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## Proton Magnetic Resonance Spectra of Cubane Derivatives.<sup>1</sup> II. Aromatic Solvent-Induced Shifts

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**Abstract:** Aromatic solvent-induced shifts (ASIS) ( $\nu_{\text{CDCl}_3} - \nu_{\text{Ar}}$ ) have been measured for a number of substituted cubanes in benzene and pyridine and an additivity rule has been derived which allows accurate prediction of these shifts. Protons remote from the substituent show the largest ASIS and these are shown to correlate with substituent electronegativity. Models are discussed for the nature and stereochemistry of the solute-solvent interaction. It is suggested that the observed additive shifts arise from independent, transient 1:1 associations of solvent molecules with the electron-deficient sites of *all* local dipoles in the solute.

Stereospecific changes in chemical shifts induced by aromatic solvents have been reported for a wide variety of solutes, and a number of different models of the solute-solvent interaction have been proposed to explain them.<sup>2-4</sup> In our studies of substituted cubanes, we found ASIS useful in removing accidental equivalences of chemical shifts when deceptively simple NMR spectra were obtained in CDCl<sub>3</sub>. The observed shifts are highly stereospecific, are additive, and show interesting correlations with substituent electronegativities. In contrast to some other systems which have been studied, the rigid, fixed geometry of the cubane system makes it an ideal model for the investigation of both the nature and stereochemistry of these solute-solvent interactions. We report here the results of our studies and confirm that the model proposed by Ronayne and Williams<sup>5</sup> satisfactorily accounts for observed ASIS, both in this study and in those of other workers.

### Results

The compounds were synthesized, and their spectra were measured and analyzed using the computer program LAOCN3,<sup>6</sup> in the manner previously described.<sup>1</sup> The observed chemical shifts and ASIS  $\Delta = (\nu_{\text{CDCl}_3} - \nu_{\text{Ar}})$  for unsubstituted,

monosubstituted, and 1,4-disubstituted cubanes are shown in Table I; a positive  $\Delta$  denotes an upfield shift on replacing CDCl<sub>3</sub> by the aromatic solvent.

The observed solvent shifts with one exception<sup>7</sup> follow a consistent pattern which is summarized by eq 1.

$$\Delta = S_0 + (S_1 + 7.0) + S_2 \quad (1)$$

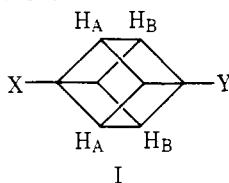
The parameter  $S_0$  is the observed ASIS of unsubstituted cubane, i.e., 9.0 Hz in benzene and 14.0 Hz in pyridine. For disubstituted cubanes,  $S_1$  and  $S_2$  are constants whose values depend both upon the substituents and their location ( $\beta$ ,  $\gamma$ , or  $\delta$ ) relative to the proton whose shift is being calculated. Values of these specific substituent shift parameters,  $S_n$ , are given in Table II. For unsubstituted or monosubstituted cubanes, only the first one or two terms of eq 1 are used, respectively. Values of  $\Delta$  calculated from eq 1 are included in Table I and agree to within  $\pm 3$  Hz with the observed shifts.

In our previous paper<sup>1</sup> we reported an additivity rule, eq 2,

$$\nu_{\text{CDCl}_3} = 403.8 + \Delta\nu_1 + \Delta\nu_2 \quad (2)$$

which accurately predicts chemical shifts of cubane and its mono- and 1,4-disubstituted derivatives in CDCl<sub>3</sub>.<sup>8</sup> Combining

