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SUBSTITUENT EFFECTS ON THE PHOTOELECTRON SPECTRA OF BENZENE DERIVATIVES

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Abstract—Systematics in the ionization energies corresponding to the different π orbitals of *para*, *meta* and *ortho*-disubstituted benzenes obtained from PES have been investigated. The data have been discussed in terms of correlations with substituent constants and such correlations are shown to provide the basis to differentiate steric from electronic effects in the case of *ortho* derivatives. Ionization energies from PES corresponding to the lone pair orbitals of substituents in related series of *p*-disubstituted benzenes are shown to vary systematically with the substituent constants.

INTRODUCTION

Recent studies on the photoelectron spectra of substituted benzenes have provided valuable information on the nature of substituent effects on benzene π levels.[1-7] In particular, these studies have shown that lone pair orbitals of electron-donating substituents like OMe and NH_2 interact with the doubly degenerate e_{1g} orbital of the benzene ring giving rise to b_1 and a_2 levels the latter being stabilized with respect to the former (Fig. 1). Electron withdrawing groups like COMe and CN interact with the e_{1g} orbital of benzene through the occupied π orbitals of the substituents. Nitro group seems to be an exceptional case in that its vacant π orbital interacts with the e_{1g} orbital giving rise to a b_1 level stabilized with respect to the a_2 level (Fig. 1). In general, the π ionization energies (IE) of substituted benzenes corresponding to the two orbitals arising from the e_{1g} orbital and to the a_{2u} orbital (11.6 eV PES band of benzene) increase with the increasing electron withdrawing power of the substituents. Most of the studies of PES hitherto have been confined to *para*-disubstituted benzenes[1] and there is little information on the effect of *meta* and *ortho* substituents. In this communication, we discuss some generalizations regarding the effects of *o*, *m* and *p* substituents on PES of benzene derivatives through correlations of IE's with substituent constants.[1] In the case of *o*-derivatives, we have attempted to distinguish electronic and steric effects of substituents. We have also examined possible additivity of substituent effects in terms of group contributions, δI, and the splitting of the first two π levels (π_2/π_1 splitting), ΔI, in several related series of disubstituted benzenes. Another aspect of interest to us is the effect of substituents on the PES bands due to ionization of lone pair orbitals of chromophoric (CO, NO_2) and auxochromic (OMe, Cl) groups.

EXPERIMENTAL

UV photoelectron spectra of the benzene derivatives were recorded employing a Perkin-Elmer PS18 spectrometer wherever necessary. The compounds were purified by subjecting them to fractionation and after ascertaining their purity by standard methods. A separate table of the IE's of all the benzene derivatives used for correlations in this paper has not been given since they may be found from the plots in Figs. 2-4.‡ Data on many of the compounds used in the study were also available in the literature.[1-7]

RESULTS AND DISCUSSION

In order to examine substituent effects in PES of benzene derivatives, we first examined group contributions, δI, in several series of *p*-disubstituted benzenes with widely varying electronic properties of substituents (Table 1). Thus, the compounds examined include *p*-dinitrobenzene at one end and N,N,N',N'-tetramethyl-*p*-phenylenediamine at the other. If the group contributions were to be purely additive, δI of a group should be constant in all the series of disubstituted benzenes. However, this is not the case, particularly in the case of electron-donating substituents like NMe_2 or OMe where the lone pair orbitals of the substituents interact with the e_{1g} orbital of benzene to give the highest occupied b_1 orbital. In the case of the chloro group, δI although small in magnitude, changes sign depending on the nature of the other substituent. This change in sign is clearly suggestive of the anomalous substituent effects of halogens wherein they act as electron-donating groups when the other *p*-substituent is a withdrawing group and as withdrawing groups when the other substituent is a donating group. Such effects have been noticed earlier in the electronic spectra of benzene derivatives.[8,9] From Table 1 we see that constancy of δI, if at all, is present only in the case of electron-withdrawing substituents like COMe, CN and NO_2.

