Carbon-13 Substituent Chemical Shifts in the Side-chain Carbons of Aromatic Systems: the Importance of π-Polarization in Determining Chemical Shifts

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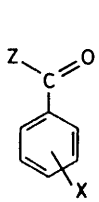
^{13}C Substituent chemical shifts of the carbonyl sites in the side-chains of *meta*- and *para*-substituted benzenes of the type XC_6H_4COZ have been measured. Analysis of this data using the dual substituent parameter method shows that inductive effects are predominant. The reverse inductive contribution observed is explained in terms of a π-polarization mechanism. Critical support for this mechanism is obtained from additional series where the carbonyl is complexed with Lewis acids. The concepts of ' extended ' and ' localized ' π-polarization are discussed.

THERE have been many reports of correlations between Hammett substituent constants and ^{13}C substituent chemical shifts (s.c.s.) of carbon atoms in side-chains of aromatic systems.[1-20] The correlations are good provided that chemical shifts are measured precisely, in an inert solvent, and at low concentration. In an earlier paper [3] we showed that the inductive (field) contribution to the chemical shift for the first atom of a conjugating side-chain was constant and negative, leading to ' reverse



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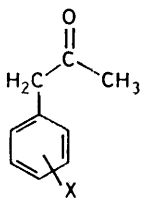

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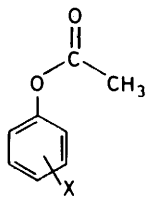

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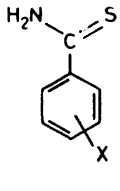
substituent chemical shifts '. This, and other evidence [11-15] has suggested the importance of the π-polarization mechanism in determining s.c.s. values.

In this paper we report s.c.s. values for a wide range of carbonyl side-chain systems (1). In a given series, the Z group remains constant whilst X is varied through a basis [21,22] set of substituents, reflecting a complete range of donor and acceptor properties. Series examined include those with Z = NH_2, F, OEt, OH, CH_3, and H.

These series have enabled us to evaluate the importance of the π-polarization mechanism. Of particular interest is the relationship between localized polarization



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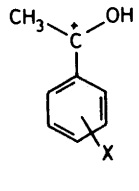

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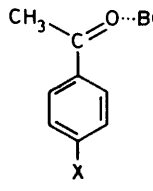

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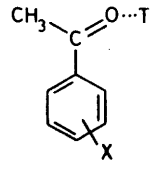

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of the side-chain compared with extended polarization of the side-chain and the benzene ring π electrons. In addition, we report data for other series containing a carbonyl moiety placed further from the substituent [(2) and (3)] and various series where other perturbations are made to the carbonyl of the basic system (1). For example, replacement of the carbonyl oxygen by a sulphur atom is examined in the thiobenzamide system (4), and protonation and complexation of the carbonyl in systems (5)—(7).

RESULTS AND DISCUSSION

The side-chain ^{13}C s.c.s. results in Tables 1 and 2 show that *meta*- and *para*-substituents have a relatively small influence on ^{13}C chemical shifts. The total range in s.c.s. values in the neutral series is less than 3 p.p.m. This is much smaller than the effects seen for ring carbon atoms,[22] where a range in s.c.s. values of up to 30 p.p.m. is observed.

Examination of the *meta*-data in series (1) shows that all substituents, except NMe_2, NH_2, and CH_3 cause upfield shifts of the carbonyl resonance. A similar trend is seen for the *para*-compounds, indicating that a reverse s.c.s. effect operates in this system. This is most clearly seen for those substituents which are both inductive and resonance withdrawing, *e.g.* NO_2 and CN. The observed upfield shift for these groups is contrary to expectation that they should withdraw electron density, decrease the shielding, and cause a downfield shift. Similar reverse s.c.s. effects have been noted for nuclei other than carbon.[2,23]

$$\text{s.c.s.} = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

Analysis of the data using the dual substituent parameter (d.s.p.) equation (1) yields correlations of good precision (Table 3), indicating that substituent effects on chemical shifts in this series are electronic in origin. This is expected, as chemical shifts have previously been related to electron densities *via* the local paramagnetic screening constant.[24] The d.s.p. analysis also shows that the ratio of resonance to inductive effects ($\lambda = \rho_R/\rho_I$) changes considerably from one series to another, showing that a single parameter equation would be inadequate for treating the data.