Table I. Chemical Shifts and ASIS in Benzene and Pyridine for I



Substituents		Solvent <sup>a</sup>	Chemical shifts, Hz, obsd (calcd)			$\Delta_{\text{CDCl}_3}^{\text{Ar}}$ , Hz, obsd (calcd)		
Y	X		$\nu_A$	$\nu_B$	Others	$\Delta_A$	$\Delta_B$	Others
H <sub>C</sub>	H <sub>C</sub>	Benzene	394.8 (394.8)	<i>b</i>	<i>b</i>	9.0 (9.0)	<i>b</i>	<i>b</i>
		Pyridine	389.7 (389.8)	<i>b</i>	<i>b</i>	14.1 (14.0)	<i>b</i>	<i>b</i>
	COOH	Benzene	410.3 (411.7)	365.6 (366.2)	362.9 <sup>c</sup>	17.9 (17.5)	36.2 (37.0)	36.1 <sup>c</sup>
		Pyridine	423.5 (423.7)	382.5 (382.2)	380.2 <sup>c</sup>	4.7 (5.5)	19.3 (21.0)	18.8 <sup>c</sup>
	CO <sub>2</sub> CH <sub>3</sub>	Benzene	411.2 (411.8)	369.3 (371.0)	367.0, <sup>c</sup> 342.1 <sup>d</sup>	12.9 (13.5)	30.9 (30.5)	30.7, <sup>c</sup> 26.6 <sup>d</sup>
		Pyridine	413.1 (413.3)	377.8 (379.5)	375.8, <sup>c</sup> 363.0 <sup>d</sup>	11.0 (12.0)	22.4 (22.0)	21.2, <sup>c</sup> 5.7 <sup>d</sup>
	Br	Benzene	401.0 (399.7)	367.1 (364.9)	365.0 <sup>c</sup>	25.2 (25.5)	42.7 (43.5)	42.4 <sup>c</sup>
		COCl	Benzene	400.0 (400.8)	347.2 (350.2)	344.9 <sup>c</sup>	43.5 (42.5)	57.7 (55.0)
CH <sub>3</sub>	CO <sub>2</sub> H	Benzene	401.4 (402.5)	336.4 (337.3)	100.0 <sup>e</sup>	10.0 (9.0)	27.8 (27.5)	27.4 <sup>e</sup>
		Pyridine	416.8 (417.0)	353.4 (353.8)	116.4 <sup>e</sup>	-5.4 (-5.5)	10.8 (11.0)	11.0 <sup>e</sup>
	CO <sub>2</sub> CH <sub>3</sub>	Benzene	403.6 (402.6)	341.9 (342.1)	104.9, <sup>e</sup> 344.4 <sup>d</sup>	4.0 (5.0)	21.2 (21.0)	22.1, <sup>e</sup> 23.9 <sup>d</sup>
		COCl	Benzene	392.8 (391.6)	323.2 (321.3)	92.3 <sup>e</sup>	34.4 (34.0)	45.4 (45.5)
Br	NHCO <sub>2</sub> CH <sub>3</sub>	Benzene	378.9 (381.3)	338.1 (339.9)	111.8, <sup>e</sup> 342.8 <sup>f</sup>	10.8 (9.5)	11.7 (10.5)	14.2, <sup>e</sup> 22.8 <sup>f</sup>
		Pyridine	424.0 (423.3)	408.0 (407.6)		10.8 (10.5)	18.2 (17.0)	
	CO <sub>2</sub> H	Benzene	389.9 (388.9)	383.3 (382.9)	333.8 <sup>d</sup>	40.7 (41.0)	40.4 (40.0)	35.5 <sup>d</sup>
		Pyridine	414.3 (412.9)	406.7 (404.9)	360.8 <sup>d</sup>	16.3 (17.0)	17.0 (18.0)	8.5 <sup>d</sup>
	CO <sub>2</sub> CH <sub>3</sub>	Benzene	378.8 (377.9)	363.0 (362.2)		67.9 (70.0)	61.9 (64.5)	
		Pyridine	405.8 (407.7)	<i>b</i>		54.7 (53.0)	<i>b</i>	
CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> H	Benzene	396.4 (394.9)	388.9 (390.2)	336.2 <sup>d</sup>	30.2 (32.0)	35.7 (34.5)	33.8 <sup>d</sup>
		Pyridine	420.1 (420.4)	411.5 (412.7)	363.6 <sup>d</sup>	6.5 (6.5)	13.1 (12.0)	6.4 <sup>d</sup>
	COCl	Benzene	383.0 (384.0)	375.2 (374.2)	333.4 <sup>d</sup>	57.0 (57.0)	50.4 (52.5)	37.3 <sup>d</sup>
		Pyridine	415.2 (414.3)	409.4 (408.2)	362.7 <sup>d</sup>	-7.6 (-7.5)	3.2 (3.0)	6.1 <sup>d</sup>
	NCO	Benzene	376.2 (373.7)	394.7 (392.8)	339.0, <sup>d</sup> 339.0 <sup>f</sup>	31.1 (32.5)	16.2 (17.5)	29.8, <sup>d</sup> 28.2 <sup>f</sup>
		Pyridine	422.1 (422.2)	405.4 (405.7)	362.8 <sup>d</sup>	-1.9 (-2.0)	17.8 (17.5)	6.7 <sup>d</sup>
	CONH <sub>2</sub>	Benzene	393.2 (395.0)	<i>b</i>	337.1 <sup>d</sup>	29.0 (28.0)	<i>b</i>	32.8 <sup>d</sup>
		Pyridine	409.1 (410.0)	<i>b</i>	364.3 <sup>d</sup>	13.1 (13.0)	<i>b</i>	7.0 <sup>d</sup>
	CH <sub>2</sub> OH	Benzene	361.2 (361.6)	402.1 (402.5)	340.6, <sup>d</sup> 337.3 <sup>g</sup>	26.3 (26.5)	11.4 (11.5)	28.5, <sup>d</sup> 37.7 <sup>g</sup>
		Pyridine	385.5 (385.1)	409.0 (409.0)	364.0, <sup>d</sup> 385.4 <sup>g</sup>	2.2 (3.0)	4.4 (5.0)	5.1, <sup>d</sup> -10.4 <sup>g</sup>
CO <sub>2</sub> H	CO <sub>2</sub> H	Pyridine	409.4 (423.1 <sup>h</sup> )	<i>b</i>		19.3 (5.5 <sup>h</sup> )	<i>b</i>	
CH <sub>2</sub> OH	CH <sub>2</sub> OH	Pyridine	384.2 (384.1)	<i>b</i>	389.5 <sup>g</sup>	-4.6 (-5.0)	<i>b</i>	-12.8 <sup>g</sup>
COCl	COCl	Benzene	362.0 (363.2)	<i>b</i>		81.6 (81.5)	<i>b</i>	

