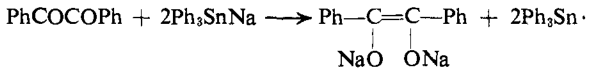
Retention in configuration in the 7-norbornenyl and 1-methyl-2,2-diphenylcyclopropyl systems requires that the coupling reaction, eq 5, be much faster than the rate of epimerization of the corresponding organoalkali intermediates. Walborsky and Impastato have shown that the above cyclopropyllithium does indeed epimerize slowly.[11] On the other hand, reactions proceeding from *syn*-7-bromonorbornene through the Grignard and lithium reagents are not stereospecific.[12] However, it is not known whether the epimerization occurs in the organometallic or at the free-radical stage in its formation. The 7-norbornenyl free radical epimerizes faster than it reacts with tri-*n*-butyltin deuteride.[13]

Triphenyltin sodium reacts with benzoyl chloride to form the dibenzoate of *cis*-stilbenediol and hexaphenylditin.[5] The pathway to this product involves electron transfer processes, eq 9–13. Thus, the possibility that

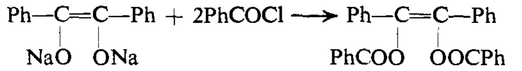
$$\mathrm{Ph_3SnNa + PhCOCl \longrightarrow Ph_3Sn\cdot + Ph\dot{C}O} \tag{9}$$

$$\mathrm{2Ph_3Sn\cdot \longrightarrow Ph_3SnSnPh_3} \tag{10}$$

$$\mathrm{2Ph\dot{C}O \longrightarrow PhCOCOPh} \tag{11}$$



$$\mathrm{PhCOCOPh + 2Ph_3SnNa \longrightarrow Ph{-}\underset{NaO}{\underset{|}{C}}{=}\underset{ONa}{\underset{|}{C}}{-}Ph + 2Ph_3Sn\cdot} \tag{12}$$



$$\mathrm{Ph{-}\underset{NaO}{\underset{|}{C}}{=}\underset{ONa}{\underset{|}{C}}{-}Ph + 2PhCOCl \longrightarrow Ph{-}\underset{PhCOO}{\underset{|}{C}}{=}\underset{OOCPh}{\underset{|}{C}}{-}Ph} \tag{13}$$

electron transfer occurs in the reactions of alkyl halides with organotin alkalis cannot be dismissed out of hand. Fortunately, this is subject to test. A carbonium mechanism has also been proposed.[8]

**Acknowledgments.**[14] This work was supported by the National Science Foundation. Trimethyltin chloride was kindly provided by M & T Chemicals, Inc.

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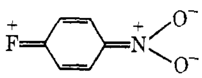
## Regarding Aprotic Solvent Effects on the Fluorine Nuclear Magnetic Resonance Shifts of Para-Substituted Fluorobenzenes[1]

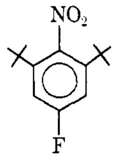
*Sir:*

We wish to report two new critical lines of evidence which define the origin of the effects of aprotic polar solvents on the F nmr shifts of para-substituted fluorobenzenes. The two previous interpretations which have been made of these solvent effects are shown to be invalid. Taft and students have attributed the increasing downfield shifts of +R para-substituted fluorobenzenes relative to fluorobenzene with increasing polarity of the aprotic solvent to increased contribution of the trans quinoidal resonance forms,[2] *e.g.*

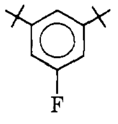


Emsley and Phillips[3] have attributed these solvent effects to the reaction field shielding contribution to the total shielding which they have related to the relative size of the solute's dipole moment.

Compounds I and II have been prepared[4] and their F nmr solvent shifts compared with those of compounds III and IV. The results are recormed in Table I. The



I



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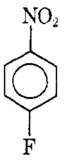

III

IV

downfield shift for the coplanar $NO_2$ group, $\int_{IV}^{III}$, as expected, is markedly larger than the corresponding shift for the twisted $NO_2$ group, $\int_{II}^{I}$. However, the solvent effects on $\int_{IV}^{III}$ are not markedly smaller as expected,[2] but instead essentially identical solvent effects are observed. Further, in cyclohexane, $\int_{II}^{I}$ is essentially the same as $\int_{H}^{m\text{-}NO_2}$ (the substituent shift for *m*-nitrofluorobenzene, −3.43 ppm).[5] This identity is expected on the basis that (a) the *tert*-butyl groups force the $NO_2$ group perpendicular to the plane of the benzene ring giving rise to complete steric inhibition of resonance[6] and (b) the polar effect of the twisted $NO_2$ is essentially the same as that for the coplanar $NO_2$ substituent in *m*-nitrofluorobenzene.[7] Previous evidence[2b,5,8] has indicated generally that the effects of meta substituents (a) involve little or no resonance or $\pi$ delocalization effects and (b) the polar effects are nearly equal from the meta and para positions.

