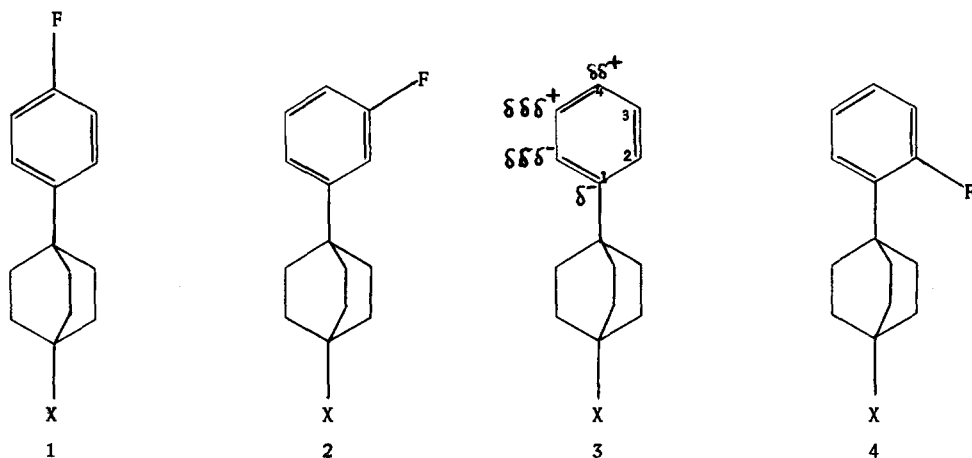


THE NATURE OF ARYL  $^{19}\text{F}$  NMR POLAR FIELD EFFECTS: EVIDENCE FOR REVERSED POLAR FIELD EFFECTS

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(Received in UK 8 August 1977; accepted for publication 2 September 1977)

Recent studies by us,<sup>1,2,3</sup> and others,<sup>4,5</sup> have demonstrated the beneficial aspects of the phenylbicyclo[2.2.2]octyl skeletal framework for assessing polar field effect phenomena in isolation of other electronic mechanisms. Herein we report further on these systems with new  $^{19}\text{F}$  nmr data for the previously reported<sup>1</sup> 1-X-4-(p-fluorophenyl)bicyclo[2.2.2]octanes (1) in an inert non-polar solvent (cyclohexane) together with similar data for a new model system (2; 1-X-4-(m-fluorophenyl)bicyclo[2.2.2]octanes) which, in conjunction with the aryl  $^{13}\text{C}$  nmr



data for 1-X-4-phenylbicyclo[2.2.2]octanes (3) in cyclohexane- $d_{12}$ , allow a definitive assessment of  $^{19}\text{F}$  nmr polar field effects in these systems. In addition, we also report  $^{19}\text{F}$  nmr data for another new model system (4; 1-X-4-(o-fluorophenyl)bicyclo[2.2.2]octanes) which we have examined since a consideration of orientational factors suggested that reversed  $^{19}\text{F}$  nmr polar field effects should be observed here, a phenomenon previously sought<sup>6</sup> after in other model aryl fluorides but to no avail. The substituent chemical shift (SCS) data listed in Table 1 have been related to substituent parameters ( $\sigma_{\text{I}}$  and  $\sigma_{\text{R}}^{\text{o}}$ )<sup>7</sup> utilizing Taft's dual substituent parameter equation<sup>7</sup> (Table II). It can be seen that, except for C-2 in 3, the precision of fit for the correlations are excellent. The  $\rho_{\text{R}}$  values are not statistically significant.

**Table I:** Substituent Chemical Shifts (SCS)<sup>a</sup> for Systems 1, 2, 3, and 4.

Substituent (X)	<sup>19</sup> F SCS			<sup>13</sup> C SCS			
	1	2	4	3			
				C-1	C-2	C-3	C-4
CH <sub>3</sub>				-0.47	0.00	-0.02	0.00
F	1.00	0.58	-0.58	b	-0.19	0.25	0.54
Cl	1.09	0.62	-0.57	-2.27	-0.25	0.22	0.54
Br	1.17	0.65	-0.56	-2.16	-0.27	0.25	0.57
I	1.17		-0.53				
OCH <sub>3</sub>	0.51	0.26	-0.47	-1.37	-0.08	0.11	0.24
OCOCH <sub>3</sub>	0.75	0.51	-0.54				
NH <sub>2</sub>	0.37	0.18	-0.36	-0.99	0.03	0.06	0.13
NO <sub>2</sub>	1.76	0.97	-0.61	-3.06	-0.22	0.44	0.90
CN	1.49	0.90		b	-0.25	0.44	0.84
NH <sub>3</sub> <sup>+</sup>	2.18 <sup>c</sup>	1.04 <sup>c</sup>	-1.08 <sup>c</sup>	-3.84 <sup>c</sup>	-0.88 <sup>c</sup>	0.26 <sup>c</sup>	1.02 <sup>c</sup>
NH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>				-2.97 <sup>d</sup>	-0.15 <sup>d</sup>	0.34 <sup>d</sup>	0.76 <sup>d</sup>

- a. Chemical shifts (ppm) referenced to parent compound (X = H; ± 0.03 ppm) in cyclohexane; a positive sign denotes deshielding.
- b. Not observed due to low solubility of compound.
- c. Solvent, CF<sub>3</sub>CO<sub>2</sub>H.
- d. Solvent, CH<sub>3</sub>OH.

