The Nature of Substituent Electronic Effects; the Existence of the π-Inductive Effect [1]

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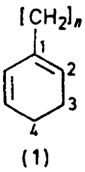
Measurements of ^{13}C n.m.r. shifts and of u.v and i.r. intensities for ω-substituted alkylbenzenes show the presence of a π-inductive effect. Various possible mechanisms contributing to such effects are analysed and the discussion is extended to related benzyl systems.

It is accepted [2] that a polar substituent in a saturated system is capable of affecting the physical properties or reactivities of a remote group. Recent evidence [3] suggests that such an inductive effect mainly arises from a through-space electrostatic interaction (field effect). The alternative transmission mechanism of relay through σ-bonds has been fairly convincingly shown to be of negligible importance for atoms further away than the one directly joined to the polar substituent. It is also accepted that where suitable substituent orbitals are available adjacent to an unsaturated system, then π-charge transfer may take place (resonance or hyperconjugation); this effect is transmitted to a remote probe site through the π-system.

The question as to whether a remote polar substituent causes disturbance in a π-system, without charge transfer (the π-inductive effect) has led to much controversy.[4-9] The occurrence of such an effect may intuitively seem reasonable but experimental evidence suggests that it is small and dependent on the method of measurement.

Origin of π-Inductive Effects.—These effects arise from any polarization of a π-system caused by a remote substituent dipole or charge which does not involve any charge transfer to or from the π-system. The three mechanisms that can be formally visualized, described previously [1] as Effects 4, 5, and 6, thus lead only to redistribution of π-electron density in the system.

The π_σ Effect.—(This has been earlier referred [10] to as a σ-inductive effect on the π-system and designated I_σ). Induction of charge difference in an underlying σ framework may lead to compensating changes in the π-electron distribution. Thus in compound (1) a substituent Y, more electronegative than carbon, can in principle induce a partial positive charge at C-1 which may, in turn, induce a redistribution of charge in the π-system as represented by the canonical forms (2).



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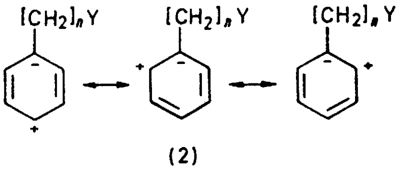
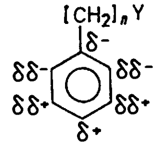


(2)

The relay of charge along a chain diminishes rapidly [3] and it is therefore reasonable to look at the effect as originating only at C-1 in the π-system, and as not being important for $n > 1$. There is also some theoretical evidence [11] to suggest that changes in σ-electron distribution do not lead to significant resulting changes in π-systems at the same location.

The π_F Effect.—The π-system may also be polarized by a through-space electrostatic interaction with a remote dipole or charged substituent. Such a field-induced disturbance would affect all positions in the π-system, with those nearest to the charge or dipole being the most influenced. It would also depend on the geometry of the system. For compounds (1), when $n = 1$—3, the effect is best represented as in (3), the polarization of the π-system being towards the *ipso*-position. There is some recent evidence [4-6] for such an effect, although it has, in the past, been included with the π_σ effect and the overall π-disturbance has been thought to be small by many workers.[4,7,12-16]



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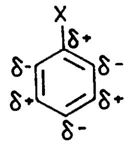

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The π_{Orb} *Effect.*—The π-system may also be disturbed by repulsive interactions with neighbouring filled orbitals on the substituent. If this was centred mainly on C-1, it would lead to a π-electron redistribution as shown in (4).

A theoretical treatment of electron densities in propene and toluene suggests [15] that the effect is based on π,π^* mixing brought about by interaction with the pseudo-π-orbitals of the substituent. The effect depends on the filled orbitals of the substituent being close to the benzene ring; the orbitals may be [17] on an atom not directly attached to the ring.

Present Work.—The systems most frequently chosen for investigation of substituent effects have been directly substituted benzenes. In these systems resonance and hyperconjugative charge transfers can occur in addition to all three effects mentioned above. Further, if one substituent is used as a probe for the other, as for example in measurements of the acidities of substituted benzoic acids, then the situation is complicated by substituent–probe interactions.

