Gas Phase UPS Investigation of *Trans*-Azobenzenes

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The first two ionization energy values of p-substituted *trans*-azobenzenes $pX\text{–}C_6H_4\text{–}N{=}N\text{–}C_6H_5$ ($X = NH_2$, OCH_3, OH, CH_3, H, Cl, COOH and NO_2) are reported. These have been obtained by U.V. (HeI and HeII) photoelectron spectroscopy (UPS). The substituent effect indicates that for electron donor substituents, the highest occupied orbital is π-type. This is confirmed by semiempirical calculations. When the substituent is H or a withdrawing group, the first two bands heavily overlap, and in these cases no certain assignment was possible, in spite of the several approaches used. The UPS data are discussed along with previous polarographic and U.V. absorption measurements.

Introduction

The U.V. absorption spectra of azobenzene are characterized by a weak $n\text{-}\pi^*$ band at 22,300 cm^{-1} ($\log \varepsilon = 2.61$) and a strong $\pi\text{-}\pi^*$ band at 31,600 cm^{-1} ($\log \varepsilon = 4.35$) [1].

The $n\text{-}\pi^*$ transition is almost insensitive to the substituent while the $\pi\text{-}\pi^*$ is strongly dependent on the substituent [1]. The previous assumption that the n level of azobenzenes is not dependent upon the substituted [2] implied that also the π^* level is substituent insensitive. However, the substituent effect on the polarographic reduction potential of substituted azobenzenes [3], which is a measure of the energy of the LUMO, seemed to disprove this. On the other hand, photoelectron spectroscopy studies [4, 5] showed that there is an appreciable substituent effect on the ionization energy (IE) of "lone-pairs" in some series of benzene derivatives. The above correlations and considerations suggested that a study of the substituent effect on the first IE of azobenzenes should be useful for a better understanding of their electronic structure. The ordering of the highest occupied orbitals in azoderivatives has been the subject of several studies [6]. The assignment of this first two bands in the UPS spectrum generally accepted for azoderivatives corresponds to that proposed [7] for azomethane. This is n_- above π_+, where n_- and n_+ are the antibonding and bonding combinations of the "lone-pair" orbitals of the two nitrogens. This situation is not found in only a few azocompounds such as those containing donor groups. Examples of this type of compounds are the tetracenes R_4N_4 [8, 9] and the ether of the bis-(trimethylsilyl)-hyponitrous acid [6], for which the HOMO is π-type. In *trans*-azobenzene the same ordering as for *trans*-azomethane has been proposed [10]. However, the bands corresponding to the $n_-(a_g)$ and to the first $\pi(a_u)$ MO (this last orbital is delocalized over the whole molecule) overlap, their separation being about 0.3 eV. This makes the relative order uncertain. We have determined the first two IE values for a series of planar para-substituted *trans*-azobenzenes $p\text{-}XC_6H_4N{=}N\text{–}C_6H_5$ ($X = NH_2$, OCH_3, OH, CH_3, H, Cl, COOH and NO_2) using UPS [11] to obtain information on their nature and sensitivity to the substituent effect. The work is part of a program intended to obtain information on the electronic structure of the azobenzene system involving bisubstituted azobenzenes and hydrogen-bonded azoderivatives.

Results and Discussion

Figure 1 shows the region of interest of the UPS spectra. Table 1 reports the first two IE values determined experimentally and the corresponding calculated (CNDO/2) data [19] of the compounds under investigation. The same Table also lists the IE values of the corresponding benzenes. When X