Since both solvent and polar effects are the same for the completely twisted $p$-$NO_2$ as for the coplanar $p$-$NO_2$ group, it is clear that the polar *not* the resonance effect[2] of the $NO_2$ group governs the solvent effect. Since $NO_2$ twisting markedly alters the molecular dipole moment,[9] the equal solvent effects on $\int_{II}^{I}$ and $\int_{IV}^{III}$ also clearly do not support the Emsley and Phillips explanation of polar solvent effects.

We have reexamined the previously reported[2] F nmr shifts for a critical selection of both −R and +R para-substituted fluorobenzenes obtained in a graded series of aprotic polar solvents. By the choice[2] of both solvents and substituents, the formation of specific complexes, *e.g.*, hydrogen-bonded complexes, or Lewis

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**Table I.** F Nmr Shifts for Twisted and Untwisted $p$-NO$_2$[a,b]

| | Solvent | | | | | | |
|---|---|---|---|---|---|---|---|
| | $c$-C$_6$H$_{12}$ | CCl$_4$ | C$_6$H$_6$ | THF | Me$_2$CO | DMF | DMSO |
| $-f_{\mathrm{II}}^{\mathrm{I}}$ | 3.32 | 3.63 | 3.75 | 4.07 | 4.45 | 4.60 | 4.67 |
| | (0.00) | (0.31) | (0.43) | (0.75) | (1.13) | (1.28) | (1.35) |
| $-f_{\mathrm{IV}}^{\mathrm{III}}$ | 9.01 | 9.37 | 9.43 | 9.84 | 10.14 | 10.26 | 10.25 |
| | (0.00) | (0.36) | (0.42) | (0.83) | (1.13) | (1.25) | (1.24) |

[a] All shifts in ppm as obtained in 0.02 $M$ solutions. [b] Values in parentheses are the additional downfield shifts beyond that observed in cyclohexane.

**Table II.** F Nmr Shifts for Para-Substituted Fluorobenzenes[a]

| | Solvent | | | | | | |
|---|---|---|---|---|---|---|---|
| Subst | $c$-C$_6$H$_{12}$ | CCl$_4$ | C$_6$H$_6$ | THF | Me$_2$CO | DMF | DMSO |
| NMe$_2$ | 15.90 | 15.62 | 15.96 | 16.36 | 16.33 | 16.45 | 16.13 |
| OMe | 11.58 | 11.54 | 11.47 | 11.56 | 11.45 | 11.45 | 11.33 |
| OC$_6$H$_5$ | 7.45 | 7.40 | 7.20 | 7.16 | 7.00 | 6.91 | 6.86 |
| F | 6.72 | 6.70 | 6.65 | 6.45 | 6.33 | 6.24 | 6.20 |
| Cl | 3.10 | 3.10 | 3.03 | 2.78 | 2.64 | 2.55 | 2.55 |
| Br | 2.53 | 2.50 | 2.50 | 2.23 | 2.11 | 2.06 | 2.04 |
| I | 1.63 | 1.56 | 1.66 | 1.51 | 1.35 | 1.42 | 1.51 |
| Me | 5.53 | 5.46 | 5.46 | 5.46 | 5.44 | 5.42 | 5.34 |
| SCF$_3$ | −4.18 | −4.31 | −4.17 | −4.43 | −4.56 | −4.61 | −4.50 |
| CN | −8.80 | −9.11 | −9.06 | −9.45 | −9.70 | −9.79 | −9.80 |
| NO$_2$ | −9.01 | −9.37 | −9.43 | −9.84 | −10.14 | −10.26 | −10.25 |
| $-\rho_{\mathrm{I}}$[b] | 7.82 | 8.13 | 8.17 | 8.81 | 9.19 | 9.35 | 9.36 |
| $-\rho_{\mathrm{R}}$[b] | 31.00 | 31.04 | 31.14 | 31.70 | 31.74 | 31.85 | 31.43 |
| $\lambda$[b] | 3.96 | 3.82 | 3.81 | 3.60 | 3.45 | 3.41 | 3.36 |
| sd[b] | 0.64 | 0.60 | 0.61 | 0.61 | 0.60 | 0.60 | 0.63 |
| sd/rms | 0.079 | 0.074 | 0.076 | 0.074 | 0.073 | 0.073 | 0.078 |