We wished to examine π-inductive effects and therefore chose to first look at π-electron disturbances in β-substituted ethyl- and γ-substituted propyl-benzenes. Here π_{Orb} and charge transfer effects should be effectively constant and π_σ absent; π-electron disturbances would thus be indicative of π_{F} effects. On the basis of these results, we later discuss effects in benzyl systems. Some ^{13}C results on a number of substituted toluenes and ethylbenzenes were reported [5] while this work was in progress and these indicated the presence of a π_{F} effect.

EXPERIMENTAL

The substituted ethyl- and propyl-benzenes were prepared by standard syntheses and their purity was checked by a combination of i.r., g.l.c. and n.m.r. techniques prior to use.

^{13}C N.m.r. spectra were measured at 25 MHz with a JEOL JNM-PS-100 PFT spectrometer with EC-100 computer operating in single pulsed Fourier transform mode with proton noise decoupling. Deuteriochloroform was used as an internal ^{13}C reference and the chemical shifts of the ring carbon atoms were then expressed relative to $^{13}C_6H_6$ under the same conditions. Concentrations were *ca.* 2M in $CDCl_3$; dilution experiments on (β-cyanoethyl)-benzene showed only small changes in ring carbon atom shifts.

I.r. intensities were measured with a Perkin-Elmer 225 grating spectrometer for solutions in spectroscopic grade carbon tetrachloride. The method of cell balancing and computer processing of results has been described previously.[18] Two solutions of each sample were made up, and duplicate determinations made of each, the result given being the average value. Concentrations were 0.3—1.0M.

U.v. absorption spectra were measured with a Varian 635 spectrophotometer. The approximate intensity values were obtained by weighing the paper corresponding to the absorption. The paper weight per area was more reproducible than the error in determining the proper absorption curve in these rather complex spectra. The weight was corrected to unit concentration and cell path length and the figures were used as relative absorptions in a qualitative sense.

DISCUSSION

Changing the substituent Y in compounds $Ph[CH_2]_nY$ should have very little effect on the electron distribution in the benzene ring for $n > 1$ unless the π_{F} effect exists. This is supported by the almost negligible change in ^{13}C chemical shift caused by substituent change at C-5 in substituted pentanes [19] and the very small changes caused by altering the substituent at C-4 in pentanes [19] or adamantanes.[20] The results reported here suggest an alteration in electron density in the π-system in the direction expected for a π_{F} effect.

Thus ^{13}C shifts in substituted benzenes are considered, at least approximately, to reflect the total electron density at the carbon atom [5,21,22] in the absence of steric or anisotropic effects. Shifts at carbon atoms α, β, and γ do show [23] anisotropic effects but at greater chain lengths reflect only the electron density. Thus where $n = 3$, all ring carbon atoms should reflect only the influence of local electron densities, as should positions other than the *ipso* where $n = 2$. In both series studied the *para*-carbon atom resonances shift as expected for electron depletion as the substituent Y becomes more electronegative (Me $\sim$ H $<$ OMe $<$ Br $<$ CN). Also with $n = 3$ (and approximately where $n = 2$), the shifts of the *ipso*-carbon atom (position of chain attachment) suggest an increase in electron density in the same order. The changes at *ortho*- and *meta*-carbon atoms are smaller and not readily assigned.

Some measure of the magnitude of the effect at the *para*-position can be obtained relative to the effect of an unsubstituted alkyl group. Thus an ethyl group causes an upfield shift of 2.72 p.p.m. at the *para*-position when attached to a benzene ring. This is diminished to 2.12 p.p.m. in $Ph[CH_2]_3 \cdot CN$ and to 1.46 p.p.m. in $Ph[CH_2]_2CN$. If we use the σ° value [24] of -0.13 for the ethyl group as an approximate measure of the total electron density, then a γ-cyano-group causes an effect equivalent to 0.03 in σ units and a β-cyano-group an effect equivalent to 0.06 units. The effect seems real here although relatively small at this distance. Its

