A Study of the π-Polarisation Effect: ^{13}C Nuclear Magnetic Resonance Chemical Shifts and SCF Electron Populations in 1-Substituted 4-Phenylbicyclo[2.2.2]octanes

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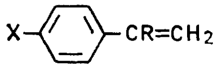
Substituent effects on the ^{13}C chemical shifts and SCF electron populations of the aromatic carbon atoms of a series of 1-substituted 4-phenylbicyclo[2.2.2]octanes have been determined. With this data and similar ^{13}C SCS and ^{19}F SCS data from the literature a model for the π-polarisation effect has been developed which provides a simple unified rationalisation of ^{13}C and ^{19}F SCS in systems in which the substituent is not directly attached to an aromatic ring.

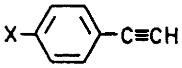
In spite of numerous investigations,[1-7] the effect of substituents on n.m.r. chemical shifts cannot yet be interpreted in a completely satisfactory way. Precise separation of mechanisms contributing to the substituent effects cannot always be achieved, and a good example [7] of this difficulty is the problem of determining the relative importance of direct field effects F_D and field-induced π-polarisation, F_π. One interpretation of ^{19}F substituent chemical shifts (SCS) in a wide variety of fluorine-substituted aromatic systems was based on the dominance of a F_D effect, *i.e.* direct electrostatic polarisation of the C–F bond by a distant substituent dipole (the view of Adcock and his co-workers [4-6]). An alternative explanation, offered by Taft and others [2,3,7] invoked π-inductive effects, *i.e.* the transmission of the substituent inductive effect to the C–F bond *via* the intervening π-electron system. This latter approach was the more difficult to substantiate using ^{19}F data alone and was vigorously disputed by Adcock.[4-6] However, extending the study of SCS to include aromatic ring carbon atoms might be expected to help resolve this dichotomy in the interpretation of ^{19}F SCS.

Reynolds and his co-workers [8,9] have shown that the side-chain ^{13}C and ^{1}H SCS in styrenes (1) and phenylacetylenes (2) can be most satisfactorily interpreted in terms of a combination of resonance, direct field (F_D) and π-polarisation effects (F_π). This last effect was envisaged as a polarisation of the side-chain π-electron system by a through-space interaction with a remote substituent dipole, a relatively neglected concept.

Subsequent work by the same group [10] with the model system (3; $n = 1$ or 2) provided some evidence for the polarisation of the aromatic π-system by the remote substituent dipole. The ^{13}C SCS and calculated electron densities (CNDO/2) in a series of benzyl and phenethyl derivatives (3; $n = 1$ or 2, X = Me, Cl, Br, or $\overset{+}{N}H_3$) indicated a polarisation of the π-electrons as shown in (4). A similar series of compounds was investigated by Brownlee *et al.*[11] using a wider range of substituents (3; $n = 2$ or 3, X = Me, OMe, OH, Br, or CN), and a slightly modified picture of π-polarisation, as shown in (5), was proposed, largely on the basis of the SCS at C-1′ and -4′. Shapiro [12] has also interpreted ^{13}C SCS in some benzyl compounds in terms of a similar π-inductive effect. Substituent effects in a wide range of naphthalene derivatives have also been discussed [13] recently in terms of a contribution from π-polarisation but this use of a directly substituted aromatic system does not lend itself to an unambiguous characterisation of this phenomenon.