Turner *et al.*[2,10] have pointed out that the separation between the two highest occupied π orbitals in *p*-disubstituted benzenes, $\Delta I = \pi_2(IE) - \pi_1(IE)$ is nearly equal to the sum of the separations in the corresponding monosubstituted benzenes. An examination of the data now available on a wide variety of benzene derivatives shows that additivity fails in the case of substituents interacting strongly with the aromatic π system, particularly those with lone pairs (Table 2). Thus, additivity of ΔI is not seen in *p*-substituted dimethylanilines when the *p*-substituent is NMe_2 or NO_2. ΔI varies considerably with the substituents in most of the series of *p*-disubstituted benzenes as well as in monosubstituted

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‡ A table containing the selected PES data on disubstituted benzenes can be obtained by those interested by writing to the author

benzenes. ΔI becomes much smaller in magnitude in the presence of electron-withdrawing groups like COMe and NO_2 and these substituents show small $\pi_2 - \pi_1$ separations in monosubstituted benzenes as well. ΔI, although not additive, remains fairly constant in derivatives containing highly electron-donating groups like NMe_2 immaterial of the other p-substituent.

The above observations on δI and ΔI would indicate that substituent effects on PES of benzene derivatives are not simply additive over a wide range of substituents. One could, in principle, employ an expression of the type proposed by Heilbronner *et al.*[11] from first order perturbation theory to calculate substituent effects or develop an empirical additivity rule based on δI values of groups for different π levels. After an examination of various ways of rationalising PES data, we considered it best to employ the substituent constants for the purpose. There seemed to be no advantage in using π electron density changes, (q − 1), caused by substituents as parameters;[12] further, (q − 1) values are not available for many substituents.

para-*Disubstituted benzenes.* The IE values of a few related series of p-disbustituted benzenes, $R_1C_6H_4R_2$ (R_1 = invariant, R_2 = variable), are plotted against the

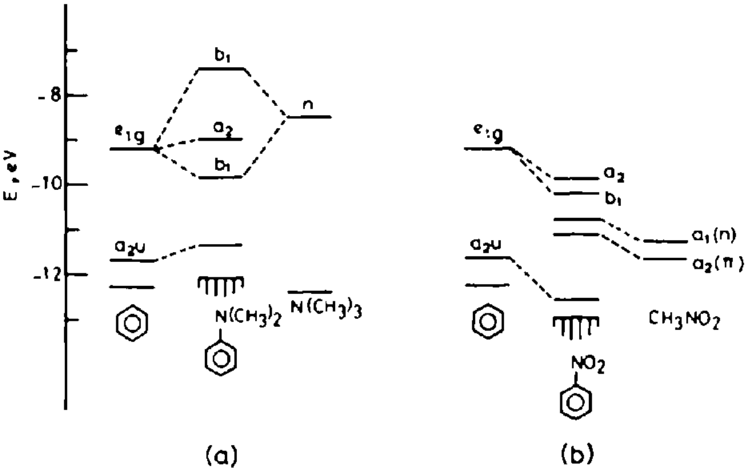

Fig. 1. Schematic energy levels diagrams for N,N-dimethylaniline and nitrobenzene. The orbital energies E are taken as negative of IE values following Koopmans' theorem.