<sup>a</sup> For chemical shifts in CDCl<sub>3</sub> see ref 1. <sup>b</sup> Same as for H<sub>A</sub>. <sup>c</sup> H<sub>C</sub> shift. <sup>d</sup> OCH<sub>3</sub> shift. <sup>e</sup> CH<sub>3</sub> shift. <sup>f</sup> NHCO<sub>2</sub>CH<sub>3</sub> shift. <sup>g</sup> CH<sub>2</sub>OH shift. <sup>h</sup> If the "normal" *S* parameters from Table II are used for both COOH groups.

Table II. Specific Substituent Shifts *S*

Substituent	Benzene			Pyridine	
	<i>S</i> <sub>β</sub>	<i>S</i> <sub>γ</sub>	<i>S</i> <sub>δ</sub>	<i>S</i> <sub>β</sub>	<i>S</i> <sub>γ</sub>
COOH	1.5	21.0	20.0	-16.0 <sup>a</sup>	0.0 <sup>a</sup>
COOMe	-2.5	14.5	14.5	-9.0	1.0
COCl	26.5	39.0	41.5		
Br	9.5	27.5	26.5	-4.0	5.0
CH <sub>3</sub>	-9.5	-8.5		-10.0	-11.0
CH <sub>2</sub> OH	-4.0	-2.0		-19.0	-7.0
NHCO <sub>2</sub> Me	2.0	4.0			
CONH <sub>2</sub>				-24.0	5.5
NCO				-27 ± 3	-12 ± 3