[a] All shifts in ppm relative to fluorobenzene. Concentration of both $p$-XC$_6$H$_4$F and C$_6$H$_5$F is 0.01 $M$; *cf.* ref 16b. [b] From DSP equation analysis of shifts in each solvent using the $\sigma_{\mathrm{R}}^0$ scale; $\lambda \equiv \rho_{\mathrm{R}}\rho_{\mathrm{I}}$.

acid–base adducts, have been excluded from making any appreciable contributions to the measured shifts. The results have been analyzed using the dual substituent parameter (DSP) equation ($P^i = \sigma_{\mathrm{I}}\rho_{\mathrm{I}}^i + \sigma_{\mathrm{R}}\rho_{\mathrm{R}}^i$)[10] and are presented in Table II. The correlations achieved by the DSP equation are all of acceptable precision and discriminating best fits are achieved in each instance with the use of the $\sigma_{\mathrm{R}}^0$ scale. It may readily be seen from Table II that the resonance effect blending parameter, $\rho_{\mathrm{R}}$, is essentially solvent independent, whereas the polar effect term, $\rho_{\mathrm{I}}$, increases significantly in magnitude with increasing solvent polarity. Thus the downfield polar solvent shifts are indeed correlated generally by the substituent $\sigma_{\mathrm{I}}$ parameter,[11] independent of the substituent $\sigma_{\mathrm{R}}^0$ parameter. The order of $\rho_{\mathrm{I}}$ values follows empirical solvent polarity parameters from reactivity (log $k_1$ values for the rates of $p$-methoxyneophyl tosylate solvolysis[12]), from ir ($G$ values for shifts of hydrogen-bonded complexes[13]), and from uv ($E_{\mathrm{T}}$ values for charge transfer complexes of betaines[14]).

Our new data provide critical evidence that $\pi$ electron delocalization between substituent (including the para F substituent) and the benzene ring (or the para F detector) plays essentially no part in the aprotic polar solvent effect. Consequently, $\sigma$ bond moments must be the predominant consideration. Recent theoretical evidence[15] strongly suggests that one mechanism of deshielding of F involves decreasing F $\sigma$ electron charge density, the latter being directly related to the $\sigma_{\mathrm{I}}$ value of the para substituent. This electron-withdrawing mechanism of the para substituent is assisted by the mobility (polarizability) of the $\pi$ electrons of the aromatic cavity. It is further assisted by the local fields created by polar solvent molecules which enhance (in approximate proportion to $\sigma_{\mathrm{I}}$) the electron-withdrawing polar effect of the substituent. The present evidence suggests that these local solvent fields involve a number of molecules acting at relatively long range. Thus, for example, the equal solvent effects for $f_{\mathrm{IV}}^{\mathrm{III}}$ and $f_{\mathrm{II}}^{\mathrm{I}}$ do not appear to support the notion of formation of weak 1:1 multipolar complexes,[16,17] since close approach of a single solvent molecule to the twisted NO$_2$ group of I is sterically hindered.

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(11) The only substantial exception known to us involves the aprotic polar solvent effects for $p$-fluoronitrosobenzene.[2] The solvent shifts for the $p$-NO substituent ($\sigma_{\mathrm{I}}$ = 0.37) are parallel but anomalously larger than the corresponding ones for the $p$-NO$_2$ substituent ($\sigma_{\mathrm{I}}$ = 0.65).

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(17) Since the net C–F bond polarities in I and III surely must be materially different, the equality of the two solvent effects appears to provide further suggestive evidence that a major component resulting from differential action of local solvent fields on the C–F bonds is not present, *i.e.*, that the F probe is not unduly complicated; also, *cf.* results reported in ref 16.

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