shift to high fields in NMR spectra.[6] The solvent effects caused by cyclopropane and by benzene in the NMR spectra of these molecules should therefore be opposite in sign. To our knowledge, this important corollary of the edge-association model has not only not been discussed previously, but also on occasion the erroneous impression has been created that the solvent effects should be qualitatively the same.[7]

Table 1.

solvent	/ temperature (deg)	Solvent shifts (ppm) on		
		CH_2Cl_2	CH_3CCl_3	CH_3CN
cyclopropane	-56	- 0.222	- 0.108	a
propene	-56	b	+ 0.043	a
toluene	-53	+ 1.078	+ 0.658	a
quadricyclene	+33			- 0.14[c]
norbornadiene	+33			+ 0.16[c,d]
cyclohexene	+34	- 0.020		- 0.008
norcarane	+34	- 0.068		
norcarane	-56	- 0.12[f]		- 0.07
cyclopropane/cyclopentane[e]	-56	- 0.14[f]		

[a] acetonitrile self-associates too strongly at low temperatures
[b] CH_2Cl_2 cannot be used as a solute because of peak overlap with propene
[c] with cyclohexane as internal standard
[d] Ref. 8. [e] Ref. 12 [f] ± 10%

Table 1. lists solvent shifts[9] (plus signs denoting upfield shifts) referred to a solution of the same solute at the same temperature in neat cyclopentane, with cyclopentane as internal standard.[10] It is seen that indeed all cyclopropane derivatives tested cause downfield shifts and comparison between cyclopropane derivatives and related hydrocarbons, particularly striking in the cyclopropane/propene[11] and quadricyclene/norbornadiene cases,[12] provides excellent evidence for predominant edge association in the general case where steric constraints are absent. Clearly the interpretation of intermolecular anisotropy effects involving three-membered rings[13,7] requires an analysis of the factors controlling collision complex geometry just as in the case of aromatic solvent-induced shifts.

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References and Notes

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9. Solute and cyclopentane concentrations were below 0.3 M.
10. The cyclopropane solvent shifts are smaller than the aromatic solvent-induced shifts because both anisotropy and association constant are lower for cyclopropane than for benzenoid hydrocarbons.[2]
11. Note that propene possesses a permanent dipole moment and is more polarizable than cyclopropane, the solvent effects should therefore be reversed if they were not due to the anisctropy effect.
12. The solvent effect in norcarane is smallest due to internal dilution. Cyclopropane, diluted with pentane to give the same molar concentration as in neat norcarane, causes a solvent shift close to that of norcarane at -56°.
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