(1)
R=H,Me or Bu^t



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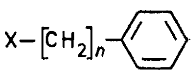
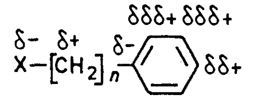
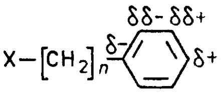


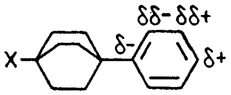
(3)
n = 1,2 or 3



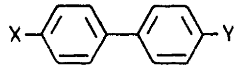
(4)
n = 1 or 2



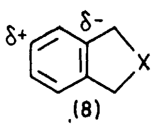
(5)
n = 2 or 3



(6)



(7)
a; Y=H b; Y=F



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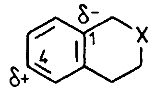

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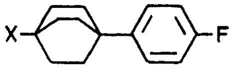

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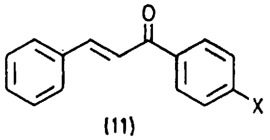

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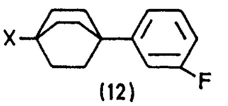

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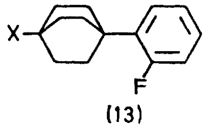

(13)

Although ω-substituted phenylalkanes are better than directly substituted benzenes for the study of F_π effects, a series of compounds of type (3) is still not a particularly good model system since the position of the substituent dipole cannot be precisely defined, and hyperconjugative interactions may vary through the series. The 4-phenylbicyclo[2.2.2]octyl system (6), however, has several advantages for the study of polar field effects [5,6,14,15] and we now report a full analysis of the ^{13}C aromatic chemical shifts in (6; X = H) and thirteen 1-substituted derivatives (X = Et, NMe_2, NH_2, CO_2Me, OMe, OH, I, Br, Cl, CN, F, NO_2, and $\overset{+}{N}Me_2H$). Adcock and Khor [16] have also reported ^{13}C SCS data for a smaller range of derivatives of (6).

EXPERIMENTAL

^{13}C Spectra were obtained on a Bruker HX 90E instrument (PCMU, Harwell) operating at 22.63 MHz. All compounds were examined as 0.1M solutions in $CDCl_3$ with tetramethylsilane as internal reference. Proton decoupling was employed in all cases with a standard 10 μs pulse width, 6024 Hz sweep width, and 4 K data points giving an uncertainty of ±0.13 p.p.m. in the chemical shifts. Several compounds in series (6) were prepared as described previously (X = H, Et, CO_2Me, OMe, OH, Br, CN,[17] X = NH_2,[18] X = I, Cl, F, NO_2[19]).

TABLE 1

^{13}C Aromatic substituent chemical shifts [a] and charge density changes [b] in 4-phenyl-1-X-bicyclo[2.2.2]octanes

	C-1′ (*ipso*)			C-2′ (*ortho*)			C-3′ (*meta*)			C-4′ (*para*)				
Substituent	$\Delta\delta$	Δq^σ	Δq^π	$\Delta\delta$	Δq^σ	Δq^π	$\Delta\delta$	Δq^σ	Δq^π	$\Delta\delta$	Δq^σ	Δq^π	$\Sigma\Delta q^\sigma$	$\Delta\Sigma q^\pi$
Et [c]	−0.33	0	2	0.0	−1	0	0.06	1	0	0.06	1	−1	1	1
NMe_2	−1.24			−0.13			0.13			0.19				
NH_2	−1.43	7	−2	−0.06	−1	0	0.13	0	1	0.23	−1	2	4	2
CO_2Me	−1.50			−0.06			0.19			0.39				
OMe	−1.89			−0.13			0.19			0.32				
OH	−2.08	22	−16	−0.19	0	1	0.13	0	4	0.32	−3	9	19	3
I	−2.08			−0.45			0.19			0.52				
Br	−2.60			−0.32			0.26			0.58				
Cl [d]	−2.73	37	−41	−0.32	2	6	0.19	−2	8	0.52	−11	25	26	12
CN	−2.80	23	−27	−0.32	1	4	0.39	−1	6	0.78	−17	17	16	10
F	−2.93	43	−38	−0.26	0	3	0.19	−2	9	0.52	−9	22	30	8
NO_2	−3.64	57	−70	−0.32	3	8	0.39	−3	16	0.84	−17	42	40	20
N^+Me_2H [e]	−3.90	256	−342	−0.39	27	20	0.45	−25	84	0.97	−90	216	170	82

[a] In p.p.m., relative to 4-phenylbicyclo[2.2.2]octane. Positive shifts are downfield. [b] From INDO SCF calculations. In units of 10^{-4} electrons relative to q^σ and q^π in 4-phenylbicyclo[2.2.2]octane. Negative sign indicates increased electron density. [c] MO calculations for Me. [d] MO calculation at CNDO/2 level. [e] MO calculations for NH_3^+.