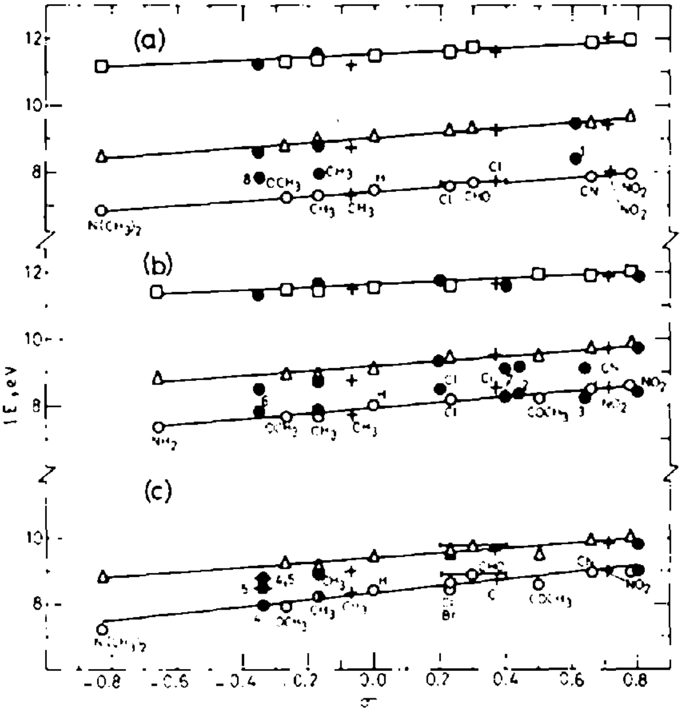

Fig. 2. Correlation of the first (open circles) and second (triangles) PES bands of related series of *para*-disubstituted benzenes with σ constants. PES bands corresponding to the a_{2u} orbital of benzene (11.6 eV) are also shown (squares). Bands of *meta*- and *ortho*-disubstituted benzenes are indicated by plus signs and closed circles respectively. Straight lines are for the correlation of the data of *para* derivatives only. (a) substituted N,N-dimethylanilines; (b) substituted anilines; (c) substituted anisoles. 1, 2-methyl-4-nitro-N,N-dimethylaniline; 2, 2,6-dimethyl-4-nitroaniline; 3, 3,5-dimethyl-4-nitroaniline; 4, 2,4-dimethylanisole; 5, 2,6-dimethylanisole; 6, 2,6-dimethylaniline; 7, 2,6-dichloroaniline; 8, 2,6-dimethyl-N,N-dimethylaniline.

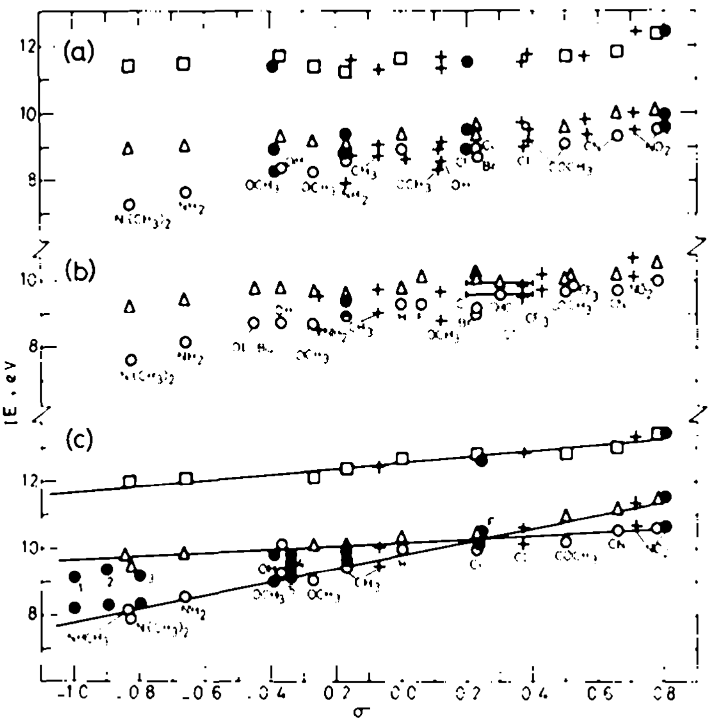

Fig. 3. Correlation of the PES bands of substituted benzenes: (a) substituted toluenes; (b) substituted chlorobenzenes; (c) substituted nitrobenzenes (see legend of Fig. 2 for other details). Straight lines are not drawn for *para* derivatives of (a) and (b) since correlations are not as good. Lines drawn in (c) show evidence of cross over of levels. 1. 3,5-dimethyl-4-nitroaniline; 2. 2-methyl-4-nitro-N,N-dimethylaniline; 3. 2,6-dimethyl-4-nitroaniline; 4. 2,4-dimethylnitrobenzene; 5. 2,6-dimethylnitrobenzene.

