A Theoretical Investigation of the π-Polarization Mechanism. The Importance of Localized and Extended Polarization

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Ab initio molecular orbital theory has been used to examine the π-polarization mechanism. 'Isolated molecule' calculations have been made for the pairs $C_3HX/H_2C=CH-HC=O$, with X being varied through a range of common substituents. The dipole of X is able to polarize the π electrons of the acrolein unit such that both polarization of the entire conjugated system and separate polarization of the individual C=C and C=O π units occurs. The relative importance of extended and localized polarization varies for different atomic positions within the acrolein probe molecule. At the terminal oxygen atom, extended polarization accounts for *ca.* 60% of the total polarization whilst for the carbonyl carbon it accounts for only 20%. Most of the polarization at this position arises from localized polarization of the carbonyl unit. These results are in agreement with ^{13}C s.c.s. data in related systems.

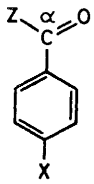
RECENTLY there has been much interest in using π-polarization to explain substituent-induced changes in ^{13}C chemical shifts.[1-9] Spectroscopic studies have shown this mechanism to be more important than had earlier been thought [10] from reactivity data. Reynolds [3,5] has provided much n.m.r. data supporting the π-polarization concept, and although some attempts have been made to quantify the mechanism,[2,3] we present here the first theoretical study specifically directed at this task.

In the accompanying paper we presented evidence showing that the reverse substituent chemical shifts (s.c.s.) noted for C-α in series (1) were controlled by a π-polarization mechanism. For a given series, the group X was varied through a range of electron-donating and -withdrawing substituents (X = NMe_2, NH_2, OMe, F, Me, H, CF_3, CO_2Et, COMe, CN, and NO_2) and ^{13}C chemical shifts of the carbonyl carbon were measured. The series examined included those with Z = NH_2, OEt, OH, F, Me, and H. In all these series, the inductive component of the ^{13}C shift at C-α is reversed. (*i.e.* inductive-withdrawing substituents cause upfield shifts) as a result of the substituent dipole polarizing the C=O bond in such a manner as to cause an increase in electron density at C-α.

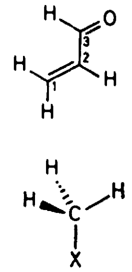
Our aim in this paper is to provide theoretical support for the π-polarization mechanism and in particular to gauge the relative importance of extended (P_E) and localized polarization (P_L). To do this we have chosen a model system (2), in which the substituent (X) and probe site (C=O) are in a similar geometrical arrangement to those in (1), but are in separate, or 'isolated molecules' (IM). The model provides a more convenient framework for examining the polarizing effects of real substituents than have previous point-dipole calculations.[11] MO calculations were done at the *ab initio* (STO-3G) level of theory, and because of their previously demonstrated importance in determining chemical shifts,[12,13] π-electron densities were examined. The IM approach has been successfully applied in the past, using similar models, to examine the through-space transmission of substituent effects.[5,14]

In our model, substituent effects transmitted *via* through-space π-polarization (π_F) [4] can be examined in the absence of other transmission modes. In particular, the lack of chemical bonding between the probe and substituent sites eliminates both π_σ and π_{orb} effects.[4] Direct resonance interactions between probe and substituent are also eliminated.

Furthermore, the substituent, X, was deliberately attached to a saturated carbon so that short range resonance delocalization is also impossible.† Such a model does not introduce any serious deficiency, as previous work has shown that the inductive effect of a substituent attached to an sp^3 centre is similar to that at an sp^2 carbon.[5,7]



(1)



(2)

Information regarding the relative importance of localized and extended polarization can be obtained by comparing the results for (2) with those of (3) and (4), where the interaction of CH_3X with the C=C and C=O π systems is examined separately. 'Localized polarization' (P_L) is represented in (2a), and the expected 'extended polarization' (P_E) in (2b). Structure (2c) indicates an alternative P_E component where the node of polarization has been displaced towards the middle of the carbonyl bond. The total polarization (P_T) was obtained directly from the π electron densities (Δq_π) in (2). Localized polarization (P_L) components were