1-*Dimethylamino*-4-*phenylbicyclo*[2.2.2]*octane* (6; X = NMe_2) was prepared from compound (6; X = NH_2) by reaction with formic acid and formaldehyde at 90—100° following a procedure described in ref. 20. Compound (6; X = NMe_2) (87%) had m.p. 74—75 °C, $\nu_{max.}$ (KCl) 2 920, 1 496, 1 455, 1 444, 1 359, 758, 693, and 538 cm^{-1}; $\delta(CDCl_3)$ 1.67—2.00 (12 H, m), 2.25 (6 H, s), and 7.17—7.43 (5 H, m) (Found: C, 83.7; H, 10.0; N, 6.1. $C_{16}H_{23}N$ requires C, 83.8; H, 10.1; N, 6.1%).

1-Dimethylamino-4-phenylbicyclo[2.2.2]octane hydrochloride (6; X = $\overset{+}{N}Me_2H\ Cl^-$) was prepared by passing dry hydrogen chloride over a rapidly stirred ethereal solution of compound (6; X = $\overset{+}{N}Me_2$). The precipitate was filtered off, washed with dry ether and dried *in vacuo*. Compound (6; X = $\overset{+}{N}Me_2H\ Cl^-$) (92%) had m.p. 238—239.5 °C; $\nu_{max.}$ (KCl) 3 520—3 420, 2 640—2 460, 1 494, 1 365, 1 020, 767, 700, and 538 cm^{-1}; $\delta(CDCl_3)$ 1.97—2.15 (12 H, m), 2.75 (6 H, s), and 7.17—7.36 (5 H, m).

DISCUSSION

The ^{13}C substituent chemical shifts for the aromatic carbon atoms in a series of 4-phenylbicyclo[2.2.2]octanes (6) are given in Table 1. Assignments were made on the basis of shift and peak intensity. The unsubstituted compound (6; X = H) has shifts of 150.65 (C-1′), 125.56 (C-2′), 127.97 (C-3′), and 125.37 (C-4′) p.p.m. indicating a significant increase in electron density at the *ortho* and *para* positions. Our data agree to within 0.2 p.p.m. with those of Kitching *et al.*[21] for X = H, OH, OMe, and F but for X = Cl the shifts for C-3′ and -4′ are reversed.

The trends in these substituents shifts provide striking confirmation that the π-system can be polarised by remote substituents. For all four different aromatic carbon atoms the shifts show almost perfect correlation with each other when listed in order of increasing magnitude, which is remarkable when it is considered that the precision of the data is ±0.13 p.p.m.*

Assuming that the changes in ^{13}C shifts reflect changes in π-electron density, then the polarisation shown in (6) is indicated. This polarisation is similar to that observed for some phenylalkanes (5) [11] but is slightly different from that originally envisaged by Reynolds [10] for series (4) (see above).

The data reported [11] for substituted propylbenzenes (3; *n* = 3) are limited but for these compounds there is a reasonably good correlation (*r* † 0.89) with series (6) for values of Δδ(C-1′) and a rather better correlation (*r* 0.92) for values of Δδ(C-4′). The corresponding shifts in ethylbenzenes (3; *n* = 2) [10,11] correlate slightly better with those in series (6) (*r* 0.98 for C-1′ and 0.97 for C-4′). The geometric relationship between the polarisable π-system and the substituent dipole is very similar in (6) to that in 1-substituted biphenyls (7a). In both cases the dipole remains fixed in position and in

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* We regard the precision of SCS as equivalent to the width of two data points. Many workers claim a higher precision.