**Table II:** Best Fit Parameters for DSP Correlative Analyses<sup>a</sup> of <sup>19</sup>F and <sup>13</sup>C SCS listed in Table I.

System	$\rho_I$	$\rho_R$	SD <sup>b</sup>	f <sup>c</sup>
1 <sup>d</sup>	2.52	0.29	0.12	0.11
2 <sup>d</sup>	1.49	0.22	0.07	0.11
4 <sup>d</sup>	-1.04	0.43	0.04	0.08
3; C-1 <sup>e</sup>	-4.73	0.52	0.10	0.05
3; C-2 <sup>e</sup>	-0.44	-0.05	0.05	0.26
3; C-3 <sup>e</sup>	0.65	0.15	0.04	0.12
3; C-4 <sup>e</sup>	1.34	0.23	0.04	0.07

- a. The appropriate form of the equation is,  $SCS = \rho_I \sigma_I + \rho_R \sigma_R$ <sup>o</sup>
- b. The standard deviation of the fit.
- c. The fit parameter,  $f \equiv SD/RMS$ , where RMS is the root mean square of the data points. Correlation of excellent precision are those for which  $f \ll 0.1$ .
- d. NH<sub>3</sub><sup>+</sup> excluded from analysis.
- e. NH<sub>3</sub><sup>+</sup> and NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> excluded from analysis.

Although the difference of opinion<sup>8,9</sup> concerning the nature of aryl <sup>19</sup>F nmr polar field effects has now been largely reconciled,<sup>4,10,11</sup> the quantitative evaluation of the relative magnitude of the components (direct field ( $F_D$ ) and field-induced  $\pi$  polarization ( $F_\pi$ ))<sup>12</sup> determining this phenomenon is still a subject for deliberation.<sup>4,11</sup> The relative magnitude of  $F_\pi$  effects within model aromatic systems can be conveniently monitored utilizing <sup>13</sup>C SCS as a charge density probe.<sup>10,11,13,14</sup> The main assumption underlying this technique is that aryl <sup>13</sup>C SCS, properly chosen, are dominated by  $\pi$  electron density perturbations.<sup>15</sup> However, it must be borne in mind that this assumption may not be valid for those carbon centres where  $\pi$  electron density changes are small and the longitudinal polarizabilities of the associated CH bonds are significant and different. A consideration of orientational factors<sup>16</sup> ( $\cos \theta/r^3$ ;  $\theta$  is the angle between a line of length  $r$  drawn between the midpoints of the CH (or CF) and CX bonds) indicates that the latter effect should be identical for carbons centers 3 and 4 in system 3. Hence  $F_\pi$  (C-3)/ $F_\pi$  (C-4) for 3<sup>17</sup> equals  $\rho_I$  (C-3)/ $\rho_I$  (C-4) = 0.65/1.34 (Table II) i.e.  $F_\pi$  (System 2)/ $F_\pi$  (System 1) = 0.5.

The direct field contribution ( $F_D$ ) to 1 and 2 can now be estimated in the following way for an arbitrary substituent ( $\sigma_I = 1$ ): If the polar field effect in I is equated to  $F_D + F_\pi$ , then the effect in 2 is equal to  $F_D + 0.5 F_\pi$  since orientational factors (vide supra) in 1 and 2 are identical. Therefore,  $(F_D + F_\pi)/(F_D + 0.5F_\pi) = \rho_I$  (System 1)/ $\rho_I$  (System 2) = 2.52/1.49 (Table II). Hence  $F_D = 0.25 F_\pi$ . Therefore, the direct field contribution to 1 and 2 is 20% and 33% respectively. The former determination is in remarkably good agreement with a recent estimate (25%) for I by an entirely different approach.<sup>4</sup> Utilizing the SCS data for NO<sub>2</sub> and CN in I (Table I) and the above determination, we have evaluated A in the Buckingham equation<sup>18</sup> ( $SCS = AE_z$  where  $E_z$  is the direct field component along the CF bond) for linear electric field effects. Standard bond lengths and bond angles<sup>19</sup> were assumed while  $\sigma$  bond moments<sup>20</sup> for NO<sub>2</sub> and CN were employed. The values are  $59 \times 10^{-12}$  and  $46 \times 10^{-12}$  respectively.

Finally, it can be seen (Table I and II) that, as expected, reversed <sup>19</sup>F nmr polar field effects are realized in system 4. Using the A value derived from the NO<sub>2</sub> data in 1 (vide supra), the Buckingham equation can be used to estimate the direct field ( $F_D$ ) contribution for NO<sub>2</sub> in 4. The value (-0.20 ppm) indicates that the  $F_D$  contribution here is approx., 33%. It is important to note that the similarity between the pattern of  $\rho_I$  values (<sup>19</sup>F SCS) for 1, 2 and 4 and the corresponding  $\rho_I$  values (<sup>13</sup>C SCS) for the appropriate carbon centers in 3 (Table II) clearly exemplifies the dominance of field-induced  $\pi$  polarization over direct field effects in determining <sup>19</sup>F SCS in 1, 2, and 4. This result is corroborated similarly by the <sup>19</sup>F and <sup>13</sup>C SCS for the positive pole, NH<sub>3</sub><sup>+</sup> (Table I).

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