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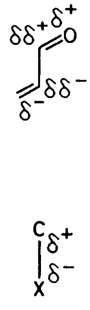
† We have shown that such delocalization into an adjacent unsaturated system can result in the formation of a π dipole, which is able to polarize (through space) a second (not necessarily attached) π system.[15] This effect is related to the field-mesomeric effect of Dewar,[16] or the resonance-polar effect of Taft,[17,18] and has been shown to be absent in model systems where the substituent is attached to an sp^3 carbon.[5]

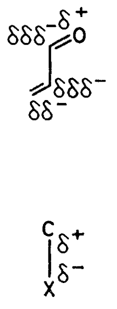
obtained from the π-electron densities of systems (3) and (4). The extended polarization component was then obtained by subtraction of the results in (3) and (4) from those in (2).

The distance and relative orientation between the substituent and probe sites were varied in order to determine their effect on polarization of the π electrons in the probe molecule. In the basic system (2) the distance between C-2 and the methane carbon was 3.0 Å, similar to that between the *para*-carbons in series (1) (2.8 Å).

(2a)



(2b)



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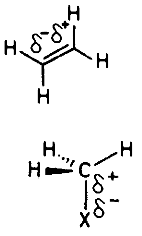
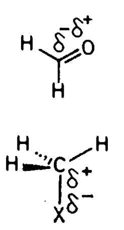


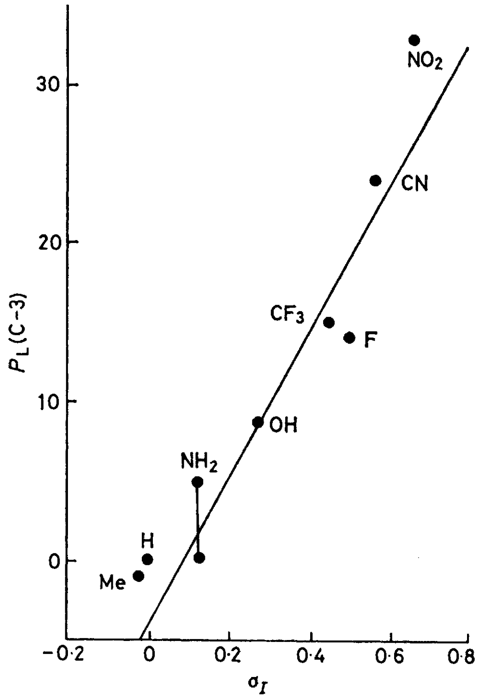
(3)



(4)

RESULTS AND DISCUSSION

The data in Table 1 show that substituents are able to polarize a distant π system in the absence of intermediate chemical bonds. This confirms that π-polarization arises from the through-space interaction of a substituent dipole with the π-electrons of the probe site. More importantly, the polarization is of the correct order of magnitude to account for the inductive component of ^{13}C s.c.s. values in (1). It is now well established that under certain conditions,[2,3,12] substituent-induced changes in chemical shifts may be related to substituent changes in electron densities. Experimentally, this requires first, that the sites examined are relatively far from the substituent so that structural distortions are minimized and secondly, that the spectra are recorded for dilute solutions of the compounds in an inert solvent, so that solvent and association effects are minimized. The theoretical justification for such correlations arises from a consideration of terms from the equation describing the paramagnetic screening constant.[19] Detailed discussions of the origin of electronic terms in this equation are given elsewhere.[19-22]



Plot of localized polarization component *versus* substituent σ_I values

That the polarization data seen in Table 1 are induc-

TABLE 1

Substituent-induced changes in π-electron density in series (2)—(4) [a]

