Tetrahedron. Vol. 25, pp. 3429 to 3440. Pergamon Press 1969. Printed in Great Britain

SOME ω TECHNIQUE CALCULATIONS ON THE VERTICAL IONIZATION POTENTIALS OF MONO- AND 1,4-DISUBSTITUTED BENZENES

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(Received in the UK 9 *December* 1968; *Accepted for publication* 24 *March* 1969*)*

Abstract—Some calculations on the effects of substituents on the vertical ionization potentials of mono- and 1,4-disubstituted benzenes are reported. The results support many of the conclusions of Baker *et al.* as to the origin of the ejected electrons. In particular, the splitting of the degenerate levels of benzene on substitution is satisfactorily reproduced.

RECENTLY Baker *et al.*[1] have published a large amount of data on the vertical ionization potentials of substituted benzenes obtained by photoelectron spectroscopy. One of us has already pointed out[2] the usefulness of such data in molecular structure calculations provided, of course, the experimental spectra can be correctly interpreted. In their paper Baker *et al.* have suggested that in a number of cases, particularly when the substituent is a halogen, the lowest ionization potentials correspond to the removal of the π electrons located largely on the benzene ring. In benzene the two highest π levels are degenerate (E_{1g}) but this degeneracy is removed on substitution. In the past calculations using the ω technique[3] have suggested that the splitting of this degeneracy is small. However, if the interpretation given by Baker *et al.*[1] is correct, then this is by no means the case. It seemed worthwhile therefore to see if the interpretation given by these authors could, in fact, be confirmed using a simple theoretical model that would retain the simplicity of their approach.

In the first part of this paper we consider how the ionization potentials as calculated on the basis of the ω technique depend on the relative magnitudes of the empirical parameters for systems of the type C_6H_5X and C_6H_5XY. In the former two electrons are contributed by X to the π electron system while in the latter one each from X and Y. We shall see that many of the spectral features discussed by Baker *et al.* can be understood on the basis of these curves. In the second part of the paper more detailed numerical calculations on the systems C_6H_5X and p-$C_6H_4X_2$, where X is now a halogen, are reported.

PART I

Theoretical model

The method used for calculating the ionization potentials in this paper is a modification of the so-called ω technique.[3, 4] This method has been used with considerable success—notably by Streitwieser[4, 5]—for the calculation of first ionization potentials of π electron systems. The essential feature of the ω technique as distinct from the well-known Hückel method is that the Coulomb integrals, α_i, are modified in the following way:

$$\alpha_i = \alpha_i^\circ - \omega\beta\delta q_i^\pi \tag{1}$$

where α_i° is the normal Coulomb integral,

β is the standard resonance integral,

δq_i^π is the excess (+) or deficiency (−) of π charge on the i'th atom brought about by the presence of the other atoms in the molecule,

and ω is a fixed numerical parameter.

As pointed out by Caldow and Coulson[3] one might also expect the Coulomb integrals to be dependent on the electron-donating or withdrawing power of neighbouring atoms transmitted through the sigma bonds. They suggested the following modification of (1) in order to account for this:

$$\alpha_i = \alpha_i^\circ - \omega\beta(\delta q_i^\pi + \delta q_i^\sigma) \tag{2}$$

where δq_i^σ is the excess or deficiency of charge on atom i brought about by the transmission of electrical effects through the sigma bonds. Caldow and Coulson assumed δq_i^σ to be the same in the molecule and the ion, an approximation that was not expected to be too serious for large π electron systems. It is probable that this assumption is less valid for the calculation of ionization potentials of electrons originally localized within restricted regions of the molecule; i.e. lone-pair electrons. Nevertheless, an examination of the experimental data[1] suggests that some account of inductive effects is necessary if, as happens in the halo-benzenes, one or both of the first two ionization potentials in the substituted benzene is greater than the first ionization potential of benzene. We have, therefore, used the above—admittedly crude—method of incorporating σ effects into our model for π electron systems. However, new methods of estimating the inductive parameters are required since the calculations of Caldow and Coulson on the halobenzenes seem to have badly underestimated the separation of the highest π levels in these molecules.

The method also allows us to calculate values for the lone-pair ionization potentials reported by Baker *et al.* for example, the lone-pair ionization potential for a substituent X, i.p.X) should be given by the expression:

$$\text{i.p.}(X) = E(X^+) - E(X) = \alpha_{X+} - 2\alpha_X \tag{3}$$

where α_{X+} is the Coulomb integral for X in the ion and α_X that in the molecule. Allowing for the variation of α_X with charge as given by Eq. (2) leads to the expression

$$\text{i.p.}(X) = -\alpha_X^\circ + \omega\beta + \omega\beta(2\delta q_X^\pi - \delta q_{X+}^\pi + \delta q_X^\sigma) \tag{4}$$

where δq_{X+}^π is the excess or deficiency of π charge on atom X in the positive ion.

