Analysis of the Electronic Factors Controlling the N_{1s} and the First two $\pi(a_2, b_1)$ Photoelectron Ionizations in N-Containing Monosubstituted Benzenes (Ph—NRR′ and Ph—N=X)

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The first two $\pi(a_2, b_1)$ IE's of monosubstituted benzenes containing di- and tri-coordinated nitrogen directly linked to the ring have been measured and analysed together with the N_{1s} IE. These photoelectron properties are found to respond in the same sense, though to different extents, to inductive and mesomeric interactions that the N-containing substituents sustain with the aromatic ring. The different sensitivities of these properties to substituent changes are discussed in connection with mechanisms of transmission of electronic effects with the aid of the ground state electronic structures determined by means of ab-initio calculations. The relative contribution of the relaxation energy to the considered core and valence IE's is also examined by referring to the model used by Gelius and Siegbahn. The factors determining the apparently anomalous behaviour of nitrobenzene are discussed.

Introduction

The π valence ionization energies (IE_v) of monosubstituted benzenes are quite suitable for distiguishing between the inductive (I) and the mesomeric (M) effects exerted by the substituents [1, 2]. Also, the core ionization energy (IE_c) of a given atom within a series of congener molecules correlates linearly, to a first approximation, with the atomic charge [3] reflecting the I and M [4] effects upon the given atom. (The importance of excited state or relaxation effects on this observable has also been discussed [5].)

Inasmuch as both the IE_v's and IE_c's of aromatic systems reflect the combined action of the mesomeric and polar interactions, these observables are expected to be in some way correlated within series of related molecules as has been found, for instance, in ionizations localized at the heteroatom in alkyl iodides [6], alcohols and amines [7–10].

In this work, using UPS and XPS data and ab-initio STO-3G calculations, attention is focused on monosubstituted benzenes containing di- and tri-coordinated nitrogen directly linked to the ring of the Ph–NRR′, and Ph–N=X type, with R, R' and X groups covering different bonding situations, with the primary aim of rationalizing in terms of electronic factors the behaviour of the IE_v's associated with the $\pi(a_2)$ and outermost $\pi(b_1)$ MO's and of the $IE_c(N_{1s})$ orbital along and between these two series of molecules.

Experimental and Calculations

The X-ray photoelectron spectra were recorded on an AEI ES200B electron spectrometer using Al K_α radiation. The samples were sublimed in vacuo onto a cooled Cu surface before and during the measurements. Calibration of the N_{1s} signals was achived by measuring the distance between the N_{1s} peak and the main C_{1s} line of the same compound assuming for the latter a constant reference value of 285.0 eV. The reproducibility of the XPS IE_c values was ±0.1 eV. Although the absolute values of the reported N_{1s} IE_c's may be in error by as much as 1 eV or more, the relative error along the series of investigated compounds should not exceed ±0.3 eV. Indeed, in order to have an independent check on the reliability of the N_{1s} values, pairs of

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samples, when possible, were sublimed simultaneously and the energy gap between the two N_{1s} lines measured. The energy separations (ΔN_{1s}) so obtained agreed within ±0.2 eV with those obtained from calibration with the C_{1s} lines.

Rather intense shake-up peaks were observed in the O_{1s} and N_{1s} energy region of nitrosobenzene (their main features have been discussed elsewhere [11].

The ultraviolet photoelectron spectra (UPS) of several of the investigated compounds were already available in the literature. The spectra of all the compounds were however recorded again in order to have a mutually consistent set of data available. These spectra were assigned by analogy with those previously published and, in some cases, with the aid of further data obtained by inserting into the ring of the compounds one halogen and/or one methyl group. The error of the IE_v values is estimated to be ±0.05 eV.

Ab-initio calculations were performed using the Gaussian-70 package of Hehre et al. [12] and the STO-3 G basis set. Unfortunately, convergence difficulties were encountered for Ph – NSC and Ph – NSO which could not be circumvented by changing the geometrical model. Experimental geometries were used where these were known [13], in other cases geometries were estimated from standard bond lengths and angles [14].

The experimental and theoretical $IE_c(N_{1s})$ and $IE_v(\pi a_2, \pi b_1)$ are reported in Table 1 and the experimental data are diagrammed in Fig. 1, where different scales are used to take into account in some way, the different accuracy of the relevant inner shell and valence IE's. (The experimental data for Ph – $NHCH_3$ have been taken from the literature [15].