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magnitude is proportional to the polar effect (that is σ_I) of the substituent. The *para*-^{13}C shifts for the Ph[CH$_2$]$_3$Y series are found to represent a change of *ca.* 0.05 σ° units per unit change of σ_I in the substituent Y, and the Ph[CH$_2$]$_2$Y series a change of *ca.* 0.1 σ° units per unit change in σ_I in accord with this expectation. It seems certain that this effect originates in the π-system since the theoretical and ^{13}C n.m.r. evidence mentioned above shows that little alteration occurs in charge density at carbon atoms removed from the substituent in purely σ-bonded systems. Furthermore, the changes in σ-electron density at the *meta*- and *para*-carbon atoms in various monosubstituted benzenes, when corrected for the charge alteration in a corresponding purely σ-system (1-substituted bicyclo[2.2.2]octane), are found[11] to be inversely proportional to the π-charge alteration. A similar result is found[22] for *ab initio* calculations in monosubstituted benzenes. The change in π-density at the *para*-positions here has been shown[22] also to be a function of the polar nature of the substituent as well as of its charge transfer ability, thus showing the presence of a π-inductive effect.

TABLE 1

Spectral properties of compounds Ph[CH$_2$]$_n$Y

	I.r.[a]	U.v.		^{13}C N.m.r. (p.p.m. from benzene)[c]		
(I) Ph[CH$_2$]$_2$Y	A/ l mol^{-1} cm^{-2}	A[b]	$\lambda_{max.}$	C-1	C-4	C-2, -3, -5, -6
Y = Me	376	751	261.0	−14.31	2.68	−0.17, 0.06
H	332	811	261.0	−15.87	2.72	0.01, 0.49
OMe	312	647	257.8	−11.58	2.24	−0.43, 0.05
OH	303	686	258.0	−10.19	2.19	−0.48, 0.05
Br	286	(664)	257.6	−10.43	1.56	−0.24
CN	318	603	257.4	−9.61	1.46	−0.19, 0.30
(II) Ph[CH$_2$]$_3$Y						
Y = Me	389	772	261.0	−14.49	2.77	−0.07, 0.13
H	376	751	261.0	−14.31	2.68	−0.17, 0.06
OMe	283	739	261.0	−13.54	2.66	−0.01
OH	314	690	261.0	−13.44	2.67	0.10
Br	306	672	258.2	−12.14	2.24	−0.13
CN	312	664	258.2	−11.23	2.12	−0.01

[a] In CCl$_4$. [b] Relative intensity units only. [c] Negative shifts are downfield.

Changes in ^{13}C resonances at the *ipso*-position confirm the nature of the effect. In the series Ph[CH$_2$]$_3$Y, there is a shift to higher field as the electronegativity of the substituent increases, as expected if the π-system is polarized towards that position. A similar but less precise relationship is found for the Ph[CH$_2$]$_2$Y series but here some γ-effects may occur.

The u.v. results support these conclusions, although these measurements cannot give as precise an estimation of the magnitude of the effect as ^{13}C n.m.r. measurements. Thus it is known[25] that the intensity, and to some extent the frequency, of the secondary band of monosubstituted benzenes ($\pi\rightarrow\pi^*$ 254 nm in benzene itself) correlates with π-electron disturbance as measured by substituent constants. In both series investigated, the relative intensity of this absorption is seen to generally decrease as the electronegativity increases, in accord with the observed result[25] for electron-attracting substituents. The order of the effect is not as precise as with the ^{13}C n.m.r. results, but the accuracy of the measurements was limited because of the complex nature of the absorption curves in the wavelength region of interest. The frequency changes observed also indicate that changes occur in π-electron distribution in the series.

We earlier showed[26] that the intensities of the ν_8 i.r. absorptions of monosubstituted benzenes could be accurately related to σ_R° values according to the relation (i) with A in l mol^{-1} cm^{-2} and the 137 units representing

$$A = 20,340(\sigma_R^\circ)^2 + 137 \qquad \text{(i)}$$

an overtone absorption in the region. For the ethyl substituent, the intensity (A = 332, Table 1) leads to a σ_R° value of about −0.10. However, an analysis[27,28] of ν_8 intensities for a wide variety of substituents against substituent parameters shows that in contrast to ^{13}C n.m.r. or u.v. results they depend only on σ_R° and not on σ_I. Thus they apparently mirror charge transfer between the ring and the substituent rather than any overall disturbance of the π-system and should here only reflect any secondary effects on the hyperconjugation between the α-methylene group and the ring. The effects observed are indeed small. For the Ph[CH$_2$]$_2$Y series,, the change from Y = H to Y = CN causes a change of intensity of only 14 units, while the maximum substituent effect seen in the series (Br) reflect a σ_R change of only 0.015 unit. There does seem however to be some definite diminution of the hyperconjugative donation by groups such as Br, CN, and OR and, most obviously, quite an increase for Me in the Ar[CH$_2$]$_2$Y series. A rather similar pattern was found in *ab initio* calculations[29] for the charge transfer into the formally unoccupied orbital on substituted cations $YCH_2\overset{+}{C}H_2$ and $YCH_2CH_2\overset{+}{C}H_2$ where Y was Me, H, F, OH, or CN. It

