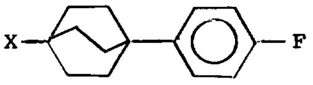
Tetrahedron Letters No. 8, pp 675 - 678, 1977. Pergamon Press. Printed in Great Britain.

CONCERNING THE TRANSMISSION OF POLAR SUBSTITUENT EFFECTS IN CONJUGATED VERSUS UNCONJUGATED SYSTEMS

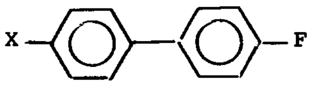
William F. Reynolds
(Department of Chemistry, University of Toronto,
Toronto, Ontario, Canada M5S 1A1)

(Received in USA 20 December 1976; received in UK for publication 26 January 1977)

Adcock and Khor have recently reported ^{19}F chemical shift data for 1-substituted 4-p-fluorophenylbicyclo[2.2.2]octanes, 1.[1] Correlation with Taft's σ_I and $\sigma_R°$ parameters[2] indicated a substantial field/inductive dependence for ^{19}F chemical shifts in 1 ($\rho_I = -1.82$ in C_6H_6) but negligible resonance dependence ($\rho_R = -0.07$)[1]. This is approximately half of the field/inductive dependence for ^{19}F chemical shifts in 2 ($\rho_I = -3.35$ in C_6H_6[3]). These results were claimed to unambiguously demonstrate the dominance of field effects over π inductive effects in derivatives such as 1 and 2[1], thus apparently resolving the continuing controversy concerning the relative importance of field effects[4] and π inductive effects[5,6] upon aryl ^{19}F chemical shifts.

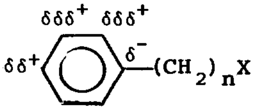


1



2

However, it has recently been shown that the field/inductive dependence of ^{13}C and ^{19}F chemical shifts in 2 is mainly due to field-induced polarization of the intervening π electron system[7]. Similar π polarization effects have been noted from ^{13}C chemical shifts and carbon electron densities in 3, where X is an electronegative group[8,9]:



3

Since 3 and 1 are closely related, it was anticipated that 1 should also show π polarization effects. Evidence supporting this view is presented below.

CNDO/2 molecular orbital calculations were performed for 4-ammoniobiphenyl in conformations with coplanar and orthogonal phenyl groups and for 4-ammonio-1-phenylbicyclo[2.2.2]-octane[10]. It is seen that in all three cases, the phenyl groups show π polarization similar to 3. The magnitude of this effect (as measured by the π electron density change at C(4)') is nearly equal for 4-ammoniobiphenyl and for the bicyclooctane derivative, with both showing π polarization effects approximately one-half of that for coplanar 4-ammoniobiphenyl (see Table I). The π polarization effect in the former two compounds can be attributed to through-space transmission of the polar effect of the NH_3^+ group[8]. The additional π polarization effect in coplanar 4-ammoniobiphenyl is due to polarization of the entire conjugated system, resulting in π electron transfer from one phenyl group to the other. This is primarily reflected by π electron density changes at C(2), C(4), C(2)' and C(4)' on going from orthogonal to coplanar 4-ammoniobiphenyl.

Thus π polarization could account for the two fold decrease in polar effects upon ^{19}F chemical shifts on going from 2 to 1. In support of this view, CNDO calculations for several polar derivatives of 1 show both phenyl π polarization and changes in fluorine 2p(π) electron density which are 13-15% of the π electron density changes at the adjacent carbon C(4)' (see Table II). A similar relationship between F and C(4)' π electron density change has been demonstrated for a series of derivatives $X\text{-}C_6H_4\text{-}G\text{-}C_6H_4F$[7]. Thus it appears that π polarization leads to concomitant changes in fluorine 2p(π) electron density. Assuming a proportionality factor of approximately 2000 ppm/π electron[11-13], it is seen that, within the limits of accuracy of the calculation[14], π polarization can account for a major part of the polar effects upon ^{19}F chemical shifts in 1 (see Table II). The only major discrepancy concerns the ammonio derivative where the calculations markedly overestimate the polar effect of this group. Presumably this occurs because the calculations do not allow for solvation and ion pairing of the charged group[8].

The alternative explanation of direct field effects to account for polar effects on ^{19}F chemical shifts in 1 does not seem viable. Direct field effects act mainly by polarizing the C-F σ bond[7]. These effects can be estimated, using the Buckingham equation[15] and a previously estimated value of $A \simeq 3x10$" for $C(sp^2)\text{-}F\sigma$ bonds[7]. A calculation of this nature indicates that direct field effects account for only about 25% of the polar effects upon ^{19}F chemical shifts in 1 (Table II)[16]. Furthermore a dominant direct field effect is inconsistent with the observed two-fold decrease in polar effects from 2 to 1. While the magnitude of the field effect depends upon the nature of the intervening molecular framework[1,17,18], previous calculations indicate that the bicyclo[2.2.2]octane group is only about 20% less effective than the phenyl group in transmitting field effects[18].

In conclusion, it is important to realize that the controversy cited in reference 1 is more apparent than real. Adcock regards π polarization as a form of field effect[4] while Taft classified it as a π inductive effect[12] (following the earlier classification of Katritzky and Topsom[19]). While a case can be made for either view[7], there is no real disagreement between the two groups, provided that it is accepted that π polarization is the dominant mechanism of transmission of polar effects in 1 and 2. The available evidence all seems consistent with this view[20].

Financial support from the National Research Council of Canada is gratefully acknowledged.