† In all correlations of substituent effects the point for H is included.

orientation throughout the series of compounds. However, direct comparison of the ^{13}C SCS in (6) and (7a) [22] reveals a poor correlation (r 0.72 for the C-1′ SCS) since π-polarisation is not the only mechanism resulting in perturbation of the π-electrons in the remote benzene ring of system (7a).

Adcock *et al.*[23] have interpreted the ^{13}C SCS in systems (8) and (9) in terms of a combination of hyperconjugative and field effects. These workers noted the substantial SCS in system (8) where hyperconjugation is minimal from structural considerations, expressing surprise at such a large field effect. Detailed examination of the data for these systems,[23] particularly the SCS values obtained by comparing $X = CH_2$ with X = NH, CO, O, and SO_2 shows a clear picture of π-polarisation, with exactly the trend in SCS to be expected for the orientation of the net substituent dipole, *i.e.* orthogonal to one edge of the benzene ring in (8) and approximately parallel to an edge of the benzene ring in (9). Assignments are uncertain for some of the intermediate carbon atoms in these systems but for $X = SO_2$ the SCS range from -8.1 (*ipso*) to $+3.3$ (*meta*) in (8) and from -12.6 (nearest, C-1) to $+2.9$ (farthest, C-4) in (9). It is difficult to compare directly the SCS in (6) and (8) [or (9)] since there can be no exact correspondence in substituent type but the trend along the series (SCS for $X = NH < X = O < X = CF_2$) in both systems clearly parallels that found for analogous substituents in the ideal system (6).

TABLE 2

Parameters for the correlation of ^{13}C and ^{19}F SCS with σ_I

System	Atom	Solvent	ρ_I	n [a]	r [b]	d [c]	Ref.[d]
(6)	C-1′	$CDCl_3$	-4.50	12	0.95	2.63	*e*
(6)	C-2′	$CDCl_3$	-0.54	12	0.79	3.15	*e*
(6)	C-3′	$CDCl_3$	0.47	12	0.87	4.00	*e*
(6)	C-4′	$CDCl_3$	1.16	12	0.97	4.35	*e*
(7a)	C-1′	Acetone	-2.86	14	0.96	2.70	7
(7a)	C-2′	Acetone	0.53	14	0.95	3.23	7
(7a)	C-3′	Acetone	0.37	14	0.91	4.08	7
(7a)	C-4′	Acetone	1.94	14	1.00	4.45	7
(3; $n = 3$)[f]	C-1′	$CDCl_3$	-5.66	5	0.95	2.45	11
(3; $n = 3$)[f]	C-4′	$CDCl_3$	1.11	5	0.86	4.18	11
(3; $n = 2$)[f]	C-1′	$CDCl_3$	-10.55	6	0.96	1.57	10, 11
(3; $n = 2$)[f]	C-4′	$CDCl_3$	2.53	6	0.97	3.17	10, 11
(11)	C-1′	$CDCl_3$	-0.47	8	0.96	4.78	26
(11)	C-4′	$CDCl_3$	0.38	8	1.00	6.18	26
(10)	F	Cyclohexane	2.52 [g]	10		5.25	16
(10)	F	Benzene	1.82 [g]	7		5.25	*h*
(10)	F	DMF	1.48 [g]	7		5.25	*h*
(7b)	F	Benzene	3.35 [g]	6		5.35	*h*
(12)	F	Cyclohexane	1.49 [g]	8		4.67	16
(13)	F	Cyclohexane	-1.04 [g]	8		3.10	16

[a] Number of substituents including H. [b] Correlation coefficient. [c] Distance (Å) from atom to the carbon bearing the substituent. [d] Source of SCS data. [e] Present work. [f] Excluding Me substituent. [g] Taking positive SCS to denote deshielding. [h] S. K. Dayal and R. W. Taft, *J. Amer. Chem. Soc.*, 1973, **95**, 5595.