The Inductive † *Component of Substituent Effects.*— For the *para*-series where the carbonyl is directly ad-

† Inductive effects are defined as those which contribute to the ρ_I term of a d.s.p. equation. Through-bond or through-space (field) effects are included, with the latter being more important.

TABLE 1

Side-chain carbonyl ^{13}C substituent chemical shifts in *para*-disubstituted benzenes [a]

Substituent	Side-chain											
	$CONH_2$ [b]	COF	COOEt	COOH [b]	COMe	COH	CH_2CO_2H [b]	OCOMe	$CSNH_2$ [b]	COMe [c] (H+)	COMe (BCl_3)	COMe [d] ($TiCl_4$)
NMe_2	0.05		0.44	0.16	−1.70	−2.19		0.78	−2.42			
NH_2	0.15		0.10	0.23	−1.60	−1.88	0.73	0.63	−2.23			
OMe	−0.44	−0.10	−0.24	−0.39	−1.22	−1.60	0.29	0.44	−1.60	−10.25	−6.92	−3.03
F	−1.02	−0.99	−0.97	−1.01	−1.70	−1.92	0.10	0.00	−1.60	−2.67	−2.31	−2.18
Cl	−1.07	−0.78	−0.87	−0.90	−1.41	−1.55	−0.30	−0.29	−1.55	−1.27	−1.33	−1.82
Br	−0.97	−0.63	−0.83	−0.78	−1.07	−1.31	−0.39	−0.39	−1.45	−0.85	−0.91	
CH_3	−0.09	0.17	0.10	−0.08	−0.34	−0.44	0.15	0.25	−0.48	−3.34	−2.00	−0.49
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CF_3	−1.12	−1.19	−1.22	−1.17	−1.22	−1.31	−0.68	−0.58	−1.21	2.25	0.61	−1.21
CN	−1.41	−1.60	−1.70	−1.32	−1.55	−1.80		−1.07	−1.60			
NO_2	−1.65	−1.90	−1.90	−1.63	−1.75	−2.09	−0.92	−1.11	−1.89			
COMe	−0.78	−0.85	−0.92	−0.70	−0.58	−0.92		−0.68	−0.87			
CO_2R	−0.87		−0.83		−0.54	−0.78		−0.63	−0.87			
H [e]	168.29	157.29	166.56	167.43	198.01	155.28	172.50	132.41	200.56	219.24	215.10	214.04

[a] ^{13}C Chemical shifts (in p.p.m.) expressed relative to the unsubstituted compound. Downfield shifts are positive. Solvent is $CDCl_3$ unless otherwise noted. [b] Solvent [$^2H_6$]DMSO. [c] Solvent H_2SO_4. [d] Solvent CH_2Cl_2. [e] Chemical shifts of the parent compound relative to Me_4Si.

TABLE 2

Side-chain carbonyl ^{13}C substituent chemical shifts in *meta*-disubstituted benzenes [a]

Substituent	Side-chain										
	$CONH_2$ [b]	COF	COOEt	COOH [b]	COMe	COH	CH_2CO_2H [b]	OCOMe	$CSNH_2$	COMe [c] (H+)	COMe [d] ($TiCl_4$)
NMe_2	0.68		0.63	0.58	0.87	0.82		0.15	0.92		
NH_2	0.82		0.15	0.54	0.39			0.05	1.27		
OMe	−0.24	−0.10	−0.19	−0.20	−0.19	−0.24	−0.10	−0.10	−0.29	0.73	−0.36
F	−1.31	−1.14	−1.26	−1.13	−1.41	−1.51	−0.44	−0.49	−1.79	0.91	−1.33
Cl	−1.46	−1.19	−1.26	−1.29	−1.46	−1.60	−0.49	−0.49	−1.79	0.91	−1.58
Br	−1.51	−1.38	−1.41	−0.78	−1.55	−1.70		−0.49	−1.89	0.79	−1.82
CH_3	0.19	0.19	0.14	0.04	0.19	0.14	0.00	0.10	0.25	−0.49	0.12
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CF_3	−1.51	−1.22	−1.36	−1.36	−1.46	−1.60	−0.49	−0.51	−1.79	1.58	−1.94
CN	−1.90	−2.02	−2.14	−1.71	−2.28	−2.43		−0.82	−2.33		
NO_2	−2.14	−2.06	−2.14	−1.91	−2.38	−2.67	−0.58	−0.78	−2.81		
COMe	−0.73		−0.92	−0.65	−0.73	−0.92		−0.24	−0.87		
CO_2Et	−0.97		−0.87		−0.87	−1.07		−0.34	−1.17		