	Total polarization [b]				Localized polarization				Extended polarization [e]			
	C-1	C-2	C-3	O	C-1 [c]	C-2 [c]	C-3 [d]	O [d]	C-1	C-2	C-3	O
NH_2(p) [f]	−4	12	1	0	−2	9	0	0	−2	3	0	0
NH_2(t) [g]	12	−3	5	−10	10	−6	4	−4	3	3	1	6
OH	38	−21	11	−24	28	−25	9	−9	10	4	2	−15
F	64	−41	17	−38	47	−45	14	−14	17	4	3	−24
CH_3	−11	10	−2	5	−5	6	−1	1	−6	4	−1	4
H	0	0	0	0	0	0	0	0	0	0	0	0
CF_3	64	−47	18	−39	51	−55	15	−15	13	8	3	−24
CN	111	−83	30	−66	79	−87	24	−24	32	4	6	−42
NO_2	149	−111	42	−91	104	−115	33	−33	44	4	9	−58

[a] Substituent-induced changes in electron density expressed relative to the case when X = H ($\times 10^{-4}$). A positive value denotes an increase in electron density. [b] π-Electron densities in series (2). [c] π-Electron densities in series (3). [d] π-Electron densities in series (4). [e] Obtained by subtracting the localized component from the total polarization for each atom. [f] Planar amino. [g] Tetrahedral amino.

tive * in origin can be seen from the Figure which shows the relationship between P_L for C-3 and substituent σ_I values. Least-squares correlations for the other polarization components are shown in Table 2 for two relative displacements of the CH_3X and C_3H_4O groups. In the first set, the C-2–CX distance is 3.0 Å and in the second it is 5.0 Å. These two sets of data are shown to demonstrate first that the polarization is distance dependent (as seen by the different slopes in Table 2) and secondly that the quality of the correlation is relatively insensitive to the intermediate distance.

TABLE 2

Relationships between π polarization components and σ_I values [a]

			d = 3 °A			d = 5 °A [b]	
Polarization	Atom	Slope [c]	Intercept [d]	r [e]	Slope [c]	Intercept [d]	r [e]
Total	C-3	55.1	−2.6	0.9496	20.8	−1.0	0.9430
	O	−121.7	6.4	0.9490	−42.1	2.0	0.9415
Localized	C-3	44.0	−2.1	0.9496	17.8	−0.8	0.9505
	O	−44.0	2.1	0.9496	−17.8	0.8	0.9505
Extended	C-3	11.2	−0.6	0.9448	3.5	−0.1	0.9676
	O	−77.7	4.4	0.9486	−24.3	1.2	0.9335

[a] Nine data points were used for each correlation. [b] Distance between C-2 and CX in series (2). [c] Slopes expressed in electron density ($\times 10^{-4}$) per σ_I unit. [d] Intercepts expressed in electron density ($\times 10^{-4}$). [e] Correlation coefficient.

When the average ρ_I value of −2.6 [1] obtained from a DSP analysis [23] of C-α s.c.s. values in (1) is divided by the factor relating σ_I and C-3 P_T values in (2), a slope of *ca.* 450 p.p.m./electron is obtained for the relationship between ^{13}C s.c.s. values and π-electron densities. If Reynold's [5] attenuation factor of 1.54 (for the transmission of through-space effects in IM, compared with full systems) is applied then this slope is reduced, and falls in the range 100—300 p.p.m./electron [24] generally expected for plots of ^{13}C chemical shifts *versus* π-electron densities. The fact that the magnitude of the through-space polarization of the C=O π bond is consistent with s.c.s. values in related series confirms that π-polarization is the dominant mechanism controlling the inductive component of chemical shifts.