There is also a good correlation of $\Delta\delta$(C-4′) in (6) (in $CDCl_3$) with the ^{19}F SCS values (in cyclohexane or benzene) for the corresponding 4′-fluoro-derivatives

$$\Delta\delta(\mathrm{F})_{\mathrm{cyclohexane}} = 2.10\ \Delta\delta(\text{C-4}') - 0.06\ (r\ 0.99) \quad (1)$$

$$\Delta\delta(\mathrm{F})_{\mathrm{benzene}} = 1.34\ \Delta\delta(\text{C-4}') - 0.05\ (r\ 0.96) \quad (2)$$

(10) [equations (1) and (2)], which points to a common mechanism for ^{13}C and ^{19}F substituent effects. These ^{19}F SCS values were originally interpreted [5] in terms of a dominant F_D effect but have been reassessed [15,16] and shown to be consistent with a 75% contribution from a F_π effect. The dominance of the F_π effect is confirmed by the present data, although the extent to which an F_D effect operates is open to question.[15,16] This point is further discussed below.

Analysis of SCS in aromatic systems in terms of Taft's dual substituent parameters (σ_I and σ_R)[1] has proved to be particularly valuable. Adcock and his co-workers [4-6,13,16,21,23] have convincingly demonstrated that DSP analysis can effectively separate field and mesomeric contributions to ^{13}C and ^{19}F SCS in a wide variety of systems. In system (6) mesomeric effects are eliminated (or at least reduced to an effectively constant hyperconjugative transfer through the π-molecular orbitals of the bicyclo-octane moiety) and this is confirmed by statistically insignificant values for ρ_R in a DSP analysis for the SCS at each of the aromatic carbons.

The values of ρ_I are given in Table 2. Poor correlation coefficients for $\Delta\delta$(C-2′) and $\Delta\delta$(C-3′) reflect the experimental uncertainty in these very small SCS. The point for Et has been omitted from the analysis since the SCS indicates π-polarisation opposite in sign to that expected for a substituent with a negative σ_I value. A similar anomaly is evident in the SCS for the Me group.[16] There is also kinetic evidence that the methyl group attached to the bridgehead position in (6) behaves abnormally.[24] There is considerable uncertainty about the value of σ_I for the $\overset{+}{N}Me_2H$ substituent and this point is also omitted from the correlation analysis.

The ρ_I values for the carbon atoms in the remote benzene ring in system (7a) and for the *ipso* and *para* carbons in the phenylpropanes (3; $n = 3$) and the phenylethanes (3; $n = 2$) are given in Table 2. Also included are ρ_I values [25] for the *ipso* and *para* carbons in system (11). In these chalcones rotation of the benzene ring results in an average π-polarisation for the remote benzene ring, analogous to that found in (6), but substantially attenuated by the greater distance from the substituent dipole.

The ρ_I values for (7a) and (11) were extracted by DSP analysis and so provide a means of characterising the F_π perturbation in the presence of mesomeric interactions, and of comparing a wide variety of systems in which a common polar field mechanism may be operating.

In order to quantify these qualitative interpretations of the F_π effect we propose the following simple model. (a) The π-system is polarised as a complete unit. (b) The null point in the π-electron polarisation is dependent on the distance of the π-system from the dipole. (c) The π-electron perturbation at a particular atom is proportional to the inverse square of its distance from the dipole. (d) The magnitude of the polarisation of a benzene ring is unchanged by rotation about the ring centre (the pseudo-six-fold symmetry axis). For example, the two orientations of the dipole and ring shown in Figure 1 would have the same polarisation provided that the distance *d* between dipole and ring centre was the same. Of course perturbations at individual carbon atoms are still governed by (c). (e) In-plane or out-of-plane rotation of the dipole with respect to the π-system will produce the normal angle dependence characteristic of electric field interactions.