In order to carry out numerical calculations on molecules of the form PhX using the above method it is necessary to obtain estimates of

(i) the standard Coulomb integrals α_C° and α_X°,
(ii) the standard resonance integrals β_{CC} and β_{CX},
(iii) the inductive parameters δq_{C-X}^σ and δq_{C-H}^σ, and
(iv) a value for ω.

Before giving these parameters specific values, however, it is of some interest to see how the various π ionization potentials in a substituted benzene, C_6H_5X, depend on their relative magnitudes.

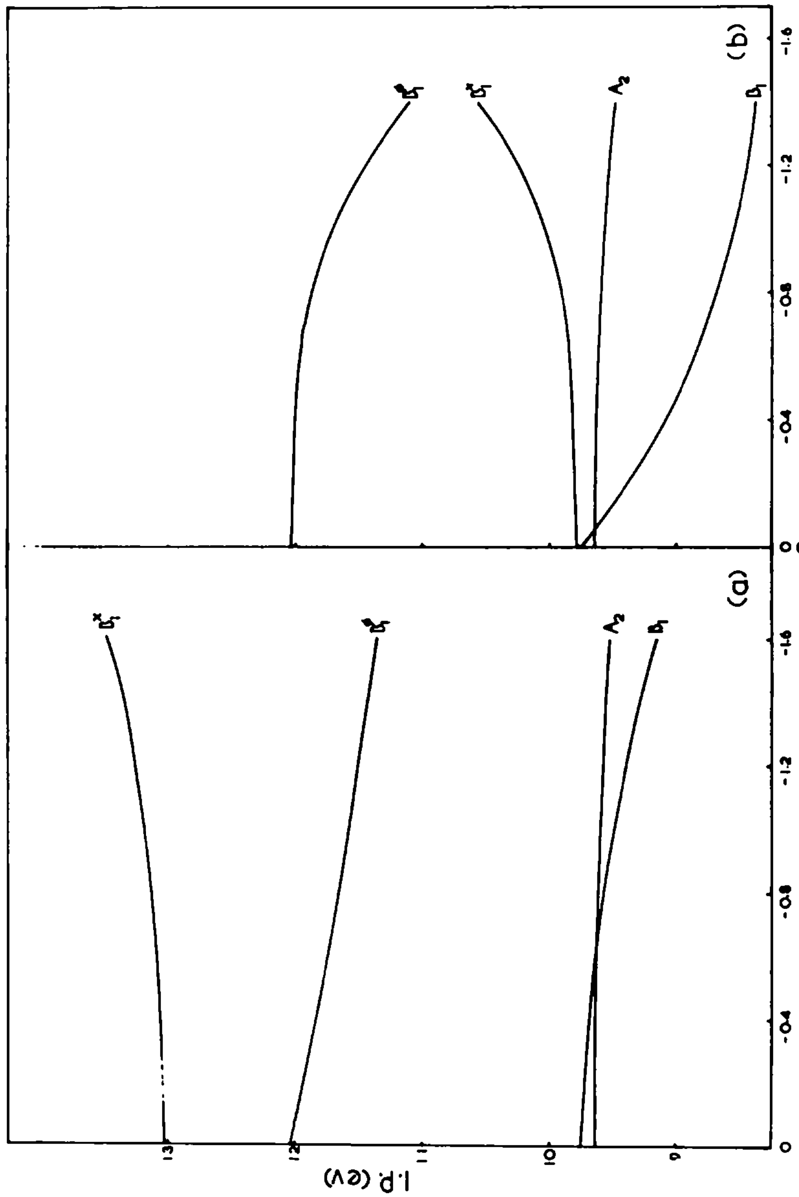

FIG. 1 The variation of orbital ionization potential with β_{CX} in C_6H_5X for : (a) $\alpha_X > \alpha_C + 2\,\beta_{CC}$; (b) $\alpha_C + 2\,\beta_{CC} > \alpha_X > \alpha_C + \beta_{CC}$.

In Figs. 1a and 1b we have plotted the ionization potential for each of the four occupied π levels in C_6H_5X as a function of β_{CX}, the resonance integral linking the substituent X to the benzene π system. Values of α°_{C}, β_{CC}, and $\omega\beta$ were determined from the ionization potential of the methyl radical and the first and second ip's. of benzene assuming that ionization from both levels corresponds to removal of $\frac{1}{6}$ of an electron from each C atom. This assumption is in keeping with our attempts to calculate vertical ionization potentials and with the results of various workers[6, 7] that the energy difference between the symmetrical and Jahn–Teller configurations of the benzene cation is small. The same sigma inductive parameter, δq^{σ}_{C-X}, was used in both sets of calculations: for convenience, the value of δq^{σ}_{C-Cl} previously used by Caldow and Coulson was selected as typical.