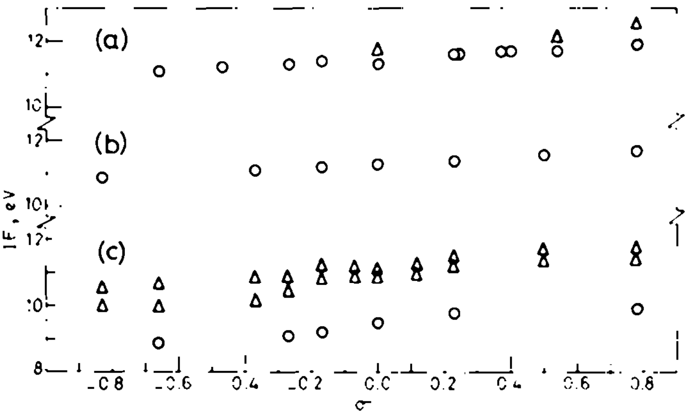

Fig. 4. Correlation of lone pair ionization bands of substituents in the PES of benzene derivatives with substituent constants: (a) chloro group in substituted chlorobenzenes. The second 3p IE values are shown (triangle) where present. (b) methoxy groups is substituted anisoles; (c) $a_2(\pi)$ $a_1(n)$ PES bands of NO_2 group in substituted nitro benzenes (triangles) and PES band due to *n* orbital of C=O group in substituted acetophenones (circles).

Hammett σ constant[13,14] of the varying substituent R_2 in Figs. 2 and 3. Other series examined by us, but not included in the figures are phenols, benzonitriles and acetophenones. In all the cases, IE's increase with the increasing electron-withdrawing power of R_2. The plots of dimethylanilines, anilines and anisoles (Fig. 2) are linear for the first two π IE's (corresponding to b_1 and a_2 orbitals) as well as for the IE corresponding to the a_{2u} orbital (11.6 eV PES band of benzene). The plots of chlorobenzenes and toluenes in Fig. 3 are not as linear for the first two IE's although proportionality to σ constants is indicated; in nitrobenzenes, the plots are again linear. It appears that linearity with σ constants is found best when the electronic effects of the invariant substituents R_1 are quite large (i.e. $|\sigma|$ of R_1 is large). Thus, while the effect of Me or Cl on the IE's of substituted anilines is properly accounted for by the linear σ correlation, the effect of the amino group on the IE's of chlorobenzenes or toluenes is not as well correlated by its σ constant.

In the case of *p*-substituted nitrobenzenes, the plots for the first two IE's (Fig. 3) seem to cross each other. This is because, in nitrobenzenes, $p\text{-}NO_2C_6H_4R_2$, the stability of the orbitals corresponding to the first two π IE's (a_2 and b_1) is reversed when R_2 becomes electron-withdrawing (starting from nitrobenzene, R_2=H, itself). It may be recalled that in nitrobenzene, unlike in anilines, anisoles

Table 1. Group contributions, δI, in p-disubstituted benzenes, 4-$R_1C_6H_4R_2$$^{(a)}$

R_2	R_1: $N(CH_3)_2$	NH_2	OCH_3	CH_3	$H^{(b)}$	Cl	$COCH_3$	NO_2
$N(CH_3)_2$	-0.7	-	-1.3	-1.6	-1.95	-1.7	-	-2.00
NH_2	-	-0.7	-0.9	-1.3	-1.4	-1.2	-1.4	-1.3
OCH_3	-0.2	-1.0	-0.6	-0.7	-0.9	-1.0	-1.0	-0.95
CH_3	-0.2	-0.4	-0.3	-0.3	-0.5	-0.5	-0.5	-0.4
Cl	+0.15	+0.15	+0.1	0.0	-0.1	-0.1	-0.1	0.1
$H^{(c)}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$COCH_3$	-	+0.2	+0.15	+0.2	+0.2	+0.3	-	+0.25
CN	+0.4	+0.5	+0.4	+0.4	+0.4	+0.4	-	+0.6
NO_2	+0.5	+0.6	+0.5	+0.6	+0.5	+0.7	+0.5	+0.7

(a) δI values are with respect to the first IE of the monosubstituted benzene. That is, effect of substituting 4-R_2 in the monosubstituted benzene $C_6H_5R_1$ on the first IE is given by δI.