[a] ^{13}C Chemical shifts (in p.p.m.) expressed relative to the unsubstituted compound. Downfield shifts are positive. Solvent is $CDCl_3$ unless otherwise noted. [b] Solvent [$^2H_6$]DMSO. [c] Solvent H_2SO_4. [d] Solvent CH_2Cl_2.

TABLE 3

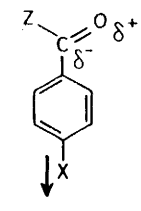
D.s.p. analysis of side-chain s.c.s. data [a]

Substituent	*para*-Series					*meta*-Series				
	ρ_I	ρ_R	Scale [b]	S.d.	f [c]	ρ_I	ρ_R	Scale [b]	S.d.	f [c]
$CONH_2$	−2.4	−0.4	BA	0.09	0.10	−3.3	−0.6	+	0.16	0.13
COF	−2.5	−1.3	0	0.12	0.12	−3.1	−0.7	+	0.15	0.12
COOEt	−2.6	−1.1	0	0.08	0.08	−3.2	−0.4	+	0.15	0.13
COOH	−2.3	−0.5	BA	0.11	0.13	−2.8	−0.5	+	0.15	0.15
COMe	−2.6	+0.8	+	0.18	0.14	−3.5	−0.6	+	0.18	0.14
COH	−3.0	+1.0	+	0.23	0.15	−3.8	−0.6	+	0.16	0.11
CH_2COOH	−1.2	−1.0	BA	0.09	0.17	−1.0	−0.1	+	0.06	0.17
OCOMe	−1.4	−1.7	0	0.08	0.12	−1.2	−0.3	BA	0.06	0.15
$CSNH_2$	−2.8	+1.1	+	0.25	0.17	−4.1	−0.8	+	0.25	0.16
COMe(H^+)	5.3	10.9	+	0.68	0.16	2.8	0.9	−	0.27	0.31
COMe(BCl_3)	2.0	6.8	+	0.54	0.18					
COMe($TiCl_4$)	−2.6	2.1	+	0.21	0.12	−4.1	−1.3	BA	0.16	0.12

[a] Results obtained by fitting the data in Tables 1 and 2 to the d.s.p. equation.[21] [b] The correlations were done for each of the four resonance scales (σ_R^-, σ_R°, σ_R^{BA}, σ_R^+), and the results for the one with the lowest s.d. (best fit) are shown. [c] f = s.d./r.m.s.[21]

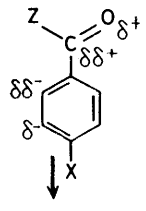
jacent to the ring, the ρ_I values are constant (mean value of *ca.* −2.6). This trend has been previously noted by us for conjugating side-chains in general.[3] The negative sign for ρ_I is indicative of a reverse s.c.s. effect, *i.e.* inductive withdrawing substituents cause an upfield shift. We consider the near constancy and negative sign of these ρ_I values to be the best evidence to date supporting the hypothesis that π-polarization is the major contributor to the inductive component if ^{13}C s.c.s. values. Structure (I) illustrates the π-polarization mechanism.