A number of conclusions which are of interest can be drawn from these ionization curves. For example, an examination of Figs. 1a and 1b shows that the ionization potentials of electrons from orbitals of B_1 symmetry are much more sensitive to variations in the resonance integral β_{CX} than those arising from the A_2 type orbital.* Indeed, the magnitude of the ionization potential of an electron from the latter orbital relative to the original E_{1g} benzene orbital is primarily determined by the inductive parameter δq^{σ}_{C-X}. It is also apparent that the sensitivity of the calculated ips. to variations in β_{CX} depends on the relative magnitudes of the Coulomb integrals; e.g. the smaller the energy difference $\alpha_C - \alpha_X$, the greater the interaction of the benzene ring with the substituent. This, of course, is a well-known result of the simple MO method.[8]

It is of some importance to note that the way the various ip's behave with increasing β_{CX} does not depend on the initial ordering of the energies (i.e. the order when $\beta_{CX} = 0$). We can compare directly, then, the variation of ionization potential with β_{CX} in the two situations. Thus, the ionization potentials of electrons in the A_2 and B_1 levels—corresponding to the originally degenerate E_{1g} levels in benzene—and the B_1 level corresponding to the benzene A_{2u} level all fall with increasing β_{CX}. On the other hand ionization from the B_1 orbital largely centered on the substituent X increases with increasing β_{CX}. For convenience we have indicated ionization from these levels in the following way: $e \leftarrow \psi_{B_1}$ and $e \leftarrow \psi_{A_2}$ indicating ionization from the originally degenerate benzene E_{1g} levels; $e \leftarrow \psi^{\phi}_{B_1}$ for ejection from the level corresponding to the A_{2u} level in benzene; and $e \leftarrow \psi^{X}_{B_1}$ for ionization originating essentially from the level associated with the substituent X. We have reserved the symbol $e \leftarrow \psi(X)$ to indicate ionization from lone-pair orbitals on X which do not possess the correct symmetry for conjugation with the π electrons of the benzene ring.

These curves allow us to predict with some confidence that when X = Cl, Br, I, NH_2, or OH the first i.p. refers to the ejection of an electron from a B_1 type orbital and the second to one in the A_2 orbital. This is because the first i.p. is always lower than the benzene value while the second is higher. Now in these molecules the inductive parameter raises both value above the benzene values with the B_1 the higher of the two. However, the latter falls rapidly with increasing β_{CX} while the A_2 ionization potential is relatively unaffected so that it is difficult to see how the A_2 value could fall below the benzene value without the B_1 ionization potential also doing so. As pointed out by Baker *et al.*,[1] the *p*-disubstituted molecules confirm this prediction since for the halogens, NH_2 and OH the first i.p. is lowered while the second is raised

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* Diagrams of these orbitals are given in Refs 1 and 3.

with respect to the monosubstituted benzenes and the splitting are remarkably additive.

Our curves also throw light on the effects on the first and second ionization potentials of changing the groups R and S in the series PhOR and PhNRS. Baker *et al.* have investigated the photoelectron spectra of a number of molecules in these series where R and S = H, Me, CMe_3 or CF_3. To a first approximation we can say that the main effect of changing R or S is to change the value of the Coulomb integral α_X in the derivation of our theoretical ionization potential curves since β_{CX} would be expected to remain relatively constant through each series. For example, we might expect the values of α_N to increase numerically through the series —NMe_2, —NHMe, —NH_2, and —$N(CF_3)_2$ because of the increasing inductive effect of the substituent groups attached to the N atom. However, from our curves we know that the greater the difference between α_X and α_C the less the effect on the A_2 and B_1 ionization potentials for a given β_{CX}. Consequently the ionization potentials of both these levels should increase as we go along each series but the change in the B_1 value will be greater than that in the A_2. The experimental results[1] support these conclusions. Thus the B_1 ionization potentials in the series C_6H_5NRS are predicted to be in the order —$N(CF_3)_2$ > —NH_2 > —NHMe > —NMe_2 and this is confirmed by the experimental order of 10·00, 8·04, 7·73, and 7·51. The same experimental order is predicted for the A_2 ionization potentials but the variation should not be so marked. The experimental results are 10·00, 9·11, 9·03, and 9·03.