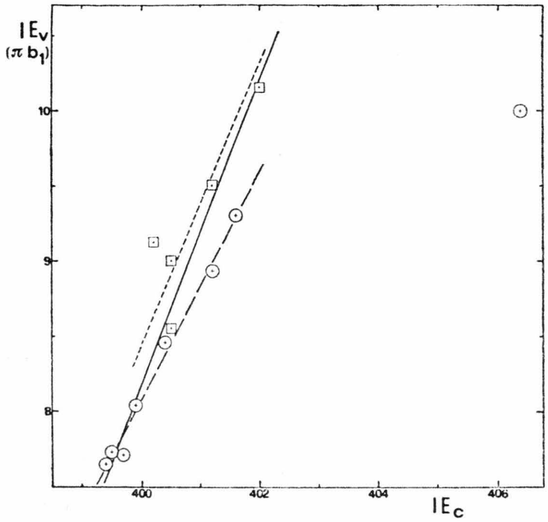

Fig. 1a. Regression of the $IE_v(\pi(b_1))$ on the $IE_c(N_{1s})$ (in eV): dotted line for the Ph–N=X series; dashed line for the Ph–NRR′ series; full line for both series.

Table 1. Experimental and theoretical $IE(N_{1s})$, $IE(\pi(a_2))$ and $IE(\pi(b_1))$ (in eV), σ and π net charges on the N atom and the σ and π charge transfers from the substituent to the ring.

Compound		Experiment			Theory						
		$IE(b_1)$	$IE(a_2)$	$IE(N_{1s})$	$IE(b_1)$[a]	$IE(a_2)$[a]	$IE(N_{1s})$[a]	Q_σ	Q_π	ΔQ_σ	ΔQ_π
1	Ph–NH_2	8.04	9.12	399.9	6.17	7.53	417.18	– 0.647	0.224	0.272	– 0.224
2	–$NHCH_3$	7.65[b]	9.03[b]	399.4[b]	5.73	7.43	417.06	– 0.505	0.148	0.158	– 0.127
3	–$N(CH_3)_2$	7.73	8.98	399.5	5.53	7.40	417.17	– 0.467	0.177	0.156	– 0.134
4	–$NCH_3Si(CH_3)_3$	7.71	9.04	399.7	5.58	7.38	415.82	– 0.665	0.193	0.129	– 0.130
5	–$NHCOCH_3$	8.46	9.35	400.4	6.29	7.56	418.39	– 0.603	0.240	0.184	– 0.080
6	–$NHCOCF_3$	8.93	9.64	401.2	6.64	7.79	418.98	– 0.611	0.251	0.199	– 0.073
7	–NCH_3NO_2	9.30	9.73	401.5	6.82	7.94	419.78	– 0.806	0.602	0.216	– 0.076
8	–NO_2	10.00	10.35	406.4	8.57	8.43	426.26	– 0.599	0.777	0.215	0.019
	–NHOH			(401.4)[c]	5.93	7.56	418.47	– 0.381	0.124	0.145	– 0.090
	–$NHNH_2$			(401.1)[c]	5.80	7.32	417.81	– 0.416	0.127	0.175	– 0.116
	–NHF			(401.5)[c]	6.03	7.66	418.90	– 0.364	0.117	0.192	– 0.122
9	Ph–NCO	9.00	9.62	400.5	6.69	7.95	417.82	0.085	– 0.434	0.207	– 0.053
10	–NCS	8.55	9.65	400.5							
11	–NSO	9.12	9.65	400.2							
12	–NO	10.15	9.84	402.0	7.97	8.06	420.45	– 0.088	0.055	0.102	0.031
13	–NC	9.50	10.03	401.2	7.86	8.25	418.68	0.045	– 0.380	0.244	– 0.016
	–NNH			(402.3)[c]	7.51	7.83	418.90	– 0.153	0.017	0.140	0.026

[a] Koopman's theorem. [b] Taken from Ref. [15]. [c] Value obtained from Equation (2).