TABLE 3

Polarization of formaldehyde as a function of distance [a,b]

	Distance [c] (Å)					
	4.46	4.96	5.46	6.46	7.46	8.46
NH_2(p) [d]	0.2	0.0	−0.1	−0.2	−0.2	−0.1
NH_2(t) [e]	3.8	2.9	2.4	1.6	1.2	0.9
OH	8.8	6.7	5.3	3.4	2.4	1.7
F	14.2	10.9	8.6	5.7	4.0	3.0
CH_3	−1.3	−1.0	−0.7	−0.4	−0.2	−0.2
H	0.0	0.0	0.0	0.0	0.0	0.0
CF_3	14.5	11.4	9.2	6.2	4.4	3.3
CN	23.7	18.6	14.8	9.8	6.8	4.8
NO_2	33.2	25.6	20.2	13.2	9.0	6.7

[a] Electron densities relative to the H substituent ($\times 10^{-4}$) for the formaldehyde carbon atom in series (3). [b] Positive values indicate an increase in electron density. [c] Distance between C-3 and CX. [d] Planar amino. [e] Tetrahedral amino.

That the reverse s.c.s. direction noted experimentally [1] is verified by the calculations can be seen, using the data for the fluorine substituent as an example. This substituent, which is inductively electron-withdrawing, sets up a dipole such that the C=O π-electrons are polarized towards C-3 and away from the oxygen atom. The *withdrawing* substituent is thus able to *increase* electron density at C-3. This is a direct consequence of the large influence that localized polarization has on the C-3 site, and is further expanded upon in the following section.

Extended and Localized Polarization.—The relative importance of extended and localized polarization can best be illustrated using a numerical example. Thus, in series (2) when X is changed from H to F, substituent induced changes in π-electron density of 17 and −38 units ($\times 10^{-4}$ electrons) for the carbonyl carbon and oxygen are observed. The respective values in a formaldehyde fragment (4) at a similar distance from the substituent are +14 and −14. These represent the contribution of localized polarization. When the additional ethylene unit is added to make up the conjugated acrolein unit (2), a further 24 units are removed from the oxygen whilst the carbon gains an extra 3 units. These values represent the contribution due to extended polarization (C-3: P_T 17, P_L 14, P_E 3; oxygen: P_T −38, P_L −14, P_E −24).

For C-3, extended polarization accounts for 18% (3/17) and localized polarization 82% (14/17) of the total fluoro-substituent-induced π-polarization. On the other hand, extended polarization at the oxygen atom accounts for 63% (24/38), whilst localized polarization accounts for 37% (14/38). Calculations of localized and extended polarization components for the other strongly inductive substituents (CF_3, CN, NO_2) give very similar values. Thus, at C-3, P_E accounts for (19 ± 2)% of the total polarization, whilst the ratio is (62 ± 2)% for the oxygen atom. Estimates of the percentage of extended polarization for the weaker inductive substituents are less reliable because of the smaller induced changes in electron density.

The model system (2) is a very simple approximation to the full systems (1), where the carbonyl is adjacent to a phenyl ring rather than an ethylene unit, and some differences in the relative importance of localized and extended polarization can be expected. These differences will arise mainly because the C=C bond of acrolein is not an exact model for a benzene C–C bond. This

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* We use the term ' inductive ' for all effects which account for the ρ_I component obtained from a Dual Substituent Parameter (DSP) analysis.[23] This can include effects transmitted both through bonds (I_σ) and through space (π_F).[4] However, in the current model system, only through-space inductive effects are observed.

may result in small changes in the nodal point of the P_E component. For example, in model system (2) the P_E component has the polarity shown in (2c). With an increase in the degree of conjugation, it is anticipated that the nodal point for the P_E component would move further away from the oxygen. Thus, extended polarization in series (1) will have nodal properties more like those in (2b).

Although some variation in $P_L : P_E$ ratios is expected for different models, the important conclusion to emerge from this analysis is that, for the carbon atom of a conjugated carbonyl, localized polarization accounts for the major proportion of π polarization and extended polarization is much less important. S.c.s. effects should be interpreted in the light of these results, as shown by the experimental data in the previous paper.* Our estimates of the approximate contributions of the components of π polarization for a conjugated carbonyl similar to (2) are as follows: C-3, $P_T = 80\%P_L + 20\%P_E$; oxygen, $P_T = 40\%P_L + 60\%P_E$.