There is one point where our interpretation through ionization curves throws light on an observation of Baker *et al.* These authors have noted that in the photoelectron spectra of both $PhOCF_3$ and $PhN(CF_3)_2$ only one band centered around 10 eV appears and have commented on the fact that even the strong inductive effect expected for such substituents does not appear to split the degeneracy of the benzene levels. On the basis of our model the explanation would seem to lie in the fact that the inductive effect raises both the A_2 and B_1 levels above the benzene value with the B_1 level the higher of the two. But this level falls more rapidly with β_{CX} (mesomeric effect) so that the two ionization potential curves eventually cross. Thus in these molecules we appear to be observing a crossing—or near crossing—point of the A_2 and B_1 ionization potential curves as illustrated in Figs. 1a and 1b.

We have constructed similar curves for molecules of the type PhXY. Examples of these systems studied by Baker *et al.* are PhCHO, PhCN, and PhNO. Hyperconjugation models of $PhCH_3$ and $PhCF_3$ are also covered by these curves. The characteristic feature of the spectra of these systems is the apparent absence of any significant splitting of the highest π level of the benzene ring.

Unfortunately the interpretation of ionization potential curves is more difficult in this model because of the additional parameters involved in the construction of the curves. Thus the ionization potentials would now be expected to be functions of α_X, α_Y, β_{CX}, β_{XY}, δq^{σ}_{C-X}, and δq^{σ}_{X-Y}. We have constructed curves to study the effects of all these factors but Figs. 2a and 2b illustrate some results for $\alpha_X = \alpha_C$ since several of the molecules studied experimentally involve C as the atom directly attached to the benzene rings. Thus in Fig. 2a we have plotted ionization potential curves as a function of β_{CX} with α_Y and β_{XY} such that $e \leftarrow \psi^{XY}_{B_1}$ is greater than $e \leftarrow \psi^{\phi}_{B_1}$ while in Fig. 2b we have plotted ionization potential curves as a function of β_{XY} for constant values of β_{CX}, α_X, and α_Y.

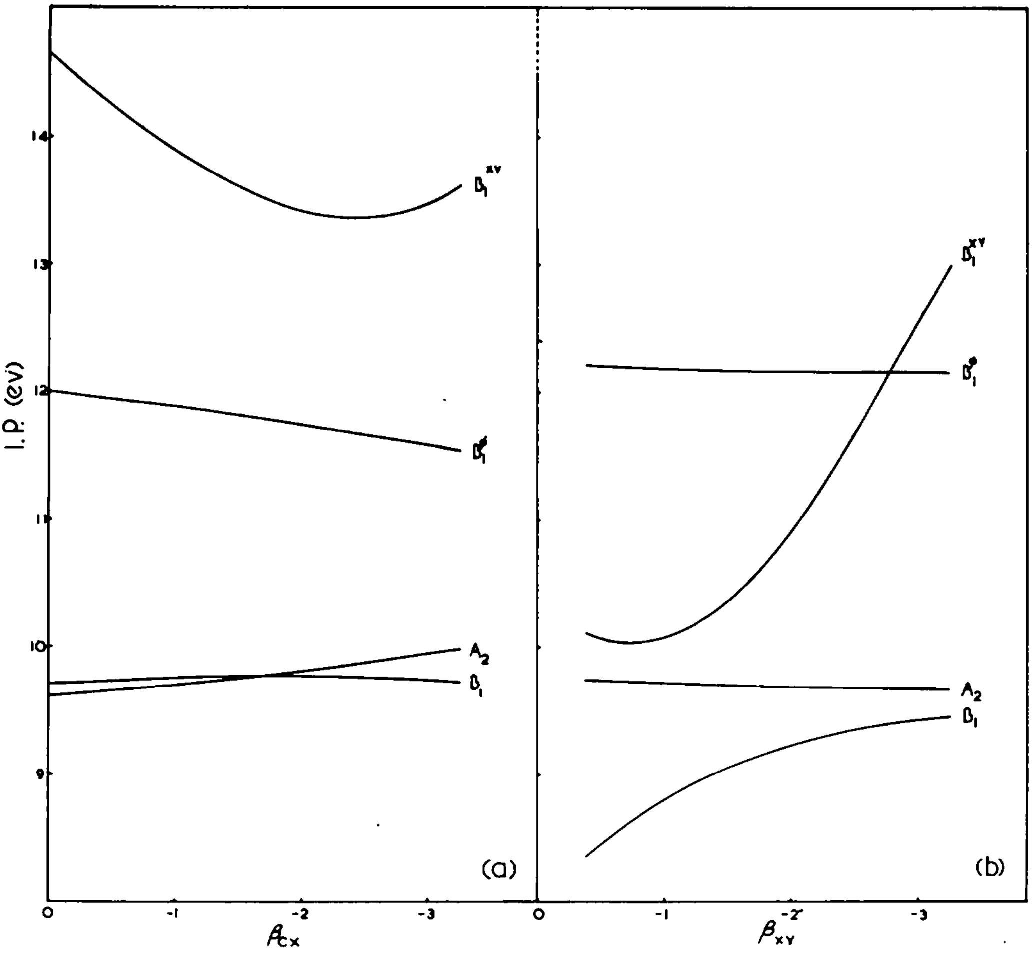

FIG. 2 The variation of orbital ionization potential in C_6H_5XY with: (a) β_{CX}; (b) β_{XY}.