<sup>a</sup> For first COOH group only. In diacid the second COOH group has *S*<sub>β</sub> = -1, *S*<sub>γ</sub> = 14.0.

eq 2 with eq 1, gives eq 3 which predicts to within ±3 Hz the observed chemical shifts in benzene and pyridine (see Table I).

$$\nu_{\text{Ar}} = 403.8 - S_0 + (\Delta\nu_1 - S_1 - 7) + (\Delta\nu_2 - S_2) \quad (3)$$

Chloroform has been used as the reference solvent in this study for reasons of solubility and because most of the cubane spectra that have been reported<sup>1</sup> were measured using it as solvent. To determine whether it is valid to consider chloroform as an "inert" reference, we have measured the spectra of several cubane derivatives in carbon tetrachloride. The observed

chemical shifts in CCl<sub>4</sub> and solvent shifts ( $\nu_{\text{CDCl}_3} - \nu_{\text{CCl}_4}$ ) are shown in Table III. Since all such solvent shifts for cage protons are <2.5 Hz, we consider their effects as negligible. However, the larger solvent shift (ca. 6 Hz) for the methyl protons of 1,4-dicarbomethoxycubane shows that this is only an approximation and confirms that CDCl<sub>3</sub> is not a truly inert reference solvent.<sup>2</sup>

## Discussion

ASIS arise from a solute-solvent interaction which results in a nonrandom orientation of the aromatic solvent molecules relative to the solute molecules.<sup>2,9</sup> The interaction is usually described as a dipole-induced dipole effect,<sup>3</sup> and is often discussed in terms of a single 1:1 solvent-solute collision complex of fixed geometry.<sup>10,11</sup> Since the lifetime of these associations is very short on the NMR time scale,<sup>2</sup> it is more correct to consider a slight time-averaged structuring of the solvent cage around the solute molecule, as the source of the shifts.<sup>9</sup> However, the 1:1 complex models are pictorially attractive and have been remarkably successful in predicting solvent shifts.<sup>2</sup> An approach that we have found especially useful is Ronayne and Williams' suggestion<sup>5</sup> that the aromatic solvent molecules solvate the electron-deficient sites of all local dipoles in the solute, in transient 1:1 associations, so that polyfunctional solutes undergo 1:1 interactions at various sites, independently.

If the benzene or pyridine molecules solvate an electron-deficient site on the cubane cage, the solvent shifts should show

Table III. Chemical Shifts and Solvent Shifts of 1 in CCl<sub>4</sub>

Substituent		Chemical shift, Hz, obsd (calcd) <sup>a</sup>			$\Delta_{\text{CDCl}_3/\text{CCl}_4}$ , (obsd), Hz, obsd		
X	Y	$\nu_A$	$\nu_B$	Other	$\Delta_A$	$\Delta_B$	Other
H	H	403.1 (403.8)	<i>b</i>		-0.7	<i>b</i>	
Br	Br	429.9 (429.8)	<i>b</i>		-1.1	<i>b</i>	
CO <sub>2</sub> Me	CO <sub>2</sub> Me	420.0 (423.0)	<i>b</i>	363.8 <sup>c</sup>	2.2	<i>b</i>	6.1
COCl	COCl	444.7 (444.7)	<i>b</i>		-1.1	<i>b</i>	
Br	COCl	426.8 (426.6)	449.0 (447.9)		-1.8	-2.3	

<sup>a</sup> Chemical shifts were calculated using the additivity rule derived for CDCl<sub>3</sub> as solvent (ref 1). <sup>b</sup> Same as for H<sub>A</sub>. <sup>c</sup> OCH<sub>3</sub> shift.