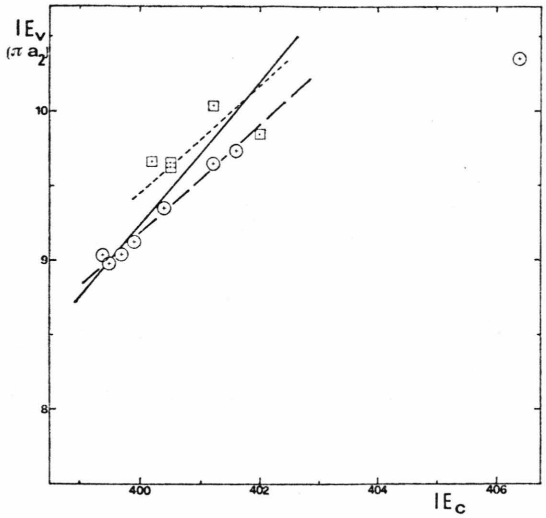

Fig. 1b. Regression of the $IE_v(\pi(a_2))$ on the $IE_c(N_{1s})$ (in eV): dotted line for the Pn—N=X series; dashed line for the Ph—NRR′ series; full line for both series.

Discussion

Relative Sensitivities of IE_c and IE_v ($\pi\, a_2$ and $\pi\, b_1$) to Substituent Effects

Perusal of Table 1 and Fig. 1 reveals that there is some correlation between IE_c's and IE_v's. Considering all compounds but Ph – NO_2* we found for the shifts:

$$\Delta IE_c \approx \Delta IE_v(b_1) \text{ and } \Delta IE_c \approx 2 \cdot \Delta IE_v(a_2)$$

over a range of 2.6 eV for IE_c, 2.5 eV for $IE_v(b_1)$ and 1.1 eV for $IE_v(a_2)$. For both the two distinct series Ph – NRR′ and Ph – N = X we found instead: $\Delta IE_c \approx 1.2 \cdot \Delta IE_v(b_1)$ and $\Delta IE_c \approx 2.8 \cdot \Delta IE_v(a_2)$. These results are then evidence that IE_c is more sensitive than IE_v's, and $IE_v(b_1)$ more than $IE_v(a_2)$, to change of substituent linked to nitrogen **. The different response of IE_c and IE_v's to substitution can be rationalized by the following arguments. IE_c is associated with the creation of a positive hole localized at a precise atomic site in the molecule and so is strongly and directly dependent on the nature of the substituents linked to nitrogen. Change of substituent causes an alteration of the average potential at the nucleus mainly by *I* effects (in the neutral molecular state) and by polarization effects (in the final ionic state). The IE_v's(π) refer instead to electron ejection from delocalized MO's. In particular, $IE_v(b_1)$ is influenced by the *I* effect of the N-substituents as well as by changes in the hybridization of N and by M effects, and $IE_v(a_2)$ is sensitive essentially to the *I* mechanism [1, 2].

However, experimental evidence shows that the inductive effect of the N-substituents is not the only cause of the IE_c and $IE_v(a_2)$ shifts. Firstly, because the Ph – NH_2, – $NHCH_3$, – $N(CH_3)_2$ and – $NCH_3Si(CH_3)_3$ derivatives exhibit lower $IE_v(a_2)$ than that (9.24 eV) of Ph – H, despite their – NRR′ group electronegativities (and so *I* effects) are greater than that of the H atom. Secondly, because all the – NRR′ substituents have electronegativities in the comparatively small range from ~3.0 (– NH_2) to ~3.4 (NO_2) [19] which does not account for the ~7(~1.4) eV range of the IE_c ($IE_v(a_2)$) shifts and also for the apparently anomalous point occupied by Ph – NO_2 in the diagrams.

Ab-initio MO calculations on the ground state of the investigated compounds were carried out and the charge distributions used to gain some information concerning the relative importance of the *I* and *M* effects on the core and valence ionizations.

Substituent Effects on $IE_v(\pi(a_2))$

Because of its nodal properties the $\pi\, a_2$ MO can not interact mesomerically with the substituent and therefore, its variations depend mainly upon polar interactions. In particular, the direction of the inductive effect is provided by $\Delta Q(\Delta Q_\sigma + \Delta Q_\pi$, see Table 1), which is the net electron density exchanged between the substituent and the benzene ring. All the present substituents are net electron withdrawing, ranging from ~0 (– $NCH_3Si(CH_3)_3$) to 0.23 (– NO_2) units of electron density, so this MO experimences an overall stabilizing effect. Since the *I* effect includes both σ and π contributions to changes in electron distribution, $I = I_\sigma + I_\pi$, some

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* In Ph-NO_2 the participation of the outermost π orbital of the NO_2 group to the outermost "benzenic" b_1 MO is very limited [16], so this MO is not mixed with the N_π lone pair MO. For this reason Ph-NO_2 can not be considered a "normal" member in the series of the compounds investigated and lies, indeed, apart in the diagrams of Figure 1. In addition, the large difference in the field effect exerted by the NRR′ and NO_2 substituents [17] could be, at least in part, responsible for the behaviour of nitrobenzene, along with differences in the electronic relaxation accompanying ionization [18].