The pattern of the ionization potentials illustrated in Fig. 2a is probably characteristic of such molecules as benzaldehyde and benzonitrile. We know, for example, that the π ionization potential of formaldehyde is considerably larger than the second π ionization potential in benzene.[9] In addition this behaviour does not change in character through wide variations in the inductive parameters, δq^{σ}_{C-X} and δq^{σ}_{X-Y}. It is not surprising then that the lowest π i.p's appear only as one broad band for these molecules. For not only do the A_2 and B_1 curves cross but neither of these ionization potentials seems to be particularly sensitive to changes in β_{CX}.

In Fig. 2b we have illustrated the variation of these ionization potentials as a function of β_{XY}. This Fig. shows that when the X–Y level lies between the two benzene π levels then considerable splitting of the A_2–B_1 levels can occur, particularly for small values of β_{XY}.

It is possible that such a situation occurs in PhNO. The measurements of Baker *et al.* indicate an ionization potential at 8·87 eV in addition to an intense band centered near 9·97 eV. Baker *et al.* have suggested that this ionization potential results from ejection of a π electron from the NO group. Our curves suggest that this is unlikely, particularly as the π level of the NO fragment might be expected to lie even lower than that of the CHO group in benzaldehyde. Another possible interpretation is that the 8·87 i.p. is in fact due to the ejection of an oxygen lone-pair electron. Introduction of chlorine into the *para* position of nitrosobenzene increases this i.p. to 9·02 eV. The inductive effect associated with the Cl atom could account for the increase in i.p. if these electrons were essentially lone-pair electrons on the O atom. On the other hand if these electrons were ejected from either a B_1 or $B_1^{N=O}$ orbital then this ionization potential would be expected to fall. This appears to occur, for example, in the analogous aldehyde situation where the i.p. of the B_1 orbital falls from around 9·80 eV in PhCHO to close to 9·6 eV in the *p*-chloro derivative. We conclude, therefore that PhCHO, PhCH, and PhNO all probably belong to the situation illustrated in Fig. 2a (i.e. energy XY > energy A_{2u} of benzene).

PART 2

Numerical calculations

In this section we present more detailed calculations on the mono- and di-substituted halogen benzenes. Two approaches to the problem have been adopted: in the first the integrals are derived purely empirically while in the second use is made of valance state ionization potential data for estimating some of the integrals.

(a) *Empirical approach.* α_C, β_{CC}, and ω were derived from the first and second vertical ionization potentials of benzene[10] and from the ionization potential of the Me radical.[11] In this derivation we are also obliged to assume a value of δq^{σ}_{C-H}; for convenience—and for want of anything better—we have chosen the value previously used.[3]

The inductive parameters, δq^{σ}_{C-X}, were derived by noting that the ionization potential of the A_2 level in both C_6H_5X and 1,4-$C_6H_4X_2$ is determined primarily by the inductive parameter (see Figs 1a and 1b). Consequently, ionization potential curves were constructed for benzene in which either C atom 1 or C atoms 1 and 4 were modified over a wide range of inductive parameters. Since the actual values of the A_2 i.p's are expected to fall slightly with increasing β_{CX}, these curves provided a means of assessing a lower limit to the inductive parameters required to fit both the mono- and disubstituted halobenzenes.

The standard Coulomb integrals for the halogens, α°_{X}, were derived from the first ionization potentials of the corresponding methyl halides. The following assumptions are implicit in this derivation:

(i) that the ionized electron is essentially a lone-pair electron on the halogen atom. This is almost certainly true of X = Cl, Br, or I but doubtful for X = F;
(ii) that no significant hyperconjugative effects are operating in either the molecule or the ion; and
(iii) that the inductive parameter for a halogen attached to a sp^3 C atom does not differ significantly from that of a sp^2 carbon.

It is difficult to assess how serious these assumptions are likely to be. But this approach seemed preferable to that adopted by Caldow and Coulson[3] since no estimate of δq_{X-H} is now required.