In (I), if X is an inductive withdrawing substituent, a



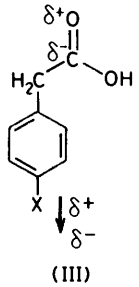
(I)

localized polarization



(II)

extended polarization



(III)

dipole on X or near the C–X bond is set up. The interaction of this dipole through the space of the molecular cavity results in the polarization shown. The net result is that the inductive withdrawing substituent increases the electron density about the α-carbon atom and hence increases the shielding to cause an upfield shift. The phenyl ring π-system is also separately polarized.

Polarization of the conjugated π-system as a whole does not play a significant part in the determination of ρ_I values for the α-C position. The polarization pattern expected in this case would be as in (II), and if significant, would lead to a positive ρ_I value for α-C (*i.e.* a normal s.c.s. direction). The observed negative ρ_I values mean that such polarization does not influence the α-C position.

Further support for the proposal that the two π-systems in these carbonyl compounds are separately polarized can be found from the data for the phenyl-

TABLE 4

D.s.p. analysis of literature side-chain s.c.s. data

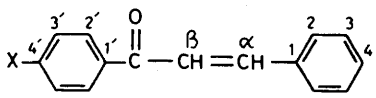
	ρ_I	ρ_R	Scale [a]	S.d.	f [b]		ρ_I	ρ_R	Scale [a]	S.d.	f [b]
Series (8a) [c]						Series (8b) [c]					
α-C	2.7	3.1	0	0.10	0.08	α-C	−4.0	−1.8	BA	0.08	0.06
β-C	−1.1	−0.06	+	0.15	0.31	β-C	4.5	6.0	BA	0.33	0.12
C=O	−2.2	1.3	+	0.23	0.17	C=O	−1.0	−0.7	−	0.13	0.34
C-1	−0.8	−0.4	BA	0.06	0.21	C-1	6.2	21.6	0	0.83	0.13
C-4	0.3	0.6	0	0.04	0.27	C-1′	−0.7	−0.5	+	0.03	0.07
C-1′	4.2	9.0	+	0.50	0.14	C-4′	0.8	0.8	BA	0.05	0.14
Series (9a) [d]						Series (9b) [d]					
CH=N	1.4	1.7	0	0.04	0.08	CH=N	−3.6	−0.7	0	0.11	0.09
C-1′	−0.6	−0.4	0	0.03	0.19	C-1	−1.1	−1.0	BA	0.04	0.09
C-4′	0.6	0.3	+	0.05	0.19	C-4	0.4	0.3	BA	0.004	0.03

[a] The correlations were done for each of the four resonance scales (σ_R^-, σ_R°, σ_R^{BA}, σ_R^+), and the results for the one with the lowest s.d. (best fit) are shown. [b] f = s.d./r.m.s. [c] Ref. 25. [d] Ref. 26.

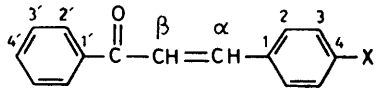
acetic acids (2). Here, the carbonyl is effectively insulated from the ring π-system, thus inhibiting the type of polarization shown in (II). The observed ρ_I value is −1.2, indicating a reverse effect (III).

An analysis of literature data also supports our hypothesis that many side-chain s.c.s. results can be explained in terms of substituent polarization of small localized π-units. An excellent illustration of this point can be seen from a d.s.p. analysis of data for the chalcone series (8).[25] The ρ_I values in Table 4 can be intepreted largely on the basis of separate polarization of the ethylene, carbonyl, and distant phenyl π-systems.

This mechanism explains the negative ρ_I values for β-C, C=O, and C-1 in series (8a) (and the positive values for C-4 and α-C), as well as the negative value of ρ_I for α-C, C=O, and C-1′ in series (8b) (and the positive values for β-C and C-4′). These results clearly indicate that in series (8a), the major polarization of the C=CHPh group is not as a whole styryl unit, but as separate ethylene



(8a)



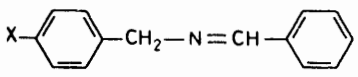
(8b)

and phenyl units. We do not suggest that polarization of the entire conjugated unit does not occur, but merely that polarization of small localized units is also very important.