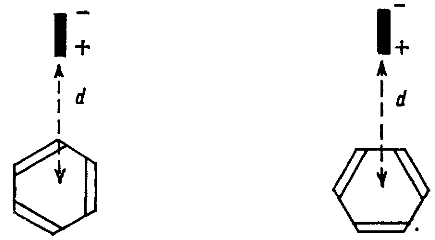

FIGURE 1 Dipole orientations with respect to a benzene ring

This model for the F_π effect requires some means of characterising the π-electron perturbation in the π-system and if the ρ_I values are used for this purpose then two crucial assumptions have to be made. First, it has to be assumed that there is a direct relationship between ^{13}C SCS {as embodied in a correlation with σ_I[equation (3)]} and the corresponding changes in π-electron populations [equation (4)]. This is widely

$$\Delta\delta = \rho_I\sigma_I \qquad (3)$$

assumed to be a valid relationship although theoretical

$$\Delta\delta = K\Delta q^\pi \qquad (4)$$

considerations [26] suggest a more complex dependence on charge density. Indeed, in system (6) the isolation of a substituent from the π-system will reduce its effect on the average excitation energy. Secondly, it must be assumed that σ-electron perturbations are not important either directly (no effect on SCS) or indirectly (no effect on π-electron population). In spite of extensive effort by many workers [1] much uncertainty still surrounds this question. Taft and his co-workers [1] find from *ab initio* calculations that for directly substituted benzenes, $\Delta\delta$(*p*-C) is roughly linearly related to the total change in charge density at the *para* position. However Δq^π and Δq^σ at the *para* carbon are accurately inversely proportional to each other and hence it is difficult to separate effectively the dependence of $\Delta\delta$(C) on Δq^π and Δq^σ. Hence the finding [1] that $\Delta\delta$(*m*-C) in monosubstituted benzenes is three times less sensitive than $\Delta\delta$(*p*-C) to the corresponding Δq^{total} may not reflect an intrinsic variation in dependence on Δq^π.

Calculated changes in σ- and π-electron population, relative to the parent unsubstituted compound have been obtained for selected substituents in the series (6) using an INDO MO method,* and results are included in Table 1. It is immediately evident that the pattern of SCS values is closely reproduced by Δq^π, *i.e.* increased charge at C-1′ and decreased charge at C-4′. The only discrepancy is the small decrease in q^π at C-2′ indicating a π-polarisation with the null point between C-1′ and -2′ rather than between C-2′ and -3′ as the SCS values suggest. Notably the Δq^σ trend is opposite to that for Δq^π [and $\Delta\delta$(C)], as was found for monosubstituted benzenes.[1]

The calculations of the field effect of the $\overset{+}{N}H_3$ substituent appear to be unreliable [7,15] and the experimental polarisation produced by a charged amino-group ($\overset{+}{N}Me_2H$) is markedly less than the calculations suggest (by a factor of 4). Solvation of the ion (by $CDCl_3$), should not be a major effect in the present case and ion-pair formation may be responsible for this marked reduction in the polar effect for $\overset{+}{N}R_3$. This substituent was excluded from all correlations of Δq, leading to significant improvement in every case, and calculations [7,15] of π-polarisation produced by the $\overset{+}{N}R_3$ group should be treated with caution.