Finally the β_{C-X} were obtained by fitting the calculated first ionization potentials

($e \leftarrow \psi_{B_1}$) with the experimental values of the monosubstituted halobenzenes. For X = F the first ionization potential of 1,4-difluorobenzene was used since the exact magnitude of the first ionization potential in fluorobenzene is somewhat uncertain. The actual numerical values of all these parameters are collected together in Table 1.

TABLE 1. PARAMETER VALUES IN eV USED IN THE CALCULATION OF IONIZATION POTENTIALS FOR HALOGEN-SUBSTITUTED BENZENES

Parameter	Ref. 3	Present (empirical)	Present (valence state)
$\omega\beta$	−5·666	−4·336	−4·804
α_C°	−11·135	−10·832	−11·420
α_F°	−23·896	−21·622	−22·864
α_{Cl}°	−19·381	−17·897	−18·164
α_{Br}°	−18·017	−16·827	−16·984
α_I°	—	−15·524	−15·654
β_{CC}	−2·79	−2·51	−2·51
β_{CF}	−1·88	−2·3	−2·21
β_{CCl}	−0·95	−1·2	−1·15
β_{CBr}	−0·70	−0·8	−0·82
β_{CI}	—	−0·62	−0·66
$\omega\beta q_{C—H}$	−0·431	−0·329	−0·526
$\omega\beta q_{C—F}$	1·808	3·686	4·434
$\omega\beta q_{C—Cl}$	0·504	2·341	2·083
$\omega\beta q_{C—Br}$	0·289	1·951	1·493
$\omega\beta q_{C—I}$	—	1·648	1·192

Also included in the Table 1 are the values previously used.[3] The most significant difference between the two sets of parameters lies, as expected in the magnitudes of the carbon–halogen inductive parameters.

(b) *Parameters derived from valence-state potentials.* By definition, the Coulomb integral, α_X, is given by

$$\alpha_X = \int \phi_X^* H_{\text{eff}} \phi_X \, d\tau \tag{5}$$

where H_{eff} is the so-called "effective" Hamiltonian for the system. In the neighbourhood of atom X the largest contributions to H_{eff} would be expected to arise from the potential of the other electrons associated with X and the nuclear charge Z_X. It is reasonable to suggest, therefore, that α_X is closely related to the ionization potential of an electron in the appropriate valence-state of the atom X in the molecule in question. This hypothesis is confirmed when we compare our empirical values of our standard Coulomb integrals, α_X°, with those obtained from the valence-state i.p. data of Skinner and Pritchard.[12] Thus within the framework of the ω technique, the valence-state ionization potential (v.s.i.p.) for a halogen atom contributing two p-type electrons to the π system is given by

$$\begin{aligned} \text{v.s.i.p.} &= E^+\,(\text{atom}) - E\,(\text{atom}) \\ &= \alpha_X^\circ - \omega\beta\delta q_{X^+}^* - 2\alpha_X^\circ \\ &= -\alpha_X^\circ + \omega\beta \end{aligned} \tag{6}$$

On the other hand for an atom contributing only one π electron to the MO then v.s.i.p. $= \alpha_X^\circ$ since there are no π-type electrons in the ion.

It is also possible to use valence-state ionization potential data in order to estimate the inductive parameters δq_{C-X}^σ. For if we assume that the experimental designation of the lone pair ionization potentials of Baker *et al.* is correct then their magnitudes are given by Eqn 4. Since for the halogens δq_X^π and $\delta q_{X^+}^\pi$ are calculated to be small by our previous method, then to a first approximation

$$\omega\beta\delta q_X^\sigma = \text{lone-pair i.p.} + \alpha_X^\circ - \omega\beta \qquad (7)$$

We can then determine β_{CX} as before by fitting to the first ionization potential of the monosubstituted benzene. The method can be made self-consistent since we can now calculate $\omega\beta\delta q_X^\pi$ and $\omega\beta\delta q_{X+}^\sigma$ and thus by Eq. 4 arrive at a new estimate of $\omega\beta\delta q_X^\sigma$. The cycle of calculations is repeated until the calculated lone-pair ionization potential agrees with the experimental value—usually two or three iterations.

The values of all the parameters based on the present approach are collected together in Table 1. As before, β and $\omega\beta$ were derived from the first and second ionization potentials of benzene while $\omega\beta q_{C-H}^\sigma$ was derived from the ionization potential of the methyl radical. It is interesting to compare the present parameters with those derived empirically. The agreement is remarkable considering the differences in approach. The most significant changes occur for α_F° and $\omega\beta q_{C-F}^\sigma$ but we have already suggested that the empirical parameters for fluorine are somewhat suspect.