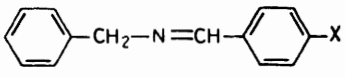
Care must be taken to avoid confusion between resonance effects and inductive polarization of a conjugated system. So far we have considered only the substituent's inductive effect. The presence of a conjugated system certainly plays an important role in determining the response of a carbon atom in a side-chain to the resonance effects of distant substituents. This resonance contribution appears in the ρ_R term of the d.s.p. equation and will be discussed later.

Other literature data which supports the π-polarization mechanism includes much of the work of Reynolds [11–15] and also some data of Cook [26] for series (9a and b). Our d.s.p. analysis of this later data is in Table 4 and the ρ_I values are readily explained in terms of π-polarization of the side-chain CH=N and Ph units. That π-polarization of a distant π-system by a substituent need not be transmitted *via* an intervening π-system can be seen from s.c.s. data of Morris and co-workers.[27] For series (10) these workers found reverse ^{13}C s.c.s. effects for both carbonyls. We believe that once again a π-polarization mechanism is responsible for this effect and that it occurs *via* a through space interaction of the subsituent dipole and the carbonyl π-electrons.

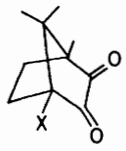
To examine the relative importance of the two possible polarization pathways we introduce the following terminology. 'Localized polarization' (P_L) refers to substituent-induced polarization of a small π-unit as shown in (I). 'Extended polarization' (P_E) refers to polarization of a much longer (conjugated) π-system as, for example, is shown in (II). The net polarization for any π-system will be the sum of these two components.



(9a)



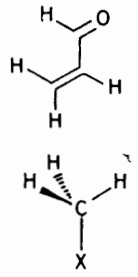
(9b)



(10)

Reynolds,[15] in his pioneering work on the π-polarization effect, recognised the existence of both of these terms and in fact calculated, for the β-C position of *p*-styrenes that the relative importance of localized polarization of the vinyl unit to extended polarization of the whole styryl unit was in the ratio $P_L : P_E = 3 : 7$. His estimate was based upon s.c.s. data for the trimethylammonio-substituent, which he assumed to have a negligible resonance effect. It has been suggested [28] that this group does have a measurable resonance component, and allowing for this, we have recalculated the $P_L : P_E$ ratio to be *ca.* 4 : 6. The actual ratio is open to debate, but the important point is that for this β-C position, the localized and extended polarization components are of comparable magnitude. We also propose that a similar ratio holds for the oxygen atom in our carbonyl systems.

There is no reason to expect that there will be a similar ratio of P_L to P_E at the α-C position. In fact, the P_L component at α-C will be exactly equal and opposite that at the oxygen atom (I), however, the magnitude of the P_E component will certainly be smaller than that at the terminal atom. On the basis of MO calculations in series (11) [29] we predict that polarization of a conjugated unit produces by far the largest changes at terminal atoms of the π unit and quite small changes at intermediate atoms. At α-C more than 80% of the polarization is due to polarization of the localized C=O bond and only 20% due to extended polarization.[29]



(11)

This shows that it is possible to predict qualitatively the correct direction of s.c.s. values for side-chain π-systems by assuring that each π-system is separately polarized. This is because localized polarization is either much more important than extended polarization (*e.g.* positions like α-C) or, for those positions where localized and extended polarization are of comparable magnitude (*i.e.* at the terminal atoms of a π-system), they work in the same direction.

For all the series with the general structure (1), the d.s.p. analyses in Table 3 show that inductive effects at the α-C carbon become larger when the substituent is moved from the *para*- to the *meta*-position. In most cases the ρ_I value increases in magnitude by 20—30%, and the negative sign is retained. The larger magnitude in the *meta*-series, where the substituent is closer to the carbonyl group, is consistent with a through-space interaction of the C-X dipole with the carbonyl π-electrons. This distance factor appears to have overriden any effects due to the differing relative orientation of the C=O and C–X bonds in the *meta*- and *para*-series. The *meta*-data also confirms that the transmission of inductive effects is not dependent on conjugation between the substituent and the carbonyl site, for if this were the case, ρ_I values would be larger for the *para*-series.