a correlation with substituent electronegativities. Aromatic solvent shifts in substituted benzenes have been correlated with Hammett  $\sigma$  parameters.<sup>12</sup> Figure 1 shows the variation with  $\sigma_1$  of the solvent shifts for protons on cubane  $\beta$  and  $\gamma$  to the substituent. The correlation shown uses  $\sigma_1$  values of Charton,<sup>13</sup> calculated from the  $\text{p}K_a$ 's of substituted acetic acids. Charton's compilation was used because of its completeness, but similar correlations obtain using  $\sigma_1$ 's calculated from <sup>19</sup>F NMR shieldings in weakly protonic solvents<sup>14</sup> or from  $\text{p}K_a$ 's of bicyclooctanecarboxylic acids,<sup>15</sup> or "average"  $\sigma_1$ 's.<sup>16</sup> Since measurements in two different solvents are being correlated, the sensitivity of these  $\sigma_1$ 's to solvent should be considered. The negligible solvent shifts we have observed between CDCl<sub>3</sub> and CCl<sub>4</sub> (which is similar to benzene in its effect on  $\sigma_1$ <sup>14</sup>) suggest that this effect is unimportant for most of the substituents. However, the CONH<sub>2</sub> group may be an exception. It is one of the most solvent-sensitive substituents in Taft's extensive tabulation,<sup>14</sup> its  $\sigma_1$  value (from <sup>19</sup>F NMR) varying from 0.10 in pyridine through ca. 0.21 in weakly protonic solvents to 0.65 in trifluoroacetic acid. Although Taft did not study the CONH<sub>2</sub> group in chloroform, that solvent's behavior was moderately protonic toward other substituents, so that it may not be entirely valid to discuss the chemical shift effects of the CONH<sub>2</sub> group in CDCl<sub>3</sub> and pyridine in terms of a single  $\sigma_1$ . The COOH group was excluded from the correlation in pyridine because it reacts chemically with the solvent. Examination of Figure 1 shows that there is a very good linear correlation for the  $\gamma$  position in both solvents, but only a poor one with benzene and practically none with pyridine for hydrogen atoms  $\beta$  to the substituent.

We suggest that the  $\gamma$  shifts arise almost entirely from association of solvent with an electron-deficient site on the cubane cage, but that, in some cases at least, there is a second solvent-solute interaction which makes an important contribution to the  $\beta$  shifts. These additional 1:1 interactions can occur when the substituent itself contains a local dipole. These additional effects will be discussed after a consideration of the nature and stereochemistry of the basic association that gives rise to the large  $\gamma$  shifts.

Many models and variations on them have been proposed to account for observed ASIS, but these are often very similar and we therefore consider in detail only two. From a study of a wide range of compounds Ledaal<sup>10</sup> has proposed that the aromatic solvent molecule associates with the positive end of the molecule, with the dipolar axis along the sixfold axis of symmetry of the benzene ring. Figure 2a illustrates the predicted geometry for the monobromocubane-benzene complex using this model. The  $\gamma$  and  $\delta$  protons, lying nearest to the benzene ring, are correctly predicted to have the largest positive  $\Delta$ .