(b) This column corresponds to monosubstituted benzenes and δI of a group here is the effect of R_2 on the first IE of benzene.

(c) δI in this row is zero since it represents the effect of H on the first IE of $C_6H_5R_1$.

Table 2. ΔI in p-disubstituted benzenes, 4-$R_1C_6H_4R_2$$^{(a)}$

R_2	R_1: $N(CH_3)_2$	NH_2	OCH_3	CH_3	$H^{(b)}$	Cl	$COCH_3$	CN	NO_2
$N(CH_3)_2$	1.6	-	1.7	1.6	1.55	1.6	-	1.55	1.6
NH_2	-	1.7	1.2	1.3	1.1	1.25	1.2	1.15	1.2
OCH_3	1.7	1.2	1.3	0.9	0.9	1.0	0.8	0.95	1.0
CH_3	1.6	1.3	0.9	0.45	0.4	0.6	0.5	0.4	0.5
$H^{(b)}$	1.55	1.1	0.9	0.4	0.0	0.4	0.2	0.25	0.4
Cl	1.6	1.25	1.0	0.7	0.4	0.8	0.4	0.45	0.4
$COCH_3$	-	1.2	0.8	0.5	0.2	0.4	-	-	0.7
CN	1.55	1.15	0.95	0.4	0.4	0.45	-	-	0.65
NO_2	1.6	1.2	1.0	0.5	0.4	0.4	0.7	0.65	0.8

(a) ΔI is the difference in the first two IE's.

(b) Corresponds to monosubstituted benzenes.

and such derivatives, the b_1 orbital is stabilized with respect to the a_2 orbital.[7] Thus, the correlations of IE's with σ constants show the importance of assigning PES bands of related series of molecules to equivalent orbitals.

In general, the slope of the IE–σ plot for the first π IE is significantly higher than for the second π IE or for that corresponding to the a_{2u} orbital. Apparently, the first IE is most sensitive to substitution. These slopes show why ΔI in p-disubstituted benzenes decreases with increase in electron-withdrawing power of the p-substituent.[1c] It is noteworthy that ΔI decreases in the direction of increasing electron-withdrawing power of the substituent in monosubstituted benzenes as well (see Table 2). The slope of the plot of 11.6 eV band seems to be least sensitive to substitution.

The slopes of the IE–σ plots of the first π IE's of several series of p-disubstituted benzenes are listed in Table 3. We see that the slope increases markedly with increase in electron-withdrawing power of the invariant substituent. Thus, the slope is highest for nitrobenzenes ($R_1 = NO_2$) and least for dimethylanilines ($R_1 = NMe_2$). It is indeed interesting that sensitivity of IE's to substitution is determined by the extent to which the aromatic

Table 3. Slopes of first IE-σ plots of p-disubstituted benzenes, 4-$R_1C_6H_4R_2$

R_1	Slope, eV
$N(CH_3)_2$	0.7
NH_2	1.0
OCH_3	1.2
CH_3	1.25
H	1.3
Cl	1.6
$COCH_3$	1.7
NO_2	1.8

π-system is depleted of electron density. This may be because the first IE of benzene derivatives with lone-pair substituents arises from the b_1 orbital with considerable lone pair character. Similar variation of slopes had been noted earlier in the correlation of $\pi-\pi^*$ transitions of *p*-disubstituted benzenes with substituent constants.[9,15] The slope of the second IE of *p*-disubstituted benzenes remains essentially independent of R_1 and is generally 0.6 ± 0.1.