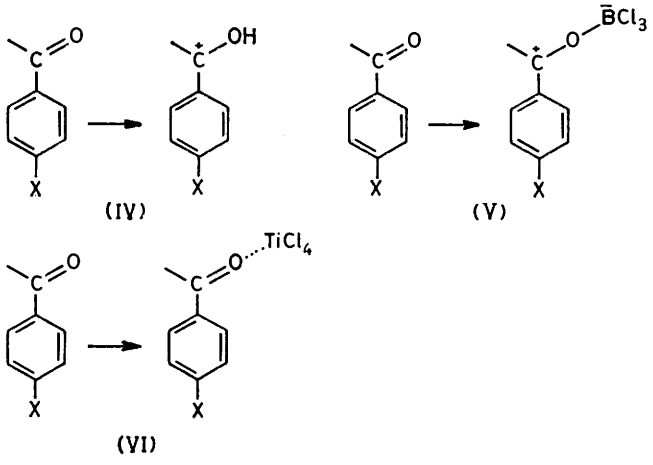
The data for series (4)—(7) provides critical support for the proposed inductive transmission mechanism in series (1). A direct corollary of our proposal that π-polarization of the carbonyl electrons is responsible for the reverse s.c.s. values is that when those π-electrons are removed then the reverse s.c.s. effect will also be eliminated. This is illustrated by a comparison of the data in Table 3 for the acetophenone, and protonated aceto-

phenone series.* Upon protonation, the C=O π-bond is broken (IV) and the ρ_I value changes from reverse (−2.6) to normal (+5.3).

Complexation with boron trichloride (V) produces a similar effect (ρ_I +2.0), although surprisingly, a reverse effect (ρ_I −2.6) is still noted for the titanium tetrachloride complexes of acetophenone. This shows that there is still considerable double-bond character in the carbonyl group (VI), a conclusion supported by i.r. studies.[30,31] The sensitive response of ρ_I values to π-bonding changes therefore provides an important experimental tool for determining the π-bond character of various groups.

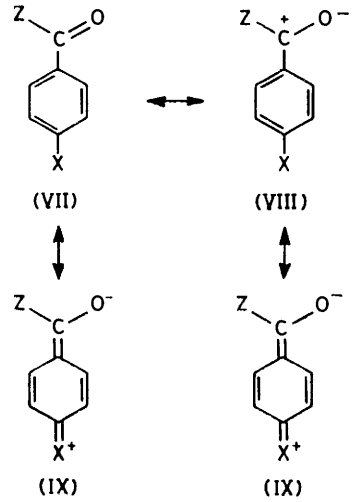
The positive sign for ρ_I which is noted when the possibility of π-polarization is removed indicates that another mechanism which produces a normal s.c.s. effect must be present. Because of the charged nature of α-C in these series, the most likely mechanism is the classical direct-field effect involving the interaction of the charge at the measuring site with the substituent dipole.[32]

A comparison of the d.s.p. results for the benzamide and thiobenzamide series shows that replacing the oxygen



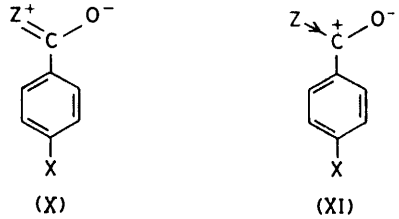
by sulphur has the effect of increasing ρ_I from −2.4 to −2.8. This negative ρ_I value is not significantly different in magnitude from that of the benzamides and indicates that π-polarization of the C=S bond controls inductive effects in the thiobenzamides.

The Resonance Component of Substituent Effects.— The sensitivity of the α-carbon to resonance effects is rather small, as might be expected for a side-chain carbon atom which is not in a direct conjugating position. An examination of the ρ_R values (Table 3) obtained from the d.s.p. analysis shows the following trends. (a) The ρ_R values (unlike ρ_I) are strongly dependent on the electronic effect of the Z group. When Z is a strong resonance donor, ρ_R is negative, and when Z is neutral (*e.g.* H) ρ_R is positive. (b) The choice of resonance scale is also related to Z. Enhanced resonance scales are preferred as Z becomes a poorer π-donor. These observations may be explained in terms of interactions of the Z group with the carbonyl function.