** In NH_3 and its Me-derivatives the IE_v (*N*, lone pair) shifts about three times faster than the $IE_c(N_{1s})$ [7, 8, 10]. (A similar behaviour has also been observed in some tervalent phosphorus compounds [18].) The lower IE_v sensitivity of the present compounds is probably related to the sizeably higher delocalization of the uppermost π MO's with respect to the *N* lone pair of amonia.

interesting features emerge if the theoretical* energies ε_i are fitted to an equation of the form: $\varepsilon_i^{\text{th}} = A\,\Delta Q_\sigma + B\,\Delta Q_\pi + C$. The values of the coefficients, which determine the direction and magnitude of the relevant calculated I effects of the substituents, obtained by a least-squares procedure on the ΔQ_i values of compounds 1 – 13 reported in Table 1 are as follows:

$$\varepsilon_i^{\text{th}} = 3.738\,\Delta Q_\sigma + 4.621\,\Delta Q_\pi + 7.448\,(\text{eV}) \quad (1)$$

(s. d. = 0.09 eV). These coefficients together with the ΔQ_i values indicate that opposing the $-I_\sigma$ stabilizing effect is a $+I_\pi$ destabilizing effect, which, ΔQ_i being equal, is more effective than the former. Therefore, according to this theoretical picture the large ΔIE_{v} beetween $-\text{NH}_2$ and $-\text{NO}_2$ derivatives must be associated mainly with the different role of the I_π mechanism. Also the constantly higher IE_{v}'s exhibited by the members of the $\text{Ph}-\text{N}=\text{X}$ series with respect to the $\text{Ph}-\text{NRR}'$ series (with the exception of $\text{Ph}-\text{NO}_2$) may be related to the fact that the $-\text{N}=\text{X}$ substituents affect the $\pi(a_2)$MO primarily by I_σ effect, the I_π effect playing a secondary role.

Substituent Effects on $IE_c(N_{1s})$

In order to account for the way in which $IE_{\text{C}}(N_{1s})$ is influenced by the I and M effects, an analysis according to the charge potential model [3] is relevant**. A correlation has therefore been made with the net Q_σ and Q_π charges carried by the N atom (Table 1): $IE_{\text{exp}} = A\,Q_\sigma + B\,Q_\pi + C \cdot Q_{\text{M}} + D$, where Q_{M} is the intramolecular Madelung-type term [3]. (A justification of treating A and B as independent parameters is that they are related to one-centre integrals of $(s_{\text{A}}/r_{\text{A}}^{-1}/s_{\text{A}})$ and $(p_{\text{A}}/r_{\text{A}}^{-1}/p_{\text{A}})$ type which assume slightly different values). The equation obtained is:

$$IE_{\text{c}}(\text{Exp}) = 8.570\,Q_\sigma + 8.758\,Q_\pi + 0.795\,Q_{\text{M}} + 403.421\ \text{eV} \quad (2)$$

(s. d. = 0.83 eV). So far, the one-centre terms A and B give the main contributions to ΔIE_{c} while only a small correction arises from the C term associated to the charges residing on the neighbouring atoms. Furthermore, it can be seen that the destabilizing influence of σ-withdrawal by N (controlled by the I effect of its substituents) appears to be virtually as effective as the stabilizing influence of π-donation by N (mainly governed by the M pover of its substituents). Therefore, for example the greater π-release (towards R and R') of N in $-\text{NO}_2$ than in $-\text{NH}_2$ seems to be the main factor responsible for the noted large IE_{c} gap between such two derivatives, where the σ-acceptor property of N seems to be similar in the two groups according to the nearly equal Q_σ. Furthermore, comparison of the σ and π N charges reveals that in the $\text{Ph}-\text{NRR}'$ series the σ-withdrawal by N is the dominant (destabilizing) factor. In contrast, the governing (destabilizing) term in the series $\text{Ph}-\text{N}=\text{X}$ is found to be the π-attraction in $\text{Ph}-\text{NC}$ and $\text{Ph}-\text{NCO}$ (and the same situation should likely hold also for $\text{Ph}-\text{NCS}$) and the σ-attraction in $\text{Ph}-\text{NNH}$, while in $\text{Ph}-\text{NO}$ the N atom experiences a virtual offset of σ-attraction and π-release actions.