RESULTS AND DISCUSSION

The calculated ionization potentials for the mono- and disubstituted halobenzenes using our two sets of parameters are given in Table 2. These are given as the π energy of the ion minus the π energy of the molecule. Also included in the Table are the lone-pair ionization potentials calculated from Eq. 4.

The experimental results reported in Table 2 are with one or two exceptions[10, 13] those given by Baker *et al.*[1] These have been assigned following the arguments of Baker *et al.* and those outlined in Part 1 of this paper. As mentioned earlier, a number of experimental values are required for fitting the parameters; these are indicated in the Table by an asterisk. An examination of the Table shows that both sets of parameters lead to substantially the same calculated ionization potentials. The two sets of results will, therefore be considered together.

For purposes of discussion it is convenient to examine first the $e \leftarrow \psi_{B_1}$ and $e \leftarrow \psi_2{}^A$ ionization potentials as a group since the experimental assignment of these is probably the most straightforward and reliable (see, however, Ref 14). In calculation 1 the monosubstituted values have mainly been used for fixing the parameters. However, the use of these parameters in calculations on the disubstituted benzenes leads to satisfactory agreement with experiment and supports the conclusions of Baker *et al.* as to the origin of these ionization potentials. The results of calculation 2 for the A_2 level are particularly gratifying since for these calculations the experimental $e \leftarrow \psi_{A_2}$ values are not used in the derivation of the parameters.

Baker *et al.* have also suggested assignments for the lone-pair ionization potentials in the spectra of the halobenzenes. These are indicated in Table 2 together with our calculated values. The agreement with experiment for calculation 1 is perhaps un-

TABLE 2. CALCULATED IONIZATION POTENTIALS FOR HALOGEN-SUBSTITUTED BENZENES

(a) C_6H_5X

	X = I			Br			Cl			F		
$e \leftarrow \psi$	Expt.	Calc. 1	Calc. 2	Expt.	Calc. 1	Calc. 2	Expt.	Calc. 1	Calc. 2	Expt.	Calc. 1	Calc. 2
ψ_{B_1}	8·78	8·78*	8·78*	9·25	9·26*	9·25*	9·31	9·30*	9·31*	(9·58)	9·58*	9·77
ψ_{A_2}	9·75	9·75*	9·73	9·78	9·78*	9·76	9·71	9·79	9·80	9·86	9·86*	9·99
$\psi(X)$	10·59	9·61	9·74*	10·78	10·62	10·77*	11·42	11·36	11·41*	13·86†	13·86	13·88*
$\psi_{B_1}^{X}$	11·70	9·68	9·81	11·36	10·73	10·87	11·76	11·58	11·56		14·49	14·45
$\psi_{B_1}^{\phi}$	12·44	12·22	12·13	12·2	12·01	10·28	12·35	10·61	10·62	≥11·8	11·36	11·27

(b) p-C_6H_4XY

	X = Br, Y = Cl			X = Cl, Y = F		
$e \leftarrow \psi$	Expt.	Calc. 1	Calc. 2	Expt.	Calc. 1	Calc. 2
ψ_{B_1}	9·04	8·78	8·79	9·26	9·06	9·11
ψ_{A_2}	9·96	9·99	9·98	10·07	10·06	10·19
$\psi(X)$	10·79	10·63	10·79	11·77	11·40	11·46
$\psi_{B_1}^{X}$	11·07	10·74	10·88	11·77	11·61	11·64
$\psi(Y)$	11·07	11·38	11·43		13·90	13·92
ψ_{B}^{Y}	11·54	11·61	11·61		14·53	14·49
$\psi_{B_1}^{\phi}$	≥12	10·65	9·34	≥12·3	10·24	10·16

(c) 1,4-$C_6H_4X_2$

	X = Br			Cl			F		
$e \leftarrow \psi$	Expt.	Calc. 1	Calc. 2	Expt.	Calc. 1	Calc. 2	Expt.	Calc. 1	Calc. 2
ψ_{B_1} (B_{2g})	8·97	8·72	8·74	9·17	8·35	8·84	9·50	9·33	9·49*
ψ_{A_2} (B_{3g})	9·95	9·98	9·94	10·01	10·00*	10·01	10·24	10·12	10·36
$\psi(X)$	10·66	10·63	10·79	11·57	11·38	11·44	13·84	13·89	13·95
$\psi_{B_1}^{X}$	10·91	10·74	10·88	11·57	11·61	11·62		14·55	14·53
$\psi_{B_1}^{\phi}$	≥11·9	12·44	12·19	≥12·7	11·39	9·63	12·72	11·00	11·04