The Δq^π values present a high degree of internal consistency since Δq^π(C-1′) correlates nearly perfectly (r 0.999) with Δq^π(C-4′). The corresponding correlation between Δq^σ values is much poorer. The pattern of π-polarisation indicated by the ^{13}C SCS is broadly confirmed by the pattern of calculated Δq^π values. These electronic perturbations are *ca.* 50 times smaller than those in directly substituted benzenes and hence very good correlations are not expected, given the inherent inadequacies of semi-empirical MO methods (particularly for substituents such as CN and NO_2 [8]). The best correlations are those for C-1′ and C-4′ (Table 3). A twofold change in slope can be noted for Δq^π but the significance of this result is uncertain since the correlation of the combined $\Delta\delta$ values with Δq^π is even

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* Pople's program (QCPE 141) was modified to cope with calculations involving up to 40 atoms and 90 orbitals. Structural parameters for bicyclo[2.2.2]octane have been published.[27] The benzene ring was taken to lie in an eclipsing conformation and mean values of Δq were taken for the two *ortho* and two *meta* positions. Separate calculations were performed for each staggered conformation of substituents without axial symmetry, and weighted average values obtained for Δq.

better (Table 3). Similar results are found for monosubstituted benzenes.[1] It is notable that net transfer of π-electronic charge from the ring is much smaller than the corresponding change in σ-electron charge.

TABLE 3

Parameters for correlation of SCS against change in electron population in (6) ($\Delta\delta = a\Delta q + b$)

$\Delta\delta$	Δq	Slope	Intercept	r [a]	n [b]
C-1′	σ	−0.05	−0.74	0.92	7
C-4′	σ	−0.04	0.17	0.88	7
C-1′	π	0.04	−1.0	0.85	7
C-4′	π	0.02	0.17	0.85	7
C-1′, C-4′	π	0.05	−0.55	0.91	14

[a] Correlation coefficient. [b] Number of data sets.

Returning to the σ_I correlations, if the individual ρ_I values can be taken to characterise the polarisation at each carbon atom [equation (5)] then the overall ring polarisation can be expressed on the basis of the model

$$\rho_I = K'\Delta q^{\pi} \qquad (5)$$

outlined above by equation (6); d is the distance of a probe nucleus from the dipole, d_o is the corresponding

$$\rho_I = P\left(\frac{1}{d_o^{\,2}} \quad \frac{1}{d^2}\right) \qquad (6)$$

distance of the null plane in the π-ring, and P is the intrinsic polarisation characteristic of the system and will vary with the nature of the π-system (*e.g.* phenyl, vinyl, conjugated phenyl) and with the nature of the bridging group. The parameter d_o, the distance at which the polarisation is zero, will vary with the distance of the dipole from the ring and should be close to the ring centre in most cases. From the plots of ρ_I against $1/d^2$ the parameters P and d_o were evaluated for various systems (Table 4). With only four points for systems (6) and (7a) and two points each for the others these values of P and d_o are necessarily approximate. The best data are those for (6) for which equation (6) has a correlation coefficient of 0.98. The dependence of ρ_I on $1/d$ and $1/d^3$ was also investigated, but such models fit the data less well. The biphenyl ρ_I values show a slightly poorer quality of plot against $1/d^2$ (r 0.92) and this may be related to the fact that these ρ_I values must be obtained by DSP analysis with the possibility of less than perfect separation of field and mesomeric effects. Nonetheless these two linear relationships at least support the notion that the π-electron system is polarised as an entity and that no angle dependence need be invoked to rationalise the polarisation at individual probe nuclei.

TABLE 4

Polarisation parameters from the application of equation (6)

System	(6)	(7a)	(3; n = 3)	(3; n = 2)	(1)
P	58.68	47.47	62.24 [b]	42.68 [b]	47.20
d_o (Å)	3.68	3.41	3.60	2.51	5.42
d_c[a] − d_o	−0.1	0.2	0.3	0.2	0.0

[a] d_c is the distance of the ring centre from the dipole. [b] Uncertain values.