It is interesting to note that the *ratio* of localized to extended polarization for a particular atom is not markedly distance-dependent. This may be seen by taking ratios of the slopes in Table 2, and confirms that the nodal points for extended and localized polarization are quite close to one another.

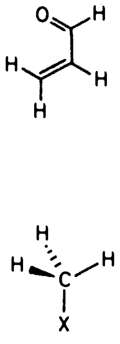
The Distance-dependency of π-Polarization.—Whilst the ratio $P_L : P_E$ does not vary with distance, the magnitude of the individual components does. This is illustrated in Table 3, which shows the polarization in a formaldehyde fragment placed successively further from the CH_3X group. The results shown are the π-electron density changes on the formaldehyde carbon atom and represent the magnitude of the localized polarization effect (the π-density changes on the oxygen atom are equal and opposite).

As our interpretation of π-polarization assumes it to be *via* a through-space interaction of the C–X dipole with the π-electrons at the measuring site, its transmission mode is formally similar to that of dipolar field effects where the interaction occurs between the C–X dipole and either a C–H or a C–F bond. One would therefore expect a similar distance dependency (d^{-3}) for both effects. To check this, we assumed that the polarization (P) of the formaldehyde unit is of the form $P = k/d^n$, where k is a constant, and plotted $\log(P)$ *versus* $\log(d)$ to obtain (from the slope) an estimate of the exponent, n. The correlation was repeated several times using different choices of d for each substituent. Angular factors were similar in all cases.

We initially chose the fluoro-substituent data to estimate n because the C–F dipole is relatively well defined. When d is taken to be the distance between the mid-point of the C–F bond and the carbon atom of the formaldehyde unit an excellent correlation is obtained: slope $= n = 2.65$, intercept $= \log(k) = 3.26$ ($r = 0.999\,8$). Choosing a more realistic distance d, from the midpoint of the C–F bond to the midpoint of the carbonyl bond, also results in an excellent correlation: $n = 2.85$, $\log(k) = 3.26$ ($r = 0.999\,7$). Both results confirm a $1/d^3$ dependency for π-polarization. This is contrary to the results of Ewing and Toyne [2] who suggested a $1/d^2$ relationship.† Our data for other substituents also support a $1/d^3$ distance dependency for π-polarization. However, we do note that the value obtained for n does depend upon the locations chosen for the end-points of the d vector and so the debate regarding the correct exponent cannot yet be regarded as fully settled. Experimental deviations from a $1/d^3$ dependency may be due to solvent effects, whilst deviations noted in theoretical calculations probably arise because the polarizable π-system is not readily approximated as a point dipole. Secondary polarization effects may also be important.

The intercept, $\log(k)$, in the correlations discussed above varies for different substituents. For a given substituent, k represents the induced polarization of the probe π-system at an arbitrary distance of d of 1 Å. Since at a given distance the polarization (P) induced by a substituent is proportional to its σ_I value (Figure), then k is also related to the substituent σ_I value. The constant k has the dimension of electron density. For example, in the correlation above for the fluoro-substituent, $\log(k) = 3.26$ and so $k = 1\,820$ ($\times 10^{-4}$) electron density units.