* used in deriving parameters.　　† high resolution spectra.[13]

expected in view of the assumptions inherent in the derivation of the halogen Coulomb integrals. There is, however, serious disagreement for the lone-pair ionization potential of iodobenzene where our calculations suggest that this i.p. lies in the same region as the A_2 level. This result is not unreasonable since the latter band at 9·75 eV is by far the most intense in the spectrum. This conclusion is confirmed by the results of calculation 2 for if one assumes that the 10·59 eV value corresponds to a lone-pair ionization potential from the I atom then Eq. 4 leads to an inductive parameter considerably larger than that calculated for Br or Cl.*

The agreement of the calculated $e \leftarrow \psi^{X}_{B_1}$ i.p's with experiment is not quite so satisfactory. Indeed, Baker *et al.* have suggested that the difference between the energy of this level and that of the lone-pair electrons increases through the series PhX for X = F, Cl, Br or I. However, our calculations suggest that this splitting should decrease down the halogen series since the calculated splitting depends primarily on the magnitude of the resonance integral, β_{CX}. In fact, in some cases the splitting is calculated to be so small that if the results have any significance whatsoever then they suggest that experimentally the two ionization potentials may not be resolved. Thus the three ionization potentials observed in the region 10·7–11·6 eV for *p*-bromochlorobenzene may actually arise from ionization from the four different levels.

Finally we can compare the calculated and experimental ionization potentials in situations where the electron comes from an orbital similar to the A_{2u} orbital in benzene; i.e. $e \leftarrow \psi^{\phi}_{B_1}$. With the exception of iodo- and bromobenzene and of *p*-dibromobenzene the results here are far from encouraging. On the other hand it is not difficult to discover the reason for the disagreement: it arises in those cases where the value of the Coulomb integral α_X—modified by the appropriate inductive parameter—is similar in magnitude to the energy of the A_{2u} level in benzene; i.e. when $\alpha_X \simeq \alpha_C + 2\beta_{CC}$, either in the molecule or the ion. Indeed, one of the most striking results of calculation 2 is the enormous effect of relatively small changes of parameters on the calculated $e \leftarrow \psi^{\phi}_{B_1}$ ionization potential particularly in the case of bromobenzene and 1,4-bromochlorobenzene. As the order of levels in 1,4-dibromobenzene is not changed from calculation 1, this illustrates how sensitive ionization from this level seems to be to our choice of parameters.

To some extent, these results support the observations of Baker *et al.* who note that the behaviour of this level on substitution is difficult to interpret in terms of the inductive and mesomeric effects of the substituents. However, another possible reason for this disagreement should be borne in mind and that is that the 11·91 i.p. which we have used as the value for the A_{2u} π level in benzene arises, in fact, from ionization of a sigma electron. A number of theoretical studies[15–17] have suggested that one or more σ levels lie between the π levels in benzene and recently it has been suggested[18] from an examination of electron impact and photoelectron results that the 12·1 i.p. in the photoelectron spectrum of benzene corresponds to ionization from the 2nd π level. The use of this value not only would lead to quite different results for our calculated ionization potentials in this region, but also might require a re-interpretation of the experimental assignments.

In the preceding section we have shown that both a completely empirical approach

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* Recent high resolution results support this prediction (D. W. Turner, *Chemistry in Britain* 4, 435 (1968).

and the use of valence-state ionization potential data leads to parameters which give a fairly satisfactory account of the experimental ionization potentials in the halogen substituted benzenes. It is worthwhile enquiring at this stage whether these methods can be extended to other substituents such as —NH_2, —OH, etc. It turns out that there are difficulties associated with both approaches. Thus, in the empirical procedure it is no longer possible to estimate the inductive parameters from the values of second ionization potentials since β_{CX} is no longer likely to be small. Nor is the valence-state approach applicable in these molecules since, in general, there are no p type lone pair ionization potentials from which to estimate δq^{σ}_{C-X} through the use of Eq. 7. It seems unlikely therefore whether the scope of the present calculations can be significantly extended.

Our main conclusions, then, from this study on the ionization potentials in substituted benzenes are:

(i) that the general features of the photoelectron spectra of substituted benzenes of the form PhX or PhXY can be understood on the basis of a simple MO model incorporating inductive effects;
(ii) that a set of parameters can be obtained which satisfactorily reproduce the observed splittings of the two highest occupied π levels in the halogen-substituted benzenes; and
(iii) that ionization from the π level corresponding to the A_{2u} level in benzene is extremely sensitive to the choice of parameters and therefore should provide a severe test for molecular wavefunctions.

Acknowledgements—The authors are grateful to Dr. D. W. Turner for useful discussions and for providing us with photoelectron spectra prior to publication. One of us (G.F.S.H.) acknowledges receipt of a Nigerian Federal Government Post-Graduate Scholarship.

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