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[29] L. Radom, J. A. Pople, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 5935.

thus appears that some of the π-disturbance observed from the ^{13}C n.m.r. and u.v. measurements is a secondary field effect on the hyperconjugation between the side chain and the ring. This secondary effect would be expected to be bigger in benzyl than phenethyl derivatives.

To summarise, the ^{13}C n.m.r. and u.v. evidence suggests a π_F effect in $Ph[CH_2]_nY$ where $n = 2$ and 3, of *ca.* 0.1 unit in σ° per unit change of σ_I in Y for the series $n = 2$. Part of this effect (perhaps a third) may arise from a change in charge transfer between the side chain and the ring; the rest can only be explained by a substituent-induced polarization of the π-system.

Reynolds [5] earlier reported similar ^{13}C n.m.r. measurements for compounds $Ph[CH_2]_nY$ (including $n = 2$, with $Y = H$, Me, Cl, Br, or $\overset{+}{N}H_3$) and found a *para*-^{13}C chemical shift of the last named compound of only 0.15 p.p.m. from benzene, suggesting a σ° value of almost zero as compared with -0.13 for the ethyl substituent. The σ_I value for $\overset{+}{N}H_3$, in trifluoroacetic acid, the solvent used, is about 0.9,[30] giving a change of about 0.14 σ° units per unit change of σ_I in Y, in reasonable agreement with the results above. Reynolds [5] also listed calculated (CNDO/2) charge densities for $Ph[CH_2]_2Y$ where Y was Me, H, Cl, or NH_3^+. The values for total density (q_t) obtained for the *para*-position, averaged over the *anti*- and *gauche*-forms approximately correlate against the observed ^{13}C shifts for the first three but the last suggests a much bigger effect than observed.

We have also used the CNDO/2 method with a ' pseudo-inductive ' [31] substituent H* in $Ph[CH_2]_2H^*$, where the parameters of H* were adjusted to simulate an electronegativity slightly greater than that of F. The results for the *anti*- and *gauche*-forms are compared with those for ethylbenzene in Table 2. The calculations do suggest a small effect in the expected direction at the *para*-position but do not show a corresponding increase in electron density at the *ipso*-position. Further, the calculations, like those of Reynolds,[5] suggest changes at the *ortho*-position similar to those at the *para*-position; the ^{13}C shifts do not substantiate this.

TABLE 2

Total atom electron densities (× 10^3) (changes from 4.000) in ethylbenzene

	C-1	C-2, -6	C-3, -5	C-4
$PhCH_2CH_3$	44	-18	14	-8
$PhCH_2CH_2H^*$ *anti*	44	-15	15	-4
$PhCH_2CH_2H^*$ *gauche*	52	$-9, -17$	15, 15	-4

α-Substituted Toluenes.[32]—From the results above we might anticipate a π_F effect of greater magnitude with an α-substituent, perhaps 0.2 σ° units per 1.0 units of σ_I in Y. The *para*-^{13}C shifts for toluene (2.9 p.p.m. relative to benzene),[33] benzylidyne fluoride (-3.2 p.p.m.),[33] and the benzylammonium ion (-2.1 p.p.m.) [5] considered in such simple terms would indeed suggest values of this magnitude.

However, the actual π-electronic effect here should be thought of as arising from a combination of π_F and π_σ effects together with any change in side-chain-to-ring hyperconjugation. The π_σ effect might still be anticipated to be small but the third effect should be more important than in the phenethyl series as found correspondingly by calculation [29] for the series $YCH_2\overset{+}{C}H_2$ as compared with $YCH_2CH_2\overset{+}{C}H$, and by use [34] of model compounds where hyperconjugation is restricted on steric grounds.