Additional Factors affecting π-Polarization.—The π-density changes (not shown) for the *cis*-acrolein unit in series (5) were almost identical with those for the *trans*-unit (2) shown in Table 1. This shows clearly that the substituent-induced polarization of the extended π-unit is not dependent on the relative (in plane) orientation of the two smaller π-units. However, when one of the ethylene fragments is twisted out of plane, extended polarization is reduced.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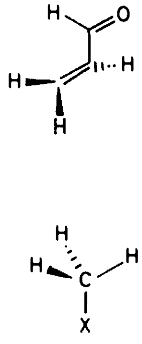
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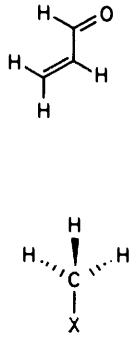
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It was thought that series (6), where the two π-units are twisted at 90° to each other, might provide a better

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* The observation of negative ρ_I values in a DSP analysis of C-α s.c.s. data in series (1) supports the dominance of localized polarization at this position.[1]

† In a personal communication, Dr. Ewing has indicated that his subsequent results (in agreement with our data) have shown that a $1/d^3$ relationship is more likely. It should also be noted that the d values in ref. 2 are in error by a constant multiplicative factor.

model for localized polarization effects than would the individual ethylene (3) and formaldehyde (4) units. However, the changes in Δq_π for C-3 and the oxygen atom were not equal and opposite, even when the CH_3X molecule was positioned at a considerable distance from the π-system. This suggests that the two π-units in (6) are not polarized solely as localized units and that there are extensive hyperconjugative interactions between the perpendicular π-units which effectively add an extended polarization component to the Δq_π values for C-3 and the oxygen. These hyperconjugative interactions make it difficult to measure separate P_L and P_E components in real molecules.[5]

To be sure that the overall results were not biased due to the choice of one particular orientation of the CH_3X group, further calculations were performed for (7) where the CH_3 group was rotated by 90° around the C–X bond axis. The results were very similar to those in (2) indicating that the rotational geometry chosen for CH_3X does not effect the results. Naturally, orientation of the C–X bond in an axis other than vertical does markedly alter the polarization of the π-system, although we have not presented these results here as we are interested in pseudo-*para*-orientations of the C–X bond to mimic the geometry of series (1).

One difficulty associated with these IM calculations is that the substituent and probe site cannot be brought too close together because of interactions between the probe molecule and the projecting hydrogen atoms of the substituted methane. Thus, in series (2), where the distance between C–X and C-2 is 3 Å, there is still some degree of overlap between the two ' isolated molecules '. In this case, the distance of closest approach of the intermediate hydrogen atoms is 1.4 Å. The effect of this overlap can be seen by noting that the sum of substituent induced changes in π-densities for C-1, -2, and -3 and the oxygen atom (termed $\Sigma\Delta q_\pi$) is non-zero. It is interesting to note that these $\Sigma\Delta q_\pi$ values accurately follow the σ_P value of the substituent. The magnitude of this overlap decreases rapidly and when $d = 3.5$ Å (intermediate hydrogen atoms 1.8 Å apart), approaches zero for all substituents. The trends in the data, at distances large enough so that no charge transfer occurred, assured us that the basic conclusions from the calculations at shorter distances are not changed significantly by the effects of this overlap.

Computational Details.—The calculations were done using a version of the GAUSSIAN 70 program [25] adapted for use on a DEC-10 computer. Co-ordinates were calculated using standard geometries.[26] All P_T, P_L, and P_E values shown in the Tables represent substituent-induced changes in electron densities ($\times 10^{-4}$) relative to the case when $X = H$. For each series (2)—(7) calculations were done for at least four different distances between CH_3X and the probe molecule for each of the nine substituents. Planar substituents were orientated such that they were coplanar with the probe π-system. Data for the two planar conformations of the OH substituent were averaged. Two conformations for the amino-substituent were studied essentially for completeness, and to facilitate comparisons with data from substituted benzenes where NH_2(pl) is often used as an approximation for NMe_2.

Conclusions.—The simple model systems used in this study have confirmed the concepts of, and enabled us to estimate the relative importance of, localized and extended polarization. The finding that, for non-terminal atoms, localized polarization is more important than extended polarization will play an essential role in explaining many substituent chemical shift phenomena in π-systems. π-Polarization effects can be transmitted through space and depend on the inverse cube of the distance between the midpoint of the substituent dipole and the midpoint of the polarizable π-system.

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