Absolute carbonyl chemical shifts have been rationalized[33] in terms of the relative contributions from canonical forms (VII) and (VIII). The substituent interaction of X in (VIII) results in a positive ρ_R value at α-C because π-electron density is directly transferred from the substituent to the carbon site (*i.e.* here α-C is conjugating site) (VIII) ⟷ (IX). On the other hand, substituent interactions in (VII) result in a negative ρ_R since π-charge density is transferred to the oxygen (the carbon is a non-conjugating site) (VII) ⟷ (IX).†

The group Z modifies the overall ρ_R value by altering the relative importance of (VII) and (VIII). If Z is a strong π-donor then an additional structure (X) contributes. As in (VII) substituent interactions result in a negative ρ_R since α-C is not directly conjugated. Inductive donors are expected to stabilize (VIII) *via* contributions from (XI) which, like (VIII), allows α-C



to directly conjugate with the substituent and hence produce a positive ρ_R value.

Evidence for this stabilizing influence of the Z group can be seen from a qualitative relationship we have

* It was not possible to measure substituent chemical shifts for a full range of X substituents in the protonated and complexed series (5)—(7) because of interactions between complexing agents and the substituents themselves, rather than with the carbonyl site. For example the NH_2 substituent could not be included in the protonated acetophenone series because under the acidic conditions it would be protonated to form an NH_3^+ group, which has vastly different substituent properties from the neutral amino-group. Its use in the $TiCl_4$ complexes was also avoided because a previous i.r. study had shown that nitrogen complexation takes place rather than oxygen complexation.[30]

† Reverse resonance effects at non-conjugating positions have been noted in other series.[34,35]

noted between ρ_I and the absolute chemical shifts of the parent compound for each series. Those series with upfield carbonyl shifts show a reverse resonance effect whereas those with a relatively downfield carbonyl shift show a normal resonance effect. This indicates that when the Z substituent can stabilize a positive charge on α-C by inductive donation, then the contribution on form (VIII) increases.

Further support for this point can be found from a comparison of data for the benzamide and thiobenzamide series. The normal resonance effect observed in the latter, and the reverse effect in the former is a reflection of an increased contribution of resonance forms involving charge separation as in (VIII) for the thiobenzamide series. General support for this may be found in the literature.[36-38]

The trend in the preference for resonance scales is consistent with some donation of π-electrons from Z to the carbonyl. The electron demand (with respect to substituent X) of the carbonyl site is controlled by the adjacent Z group. The more that Z is able to donate electrons to α-C, (VIII) ⟷ (X), the less substituent X will be called upon to supply electrons, (VIII) ⟷ (IX), and hence the more likely the series will correlate with a neutral resonance scale (*e.g.* σ_R^0). If Z is not so good at supplying electrons then the carbonyl site will demand more from substituent X, and hence there will be a preference for an enhanced resonance scale (*e.g.* σ_R^{BA} or σ_R^+).

For the *meta*-series (1), all ρ_R values are negative and smaller in magnitude than in the corresponding *para*-series. The smaller magnitude is consistent with the lack of conjugation between *meta*-groups in a benzene ring. Secondary conjugation effects transmitted *via* the common *ortho*- and *para*-positions of the two substituents are unimportant because if present they would produce similar signs in ρ_R for the *para*- and *meta*-series. The relative constancy of ρ_R and its negative sign suggest that resonance effects in the *meta*-series bear some similarity to inductive effects transmitted by π-polarization (*i.e.* resonance–polar effects [39] may be important).

Protonation or complexation of the carbonyl in acetophenone increases the magnitude of the ρ_R value. The increase is largest for protonation or complexation with BCl_3, but only marginal for $TiCl_4$ complexation. The dramatic increase in the magnitude of resonance effects is obviously related to an increase in the positively charged character of α-C, as indicated in structures (IV) and (V).