A very different model for the interaction<sup>5,9</sup> is illustrated

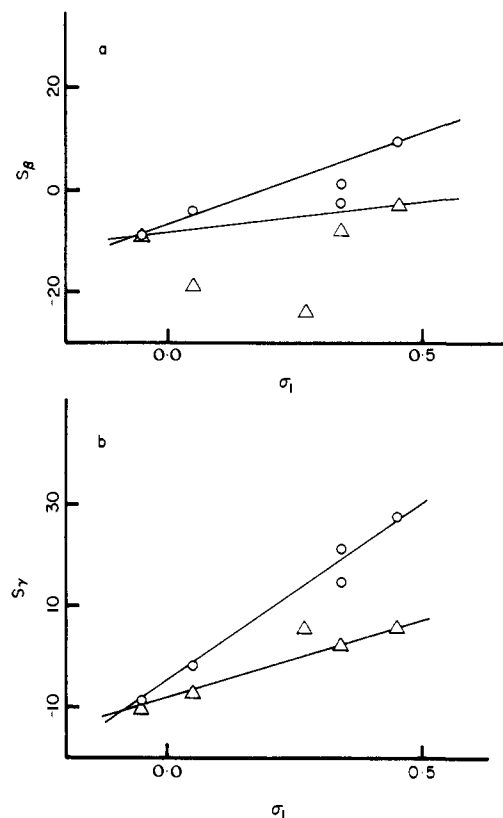


Figure 1. The variation of ASIS ( $\nu_{\text{CDCl}_3} - \nu_{\text{Ar}}$ ) for substituted cubanes with Charton's  $\sigma_1$  values: (a)  $\beta$ -hydrogen atoms, (b)  $\gamma$ -hydrogen atoms. (O) Ar = benzene; ( $\Delta$ ) Ar = pyridine.

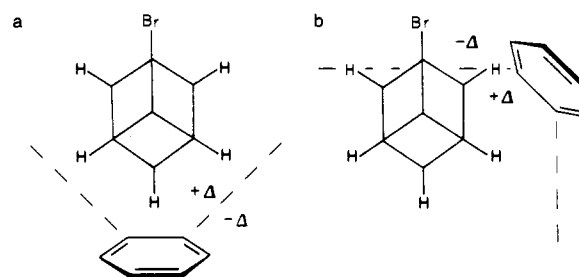


Figure 2. Models for the interaction of aromatic solvent molecules with bromocubane: (a) after Ledaal,<sup>10</sup> (b) after Ronayne and Williams.<sup>5</sup>

in Figure 2b in which the benzene molecule is oriented so as to lie as far as possible from the negative end of a local dipole while solvating the positive end. The maximum polarizability of benzene lies in the plane of the ring<sup>2</sup> but steric considerations<sup>5</sup> are argued to account for the nonplanarity shown in Figure 2b. Again the protons  $\beta$  to the substituent are correctly predicted to have a smaller solvent shift than the more remote protons, this time because the  $\beta$  protons lie near the edge of the aromatic shielding cone, whereas the  $\gamma$  and  $\delta$  protons lie near its center.

When one considers a 1,4-disubstituted cubane, the two models differ in their predictions (Figure 3). Ledaal's model (Figure 3a) requires a complete change in the geometry of the complex since there is no longer a net molecular dipole. Presumably some geometry such as that shown in Figure 3a has to be invoked and thus the observed additivity of chemical shifts is difficult to explain. However, in the alternative model (Figure 3b) the additivity relationship is preserved and logical. Each local dipole can independently form a 1:1 complex with a solvent molecule, giving rise to differing shielding effects upon each of the  $\beta$  and  $\gamma$  protons. Such differing effects imply

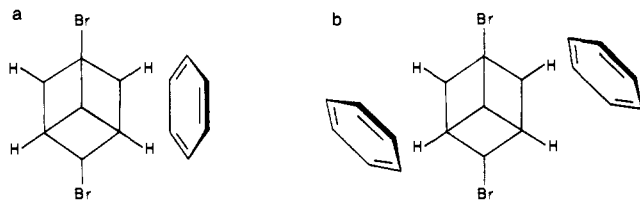


Figure 3. Models for the interaction of aromatic solvent molecules with a 1,4-disubstituted cubane: (a) after Ledaal,<sup>10</sup> (b) after Ronayne and Williams.<sup>5</sup>

an inherent additivity and the good agreement obtained between observed and predicted ASIS on the basis of Figures 2b and 3b lends very strong support to the proposal that these Figures provide the best pictures of the stereochemistry of the solute–aromatic solvent interaction. It is worth emphasizing that the “complexes” represented are transient species, and at any given time the solute molecule is probably not interacting with more than one molecule of solvent.