We have also examined correlations of IE's with Brown's σ^+ constants[16] to see if these constants were in any way superior to the Hammett σ constants. We saw no definitive advantage in using σ^+ constants in most of the series; slightly improved linear plots were found only in the correlation of the first IE's of *p*-substituted toluenes and chlorobenzenes.

meta-*Disubstituted benzenes*. In these derivatives, the ΔI values are generally smaller than in the corresponding *para* derivatives. The absence of resonance interaction of substituents in the *meta* derivatives is probably responsible for this behaviour. We have plotted the IE's of *meta* derivatives also against σ (*meta*) constants in Figs. 2 and 3 (see data points designated by the plus symbol). While a fair proportion of the data could be fitted with the σ-correlation of *p*-derivatives, there is also considerable scatter in some of the plots. Thus, while the effect of *m*-Me on IE's of anilines is fairly well accounted for by its σ constant, the effect of *m*-NH_2 on IE's of toluene does not fit in with the σ correlation of *p*-substituted toluenes.

ortho-*Disubstituted benzenes*. The ΔI values in *ortho* derivatives are considerably smaller than in the corresponding *para* derivatives and often, than in the *meta* derivatives as well. Such small ΔI values have been employed to examine steric effects of *ortho* substituents in dimethylaniline and other derivatives.[6] We have attempted to distinguish electronic and steric effects of *ortho* substituents making use of the correlations of IE's with σ constants. In Figs. 2 and 3, we have plotted the data on the *ortho* derivatives (designated ●) to compare them with those of the *para* derivatives. We see that σ correlations (of the *p*-derivatives) rightly predict the IE's of *ortho* derivatives where there is no steric effect. Thus, in nitrobenzenes ($R_2 = NO_2$), the correlations are good when σ(*ortho*) constants[17] are employed for *o*-F or NO_2. Similarly, in aniline and anisole *o*-Me and NO_2 groups seem to exert little or no steric effect as also the *o*-Me, OMe and Cl groups in the case of toluene.

When steric effects due to substituents are operative, we see that IE's of the ortho derivatives deviate significantly from the σ correlations (of the *p*-derivatives) when σ(*ortho*) constants are employed. This is obviously because, the σ(*ortho*) constants only account for the electronic effects of the *ortho* substituents which are not very different from those of the corresponding *para* substituents. From Figs. 2 and 3, the first two IE's of *ortho* derivatives where steric effects are operative can be readily identified as will be detailed later; the IE corresponding to the a_{2u} orbital is not sensitive to steric effects. In many of the systems with steric effects, the first IE is higher than that predicted by the σ correlation while the second IE is often lower than the predicted value. Such deviations from the σ correlations associated with small ΔI values could be taken as evidence for steric effects. That the ΔI value is a measure of steric effect or twisting of the S-bond (C–N or C–O) in dimethylanilines and anisoles can be understood from the following arguments.[6]

The resonance interaction between the lone pair orbital of dimethylamino or methoxy group and the benzene π system is given by,

$$E = E(\pi_{lp} \quad \pi_q) = [(A_{lp} - A_q)^2 + 4B^2]^2$$

where p refers to the highest occupied b_1 orbital of the substituted benzene with considerable lone pair character, q refers to the corresponding π orbital of much higher energy and A is the diagonal matrix element given by

$$A_i = \langle\psi_i|H|\psi_i\rangle.$$

The term B depends on the angle, θ, between the plane containing the C–N (or C–O) bond and the 6-fold axis of the benzene ring. B is given by,

$$B = \langle\psi_{lp}|H'|\psi_q\rangle$$

when $\theta = 0^\circ$ and $B_\theta = B_0 \cos\theta$. In dimethylanilines, Maier and Turner[6] have taken A_{lp} (lp = lone pair) as the negative of the IE of Me_3N and A_q as the second π IE (a_2) of toluene. They have then taken the splitting ΔE as the difference in the first and third IE values. This seems reasonable since the second IE arises from the a_2 orbital (which is nearly the basis orbital) and both the third and first IE arise from b_1 orbitals. This cannot, however, be done in anisoles where one observes only two PES bands due to π orbitals followed by a band essentially due to the lone pair. We, therefore, feel that the difference in the first two IE's ΔI, of dimethylanilines as well as anisoles may be taken as a qualitative measure of the magnitude of twist of the S bond. Accordingly, ΔI varies in the same direction as the difference in the first and third IE's in dimethylamiles. We can also see from the σ correlations in Figs. 2 and 3, that in systems where such twisting of the S bond is present, ΔI is anomalous in addition to the first IE being higher. We shall now examine a few specific systems where steric effect is operative in the light of the σ correlations.