Table I: Calculated[a] carbon π charge densities for 4-ammoniobiphenyl in coplanar and orthogonal conformations and for 1-ammonio-4-phenylbicyclo [2.2.2] octane[b]

	Carbon[c]							
Compound	C(4)	C(3)	C(2)	C(1)	C(1)'	C(2)'	C(3)'	C(4)'
4-ammoniobiphenyl (orthogonal phenyl groups)	-135[d]	+2	+19	+78	-47	+6	+7	+27
4-ammoniobiphenyl (coplanar phenyl groups)	-143	+4	+12	+79	-46	+16	+4	+46
Δ[e]	-8	+2	-7	+1	+1	+9	-3	+19
1-ammonio-4-phenyl-bicyclo [2.2.2] octane	-	-	-	-	-36	+4	+7	+24

[a] CNDO/2 calculation using a standard program (Quantum Chemistry Program Exchange program 141) and standard geometries.

[b] Actual calculations carried out for a compound with one CH_2-CH_2 bridge replaced by two C-H bonds, e.g. for the boat conformation of cyclohexane. This was necessitated by program limitations on the number of atomic orbitals.

[c] Primed carbons refer to the unsubstituted phenyl group in 4-ammoniobiphenyl and the phenyl group in the bicyclo [2.2.2] octane derivative.

[d] Charge densities for the ammonio derivative relative to the unsubstituted derivative. A negative sign indicates increased electron density. Charge densities (x10^3).

[e] Change from orthogonal to coplanar 4-ammoniobiphenyl.

Table II: Calculated carbon and fluorine π charge densities for **1**[a], observed ^{19}F chemical shifts for **1** and estimated π polarization and direct field contributions to these chemical shifts.

	π charge densities[b]							
X	C(1)'	C(2)'	C(3)'	C(4)'	F	δ_F(c)	$\delta_F(\pi)$[d]	δ_F(field)[e]
F	-37	+7	+5	+22	+3	-0.78(-0.66)	-.6	-.19
OH	-11	+2	+2	+7	+1	-0.45(-0.24)	-.2	-.08
CN	-32	+4	+7	+17	+3	-0.98(-0.77)	-.6	-.24
NO_2	-83	+14	+13	+48	+6	-1.19(-0.97)[f]	-1.2	-.30
NH_3^+	-378	+52	+64	+235	+33	- (-2.17)	-6.6	-1.79

[a] See footnotes a-c from Table I.

[b] Charge densities (x10^4) relative to the unsubstituted derivative. A negative sign indicates increased electron density.

[c] Data from reference 1. A negative sign indicates low field shifts. Unbracketed and bracketed values are for benzene and dimethylformamide solutions respectively.

[d] Chemical shift due to π polarization, estimated assuming a scaling factor of 2000 ppm/π electron.

[e] Chemical shift due to direct field effect, estimated using Buckingham equation[15] and parameters from reference 7.

[f] Estimated from correlation equations from reference 1 and $\sigma_I = +0.65$, $\sigma_R^\circ = +0.15$[2].

References

1. W. Adcock and T.C. Khor, Tetrahedron Lett, 3063 (1976).

2. S. Ehrenson, R.T.C. Brownlee and R.W. Taft, Progr. Phys. Org. Chem., 10, 1 (1973).

3. S.K. Dayal and R.W. Taft, J. Am. Chem. Soc., 95, 5595 (1973).

4. W. Adcock and B.D. Gupta, J. Am. Chem. Soc., 97, 6871 (1975).

5. G.L. Anderson, R.C. Parish and L.M. Stock, J. Am. Chem. Soc., 93, 6984 (1971).

6. J. Fukunaga and R.W. Taft, J. Am. Chem. Soc., 97, 1612 (1975).

7. W.F. Reynolds and G.K. Hamer, J. Am. Chem. Soc., 98, 7296 (1976).

8. W.F. Reynolds, I.R. Peat, M.H. Freedman and J.R. Lyerla, Can. J. Chem., 51, 1857 (1973).

9. R.T.C. Brownlee, G. Butt, C.H. Chan and R.D. Topsom, J. Chem. Soc. Perkin II, in press. We thank Professor Topsom for supplying a copy of this article prior to publication.

10. The ammonio group was chosen for its large polar effect[8].

11. R.T.C. Brownlee and R.W. Taft, J. Am. Chem. Soc., 92, 7007 (1970).

12. W.J. Hehre, R.W. Taft and R.D. Topsom, Prog. Phys. Org. Chem. 12 (1976).

13. ^{19}F chemical shifts in aryl fluorides appear to be directly proportional to changes in fluorine 2p(π) electron density (references 7 and 12 and references therein).

14. The calculations are at best accurate to 10^{-4} electron, corresponding to an uncertainty in chemical shift of 0.2 ppm.

15. A.D. Buckingham, Can. J. Chem., 38, 300 (1960).

16. Direct field effects are relatively less important in **2** (10-13%)[7], due to enhanced π polarization.

17. R.B. Hermann, J. Am. Chem. Soc., 91, 3152 (1969).

18. G.K. Hamer, I.R. Peat and W.F. Reynolds, Can. J. Chem., 51, 897, 915 (1973).

19. A.R. Katritzky and R.D. Topsom, J. Chem. Ed., 48, 427 (1971).

20. It should be stressed that the conclusion that π polarization dominates over direct field effects applies specifically to aromatic systems where the probe group is essentially neutral (e.g. ^{13}C or ^{19}F chemical shifts). In the case of benzoic acid dissociation constants, where the field effect arises from a direct electrostatic interaction between the substituent and a changing probe group, direct field effects appear to dominate over polarization effects (W.F. Reynolds and P.G. Mezey, to be published.)