As can be seen by examination of the data of Table I, the observed additivity is not perfect; eq 1 implies that the effect of a second substituent on the solvent shift is approximately 7 Hz smaller than that of the first substituent and this result is not altogether surprising. Thus the electronic interaction between the two local dipoles, together with “steric” interactions of the aromatic solvent molecules forming transient associations with these two dipoles, will tend to weaken the complexes in the disubstituted molecule, relative to a mono-substituted one. Inspection of models shows that only three or four molecules of benzene or pyridine will fit around the circumference of a cubane molecule, within range to form an association as in Figure 2b. In a disubstituted cubane, there are two dipoles competing to form such an association with one of those three or four solvent molecules, and as a result each dipole will spend slightly less of its time complexed with a solvent molecule. Since the difference in shift effect between the first and second substituents is a constant 7 Hz, relatively independent of substituent electronegativities, we believe that this solvent-crowding effect is more important than the electronic effect.

It is well known that benzene complexes with a carbonyl group to give ASIS such as those shown schematically in Figure 4. Such an interaction accounts for the “anomalously” low solvent shifts in Figure 1a for protons  $\beta$  to a carbonyl substituent. In pyridine, protons  $\beta$  to an ester group show a similar deviation (Figure 1a) but much larger deviations are evident for protons  $\beta$  to a  $\text{CH}_2\text{OH}$  or  $\text{CONH}_2$  group.

The interaction of pyridine with the carbonyl group of an amide is stronger than with that of an ester because of the larger internal dipole of the amide group. Figure 5a shows a plausible geometry for this association. In all of the cases studied here the substituent–solvent complex is sufficiently remote from the  $\gamma$  protons that it does not contribute significantly to their ASIS. The carbinol substituent probably hydrogen bonds to pyridine as shown in Figure 5b and this suggestion is supported by the large downfield shift observed for the methylene protons.

The small solvent shifts observed with unsubstituted cubane deserve some comment. Similar solvent shifts are observed for methane using an external reference,<sup>17</sup> but are not expected when using an internal reference (TMS) of approximately the same spherical shape and size as the solute. For example, adamantane is reported to show no appreciable solvent shift.<sup>18</sup> There may be a weak dipole-induced dipole interaction between cubane and the polar pyridine, but we are unable to provide any good explanation, at present, for the somewhat smaller solvent shift in nonpolar benzene.

Although the alternative model of Ledaal explains, quali-

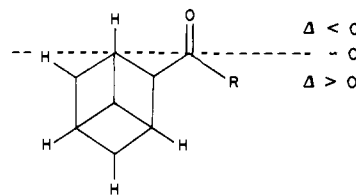


Figure 4. Aromatic solvent-induced shifts expected in the presence of a carbonyl group.

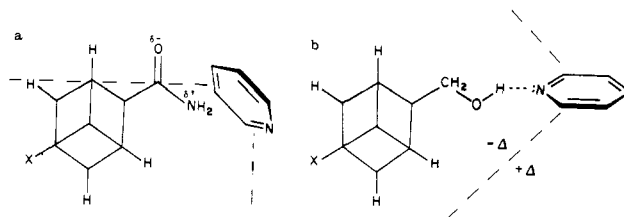


Figure 5. Models for the specific interactions of pyridine with (a) an amide group and (b) an alcohol group.

tatively, the majority of observed ASIS, an additivity of solvent shifts is not required by this model. It does not readily accommodate the differing behaviors of substituents which contain internal dipoles, such as  $\text{CONH}_2$ , and those that do not, such as Br or  $\text{CH}_3$ . The model described by Ronayne and Williams is in accord with these observations, as well as other reported effects, e.g., the effect of hexamethylbenzene upon the ring protons of 1-substituted 3,5-dinitrobenzenes in charge transfer complex interactions,<sup>19</sup> ASIS of alcohols,<sup>20</sup> etc. We believe, therefore, that our observations are most consistent with their assumption that the aromatic solvent is forming transient 1:1 associations, probably with the solvent molecules inclined as in Figure 2b, independently with the electron-deficient sites of all local dipoles in the solute. Thus, the shifts for bromocubane arise from a single such 1:1 complex, 1,4-dibromocubane forms two such complexes, and to explain the shifts for cubane-1,4-dicarboxylic acid monomethyl ester monoamide we postulate four independent transient 1:1 complexations.

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