In Fig. 2(a) we see that N,N-dimethyl *o*-toludine and 2,6-dimethyl-N,N-dimethylaniline (point 8) clearly show higher first IE's than predicted by the σ-correlation as well as small ΔI values. There is indeed considerable spectroscopic and structural evidence for the twisting about the C–N bond in this these two derivatives.[6,17] Figure 2(a) also shows that steric effect is still considerable in 2-methyl-4-nitro-N,N-dimethylaniline (point 1) despite the presence of a *para*-NO_2 group. Twisting about the C–O bond in 2,6-dimethylanisole (point 5) is known to be quite large[6,18] and the σ correlation in Fig. 2(c) clearly shows evidence for the presence of large steric effect in this compound compared to 2-methylanisole. Figure 2(b) indicates that there may be some steric effect in 2,6-dimethylaniline (point 6) as well. From Fig. 3(c) we see evidence for steric effects in *o*-nitrotoluene and 2,6- and 2,4-dimethyl nitrobenzenes. It is known that *o*-Me groups cause a twisting of the NO_2 group from the plane of the ring.[19-21] It is interesting that the σ-plots of nitrobenzenes also indicate the presence of steric effect in 2-methyl-4-nitro-N,N-dimethylaniline (point 2) just as the σ-plots of dimethylanilines in Fig. 2(a) did for this compound. Presence of steric effect in 3,5-dimethyl-4-nitroaniline (point 1) with two Me groups *ortho* to the NO_2 group is also clearly indicated in Fig. 3(c) (also see Fig. 2(b)). Presence of steric effect in 2,6-dimethyl-4-nitroaniline is similarly indicated in both

Figs. 3(c) and 2(b). From σ correlations, we also find that in 2-methyl and 2,6-dimethylacetophenones there is likely to be twisting of the C–C bond as suspected earlier.[9] Other compounds which show similar effects are di-*ortho*-substituted alkyl phenols.

Lone pair PES bands of substituents. PES of organic molecules show characteristic, and often sharp, bands due to ionization of lone pair orbitals of hetero atoms.[2,24] The sharp PES bands due to ionization of halogen atom lone pairs in organic molecules is well documented.[2,25] PES bands due to lone pair orbitals of the C=O group in aliphatic ketones,[26] NO_2 group in nitroalkanes,[27] and NO group in nitrosoalkanes[28] have been correlated with Taft's σ^* constants[29] of alkyl substituents. We have now examined substituent effects on the PES bands due to the lone pair orbitals of various groups in benzene derivatives.

In Fig. 4, we have plotted the lone pair IE's of chloro and methoxy groups in *p*-substituted chlorobenzenes and anisoles respectively against the Hammett σ constants of the *p*-substituent. The plots are indeed linear with the IE increasing, as expected, with the increasing electron-withdrawing ability of the substituent. In Fig. 2(a) we saw that in dimethylanilines, the first IE varied linearly with σ constants; the first IE arises from the b_1 level which has considerable lone pair character.

In Fig. 4, we have also plotted the IE of the *n* orbital of the C=O group in *p*-substituted acetophenones against σ constants which again shows linearity and the expected trend. A similar behaviour is also exhibited by *p*-substituted benzaldehydes. The IE's corresponding to the $a_2(\pi)$ and $a_1(n)$ orbitals of the nitro group[1,27] in *p*-substituted nitrobenzenes also vary in proportion to the σ constants of the *p*-substituents. A similar trend has been noticed with *n* IE's of the NO group in nitrosobenzenes.[28]

We seem to find some evidence for steric effects of *ortho*-substituents on the lone pair IE's of substituents. Thus, 2,6-dimethylanisole (10 eV) and 2,6-dimethylnitrobenzene (10.9 eV) exhibit lower IE's due to *n* orbital ionization that predicted by the σ correlations in Fig. 4. Decrease in the interaction between the lone-pair orbital and the aromatic π system due to twisting of bonds would be expected to lower the IE of the lone pair orbital.

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