

SUBSTITUENT EFFECTS ON FLUORINE - 19 CHEMICAL SHIFTS IN BENZOBICYCLO(2.2.2)OCTEN-1-YL FLUORIDES

William Adcock\* and Anil N. Abeywickrema

(School of Physical Sciences, The Flinders University of South  
Australia, Bedford Park, S.A. 5042, Australia)

**Summary:** Inverse  $^{19}\text{F}$  substituent chemical shifts (SCS) of *m*- and *p*-substituted benzylfluorides are shown to have their origin in hyperconjugation involving the CF  $\sigma$  - bond.

Although the perturbation of  $^{19}\text{F}$  chemical shifts of arylfluorides by the electronic effects of remote substituents is now reasonably well understood in terms of the local  $\pi$ -electron distribution round the fluorine nucleus<sup>1</sup>, the corresponding situation for stereochemically well-defined alkylfluoride systems<sup>2</sup> poses a conundrum within the framework of current chemical shift theory. Thus, for most of these latter systems, but not all<sup>2d</sup>, the  $^{19}\text{F}$  substituent chemical shifts (SCS) are in the opposite direction (inverse substituent dependence) to expectations based on the electron density parameter dominating the decisive paramagnetic contribution to  $^{19}\text{F}$  chemical shifts.

Perhaps the most dramatic exemplification of this phenomenon of inverse  $^{19}\text{F}$  SCS are the results for substituted benzylfluorides<sup>2c,2i</sup> and fluoromethylnaphthalenes<sup>2f-g</sup>. Here the effect is of such a large magnitude as to encourage an investigation of its origin in the hope that this will shed some light on the dichotomous response of  $^{19}\text{F}$  chemical shifts to substituent electronic effects in general. Thus, we present herein preliminary  $^{19}\text{F}$  nmr data for two new stereochemically well-defined model systems (6- and 7- substituted 1-fluoro-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalenes, 1 and 2 respectively) which contribute significantly in this



regard. The most important feature of these new model systems is that the CF bond is constrained to the nodal plane of the adjacent aromatic  $\pi$  system, thus, the effect of substituent electronic perturbations on the  $^{19}\text{F}$  chemical shifts of benzylfluorides can be assessed in the complete absence of hyperconjugative interactions involving the CF  $\sigma$ -bond. The  $^{19}\text{F}$  SCS for 1 and 2 are shown in Table 1 together with the corresponding values for the previously reported meta- and para-substituted benzylfluorides in order to facilitate comparisons.

A cursory examination of the data listed in Table 1 clearly indicates that for a series of substituents covering a wide range of electronic effects the  $^{19}\text{F}$  SCS for 1 and 2 (formally para and meta orientations respectively) are confined to a very narrow range (< 1 ppm). Note that this stands in striking contrast to the large effects observed in the corresponding benzylfluoride:

TABLE 1.  $^{19}\text{F}$  SUBSTITUENT CHEMICAL SHIFTS (SCS)<sup>a,b</sup>

| Substituent (X)               | Benzobicyclo[2.2.2]octen-1-yl Fluorides <sup>c,d</sup> |        | Benzylfluorides <sup>e</sup> |                            |
|-------------------------------|--|--------|------------------------------|----------------------------|
|                               | 1  | 2      | para                         | meta                       |
| $\text{NO}_2$                 | + 0.69   | + 0.31 | - 8.10(-8.86) <sup>f</sup>   | - 5.10(-4.68) <sup>g</sup> |
| CN                            | + 0.09   | - 0.20 | - 7.68(-8.41)                | - 5.03                     |
| $\text{COCH}_3$               | + 0.59   | 0.00   |                              |                            |
| $\text{COOCH}_3$              | + 0.52   | + 0.07 |                              |                            |
| F                             | - 0.04   | + 0.79 | + 2.82(+2.74) <sup>f</sup>   | - 2.82                     |
| Cl                            |  |        | - 0.49(-0.74) <sup>f</sup>   | - 2.99                     |
| Br                            | - 0.18   | + 0.46 | - 0.98                       |                            |
| $\text{CH}_3$                 | - 0.07   | + 0.11 | + 2.95(+3.03) <sup>f</sup>   | + 0.44                     |
| $\text{NH}\cdot\text{COCH}_3$ | + 0.04   | - 0.15 |                              |                            |
| $\text{NH}_2$                 | - 0.29   | + 0.73 |                              |                            |
| $\text{OCH}_3$                |  |        | + 7.79(+7.46) <sup>f</sup>   | - 0.94                     |

a. In ppm. b. A positive sign implies deshielding. c. Solvent, cyclohexane. d. Accurate to  $\pm 0.01$  ppm. e. Taken from ref. 2c. Solvent,  $\text{CCl}_4$ . f. Taken from ref. 2i. Solvent,  $\text{DCCl}_3$ . g. This study. Solvent, cyclohexane.

Moreover, the signs of the shifts for 1 and 2 do not indicate a general pattern consistent with inverse substituent behaviour. Thus, we believe the results for 1 and 2 offer compelling support for the idea<sup>2c,3</sup> that hyperconjugation involving the CF bond is indeed largely responsible for the large inverse  $^{19}\text{F}$  SCS of benzylfluorides<sup>2c,2i</sup> and fluoromethylnaphthalenes<sup>2f-g</sup>. Now since this electronic interaction provides a mechanism by which substituents in the aryl ring of fluoromethylaromatics can strongly polarize the  $\sigma$  electrons in the  $2p_y$  orbital of fluorine, but not the  $\pi$  electrons in the  $2p_z$  and  $2p_x$  orbitals which are responsible for aryl  $^{19}\text{F}$  SCS<sup>1</sup>, it is tempting to speculate that inverse substituent behaviour is a manifestation of their dominant redistribution. In other words, substituent-induced  $^{19}\text{F}$  chemical shifts depend not only on the total charge density on fluorine but also on the symmetry of its distribution. Thus, the direction of  $^{19}\text{F}$  SCS in alkylfluorides may, in some instances, be finely balanced since the relative extent of polarization of the  $\sigma(2p_y)$  and  $\pi(2p_x$  and  $2p_z)$  electrons will depend significantly on the electronic structure of the bonds in the local vicinity of the fluorine atom.

The full data for 1 and 2, including their syntheses and a  $^{13}\text{C}$  nmr study, will be presented in a main paper.

#### References and Notes

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