Conclusions.—For series of the general form (1), the *para*- or *meta*-substituent X induces changes in the ^{13}C chemical shifts at the α-C atom. These changes correlate with substituent parameters *via* the d.s.p. equation (with good precision) indicating that they are electronic in origin. The inductive effect of X is largely determined by localized π-polarization of the C=O π-electrons, and is independent of the adjacent Z group. Removal of the π-electrons of the carbonyl by complexation or protonation removes the possibility of a π-polarization mechanism and results in a change in the sign of ρ_I values. The resonance effect of X varies considerably from one series to another, and is determined by both the inductive and resonance effects of the Z group.

EXPERIMENTAL

The ^{13}C n.m.r. spectra were run on a JEOL PFT-100 spectrometer at 25 MHz using 10-mm sample tubes. For the neutral series, 8 K data points were used, with a spectral width of 5 000 Hz, giving a digital resolution of 0.05 p.p.m. Concentrations of 0.5M for the BCl_3 complexes, 0.1M for the $TiCl_4$ complexes, and 0.2M for all other series were used. Solvents are noted in Table 1. For the $TiCl_4$ complexes, a capillary containing D_2O and dioxan was placed in the sample tube to provide deuterium lock and reference respectively. The complexes were prepared immediately prior to recording of the spectrum, by dissolving equimolar amounts of the acetophenone and Lewis acid in the corresponding solvent under nitrogen. The $TiCl_4$ was used neat, the BCl_3 as a 3M solution in chloroform. The complexes were stable at room temperature during accumulation of the spectrum. A spectral width of 6 250 Hz, was used for the BCl_3 and $TiCl_4$ complexes, with 8 K (resolution 0.06 p.p.m.) and 4 K (resolution 0.12 p.p.m.) data points respectively. The protonated acetophenones were run using concentrated sulphuric acid as solvent with a capillary containing D_2O for locking purposes.

Most of the compounds used in this study were commercial samples purified by recrystallization or column chromatography whenever necessary. Spectral and physical properties of all the compounds were in agreement with expectations and literature data where available. The following derivatives were prepared.

p-Aminobenzaldehyde was obtained from the internal oxidation–reduction of *p*-nitrotoluene by alkaline sodium polysulphide.[40] *m*-Dimethylaminobenzaldehyde was prepared from *m*-nitrobenzaldehyde,[41,42] *p*- and *m*-acetylbenzaldehydes by the oxidation of the corresponding methylacetophenones,[43] and *p*- and *m*-trifluoromethylbenzaldehydes from $AlLi(Bu^t)_3$ reduction of the corresponding acid chlorides.[44,45] The *m*-carboxymethylbenzaldehyde was prepared by dibromination of *m*-toluoyl chloride,[46] subsequent hydrolysis to *m*-carboxybenzaldehyde [47] and DMS–K_2CO_3 esterification.[48]

The benzamides (except those with acid-sensitive substituents) were prepared by a standard conversion of the corresponding benzoic acid into the acid chloride and ammonolysis with aqueous ammonia. The *p*- and *m*-aminobenzamides were obtained by partial hydrolysis of aminobenzonitriles.[49] Using the same method, *p*- and *m*-carboxybenzamides were prepared and later converted into methyl esters by methyl iodide methylation of their silver salts.

Most thiobenzamides were prepared by the addition of H_2O to the corresponding benzontrile dissolved in pyridine, with an equimolar amount of Et_3N.[50] The cyanothiobenzamides were synthesized by sulphurization of the corresponding benzamide with P_2S_5–toluene.[51] *p*-Nitrobenzamide was obtained from *p*-nitrobenzonitrile and thioacetamide under acidic conditions.[52]

All phenyl acetates were prepared from readily available phenols by a standard method.[53] This failed only for *p*-trifluoromethyl and *p*-nitrophenols, and they were esterified with acetic anhydride in glacial acetic acid under reflux for 1 h.

The benzoyl fluorides were available in these laboratories from a previous study, and had been prepared from the reaction of the corresponding benzoic acid and sulphur tetrafluoride.[54]

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