Relative Contributions of the Relaxation Effects

Although the I and M effects certainly play the major role in the observed values and trends of the IE_{c}'s and IE_{v}'s, the not completely satisfactory theoretical correlations (especially for IE_{c}'s) – which may be at least in part ascribed to inadequate geometric models and the inherent limits of the theoretical approach –, and the lack of a simple correlation between core and valence IE values, show that there are further more subtle influences on the shifts as well, one of which may likely be the relaxation energy (RE) [18].

Although there is a certain basis set dependence of the Koopmans' theorem predictions [22], we found from the data in Table 1 that the estimate [23] of an average value of RE of 16.6 eV for N_{1s} ionizations accounts for most of the observed differences between Koopmans' IE_{c}'s and values measured from XPS. The difference between the (Koopmans' IE_{c} – 16.6 eV) values and the experimental data increases between the two extremes cases of $\text{Ph}-\text{NCH}_3\text{SiMe}_3$ and $\text{Ph}-\text{NO}_2$ from -0.5 to $+3.3$ eV. These findings are congruent with conclusions from sophisticated ab-initio calculations on simple compounds of NH_2X type [24] that the

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* Indeed, experimental and theoretical $IE_{\text{V}}(\pi(a_2))$ values are linearly related.

** The use of the relaxation potential model [5], which could give, in addition, an estimate of the relaxation energy involved in core ionization, does not improve significantly the correlation between calculated and experimental IE_{C}'s when compounds of molecular size similar to those presently investigated are considered [20, 21]. Financial reasons prevented us to use also this model.

RE's accompanying N_{1s} ionization are closely similar in related series of molecules, and also with the assumption that the RE is, to a first approximation, monotonically dependent on IE_c [25]. (Experimental and theoretical $IE_c(N_{1s})$ values are in fact linearly related.)

So far, the relative differences of RE along each series of molecules and between the two series seem to contribute only to a minor, even if non-negligible, extent to the core *IE* shifts.

The RE involved in one valence ionization process is about one order of magnitude less than that of the N_{1s} core ionization and bears, therefore, comparatively less importance.

Higher π-RE's are expected to be associated with the unsaturated $-N=X$ substituents, which can interact more strongly than the $-NRR'$ groups with the aromatic network. σ-RE should be instead greater in IE_c of $Ph-NRR'$ because of higher ligancy of the N atom [26].

Concluding Remarks

The conclusions from the present analysis of the electronic effects on the $IE_c(N_{1s})$ and the first IE_v's (πa_2 and πb_1) of a representative sample of $Ph-NRR'$ and $Ph-N=X$ molecules covering a variety of bonding situations may be summarized as follows:

1) The destabilizing influence of σ-withdrawal by N from its bonded groups appears to be of equal importance as the stabilizing influence of π-donation by N, the Madelung-type interaction playing a minor role. The factor controlling the IE_c is surely the former in the $Ph-NRR'$ series; in the $Ph-N=X$ series there appears to be no single decisive factor.

2) Both the IE_v's considered respond linearly to electronic interactions that the N-containing substituent sustains with the π aromatic cloud, $IE_v(b_1)$ being more sensitive than $IE_v(a_2)$ to variance of substituent effects. In particular, for $IE_v(a_2)$ the stabilizing $-I_\sigma$ effect prevails over the destabilizing $+I_\pi$ effect of the N-containing substituent to a larger extent in the $Ph-N=X$ series.

3) The noted correlations IE_v vs. IE_c for series of closely related compounds are coherent with the like response of these properties to inductive and mesomeric effects propagated through the N atom within the various substrates. This picture is also supported by both the σ and π N atomic charges and the σ and π charge-transfers between the ring and the N-containing substituents as obtaned by ab-initio STO-3 G calculations.

4) The apparently anomalous position of nitrobenzene in Fig. 1 could derive from the combination of several factors such as the different nature of its $\pi(b_1)$MO, the different role of the I_π mechanism on the $IE_v(\pi a_2)$ value, the different field effect of the $-NO_2$ group with respect to the $-NRR'$ groups and the greater π-release of N in $-NO_2$.

Bearing in mind the different types of environements experienced by the N atom in the examples chosen, we feel that the analysis reported here provides a reasonable description of the relevant electronic factors leading to the IE_c and IE_v shifts observed in monosubstituted benzenes containing di- and tri-coordinated nitrogen directly linked to the ring.

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