Ab initio calculations [35] (STO-3G) of the π-densities in toluene, benzyl fluoride, and benzylidyne fluoride show an overall redistribution of π-density much greater than corresponding to changes in charge-transfer between the substituent and the ring. The effect of replacing H atoms by F atoms in the methyl group is to increase the π-density at the *ipso*-position and reduce it at the *para*-position; the *ortho*-positions are affected about as much as the *para*-positions while the π-electron density increases at the *meta*-positions. Similar trends were found[5] in CNDO/2 calculations on benzyl chloride. This may indicate a π_σ effect although ^{13}C shifts at the *ortho*-positions relative to benzene do not support this finding (see below).

TABLE 3

Changes (× 10^3) in total and π atom electron densities in some substituted toluenes by CNDO/2

PhY	C-1	C-2, -6	C-3, -5	C-4
$Y = CH_3$	42 (28)	-10 (-24)	12 (12)	-3 (-15)
CH_2H *†	25 (18)	$-3, -9$ ($-16, -31$)	4, 13 (15, 13)	0 (-9)
$CH_2\overset{+}{N}H_3$	-6 (-71)	11 (6)	17 (18)	32 (46)

† C–H * in plane of ring.

We have made CNDO/2 calculations on $PhCH_2H^*$ and on $PhCH_2\overset{+}{N}H_3$ (Table 3); our values for $PhCH_2\overset{+}{N}H_3$ are in accord with those previously published.[5] The results for $PhCH_2H^*$ with the CH* bond orthogonal to the π-system of the ring show a decrease in electron density at the *para*-position, an increase at the *ipso*-position, and little change elsewhere in accord with ^{13}C measurements in α-substituted toluenes. The calculations for the $CH_2\overset{+}{N}H_3$ substituent are more typical of what one expects from a π_F effect; similar figures are found with an *ab initio*, STO-3G calculation [36] for the π-system (C-1 q_π -0.093; C-2, -6 0.009; C-3, -5 0.023; C-4 0.053; with an overall q_π transfer from ring to side-chain of 0.024). Bringing up an ammonium ion to a similar

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[30] R. W. Taft, personal communication.

[31] N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1969, **91**, 352.

[32] See T. J. Broxton, D. G. Cameron, R. D. Topsom, and A. R. Katritzky, *J.C.S. Perkin II*, 1974, 256, for some general discussion and relevant references.

[33] G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, 1972, **94**, 3089.

[34] W. Adcock, M. J. S. Dewar, and B. D. Gupta, *J. Amer. Chem. Soc.*, 1973, **95**, 7353.

[35] W. H. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

[36] L. Radom, personal communication.

distance from a benzene ring caused[5] a similar calculated (CNDO/2) change in electron densities. The ^{13}C shifts[5] follow the order of these predictions but the calculations seem to overemphasize the charge differences.

Overall then, ^{13}C shifts and theoretical calculations indicate the presence of a π_F effect here although it is more difficult, and less realistic, to treat it separately from the other perturbations than was the case for the phenethyl and phenylpropyl series. The situation in monosubstituted benzenes is much more complex since resonance, π_F, π_σ, and π_{Orb} effects can all be present, and any such division is now rather artificial.

^{19}F N.m.r. measurements of substituent π-effects do not provide a useful probe for π_F effects. Differences in fluorine shifts for the corresponding *meta*- and *para*-substituted fluoro-substituted benzene derivatives have been related to $\sigma_R{}^\circ$ values. The method, however, assumes[37] that any resonance effect (π-disturbance) at the *meta*-position is less than but proportional to that of the *para*-position. This is reasonable for substituents where a combination of resonance, hyperconjugative, or π_σ effects are dominant since they will all cause a fairly constant relative change at the two positions. However the π_F effect represents a different relative change on the densities at various positions in the ring; it may be approximately the same in the *meta*- and *para*-positions and therefore the relative *para–meta* ^{19}F shifts do not provide a suitable probe.

Overall, this and the complementary work by Reynolds[5] form a firm foundation for the idea of π-inductive effects in substituted aromatic systems.

We are grateful to Dr. R. Wilson for performing some of the CNDO calculations with the pseudohydrogen substituent, and to the La Trobe Computer Centre for computer time.

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[37] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343.