Comparison of systems (6) and (7a), in which the dipole is almost the same distance from the remote benzene ring shows that the polarisation P is smaller suggesting that in (7a) the polarisable π-system must be extended to some extent over both rings resulting in a less severe perturbation of the remote ring. A similar result is found for system (11). The null plane in (7a) is displaced from the ring centre (Table 4) towards C-1′ and ρ_I(C-4′) shows the expected increase relative to the corresponding position in (6). Furthermore, comparison of the ^{19}F SCS values of fluorinated derivatives of (6) and (7a) [*i.e.* (7b) and (10)], shows that the ρ_I value in (7b) is twice as large as that in (10) confirming that the polarisation in system (7) is enhanced and offset with respect to the phenylbicyclo[2.2.2]octyl system and that the ^{19}F SCS values can be adequately interpreted in terms of π-polarisation.[15,16]

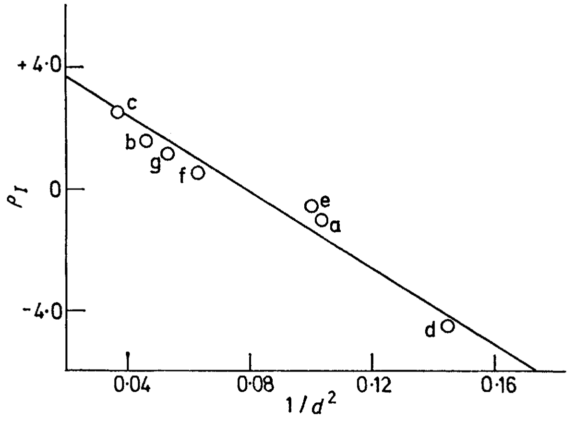

FIGURE 2 Plot of ρ_I for aromatic carbon atoms in (6) and fluorine atoms in (10), (12), and (13) against $1/d^2$: a, *o*-F (13); b, *m*-F (12); c, *p*-F (10); d, C-1′ (6); e, C-2′ (6); f, C-3′ (6); g, C-4′ (6)

For all systems d_o is close to the ring centre and although the polarisation parameters for the phenylalkanes are not very reliable (very small data sets), there is evidence for displacement of the null plane.

Adcock and Khor[16] have interpreted the SCS for ^{19}F in systems (12) and (13) in terms of 67% F_{π} and 33% F_D [compared with 20% F_{π} for ^{19}F in (10)], on the basis of the deduction that P in system (12) is approximately half P in system (10). On the basis of the present model for π-polarisation it seems most unlikely that P would be significantly different in these systems. If the ρ_I values for ^{19}F in (10), (12), and (13) are plotted against the corresponding values of $1/d^2$ the points all fit reasonably well onto the line [equation (6)] for the carbon atoms in (6) (Figure 2; the ^{19}F data and ^{13}C data are for cyclohexane and $CDCl_3$ solutions respectively). This remarkable result may be coincidence. However, it may be noted that (a) ^{19}F π-charge density in *p*-disubstituted benzenes is *ca.* 7 times smaller than the *p*-^{13}C π-charge density in monosubstituted benzenes[1] [a similar ratio is evident between π-charge density at ^{19}F and the attached carbon in (10)[15]], and (b) ^{19}F chemical shifts are 9 or 10 times more sensitive than

^{13}C chemical shifts in benzene derivatives to changes in π-charge density.[1]

To a first approximation these effects cancel and ^{19}F SCS and ^{13}C SCS in systems (6), (10), (12), and (13) can be regarded as a measure of a single phenomenon, π-polarisation. That is to say that the greater sensitivity of ^{19}F chemical shifts is just offset by the reduced charge (*i.e.* reduced polarisability of the intrinsically polar C–F bond) at the ^{19}F atom, arising from the operation of an F_π effect on the total π-system constituted by the benzene ring and the C–F bond. Hence the ρ_I values for ^{19}F in (10), (12), and (13) are adequately explained by equation (6), without invoking any angular dependence as would be required for a contribution from a direct field effect (F_D). Whilst this interpretation may be oversimplified it provides a convenient, unified rationalisation of ^{13}C and ^{19}F SCS in systems free from mesomeric interaction.

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