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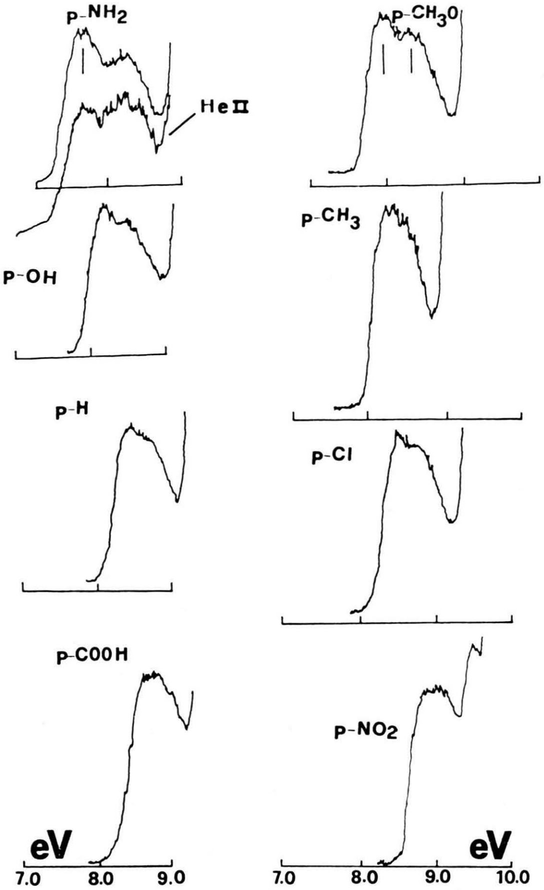

Fig. 1. First two bands of the photoelectron (HeI) spectra of para-substituted trans-azobenzenes. For the NH_2 derivative the He II spectrum is also reported.

is CH_3, OH, OCH_3 or NH_2, the experimentally observed splitting of the first two IE values increases with the electron-releasing ability of the substituent. In particular, on going from the CH_3 to the NH_2 derivative, IE_1 is destabilized by about 0.6 eV but IE_2 by only 0.2 eV. This different sensitivity to substituent effects indicates that, when electron-releasing substituents are present, IE_1 is related to ionization from a πMO, while IE_2 corresponds to the n_- MO. In fact, the mesomeric effect of the substituent is certainly stronger on the π than on the n MOs owing to the much larger wavefunction coefficient (CNDO/2) at the substituted carbon atom. The small variation of the energy of the n_- MO probably derives from the variation of the charge density at the nitrogen atoms brought about by the π MOs delocalized over the whole molecule*. Note that CNDO/2 calculations reproduce the ordering $IE_\pi < IE_n$, as well as the increasing energy gap between the first two IE values on going from $X = CH_3$ to $X = NH_2$. The assignment is much less straightforward when the other azobenzenes are considered, since the first two bands heavily overlap. The situation is even more involved for the nitro derivative, where doubts exists as to whether both the π and n_- ionizations contribute to the same (first) band or not.

As pointed out in the introduction, the ordering n_- above π has been proposed [10] for the first two IE values of unsubstituted *trans*-azobenzene. In order to obtain information on the π or n character of the HOMO when the substituent is H or an electron withdrawing group we used the following approaches.

1) We plotted the experimental IE_1 and IE_2 values for all the derivatives vs. the IE_1 value of the corresponding monosubstituted benzenes. The better correlation is obtained for IE_1 (azobenzenes) vs. IE_1 (benzene) indicating that the ordering π above n is maintained along the series and that ionization from the π MO of the NO_2-derivative contributes to the first band.

2) A very good linear relationship is found between both IE_1 and IE_2 and the σ_p^+ values for all the considered azobenzenes, the slope of the correlation line for IE_1 being higher. This approach also indicates that the ordering π above n is maintained.

3) The experimental IE_1 and IE_2 values were plotted against the corresponding calculated data. The best correlations were obtained by inverting the π/n ordering for X = H, Cl, COOH and NO_2. These correlations indicate that the first band in the spectrum of nitro-azobenzene derives from the n ionization process only. Note that, despite the linear correlations found ($I_{\pi\,\mathrm{exp}} = -7.77 \pm 0.84 + (1.43 \pm 0.07)\, I_{\pi\,\mathrm{th}}$; $r = 0.99$ and $I_{n\,\mathrm{exp}} = -2.64 \pm 1.93 + (0.96 \pm 0.16)\, I_{n\,\mathrm{th}}$; $r = 0.92$) the calculated figures do not reproduce such an inversion, the π MO lying above n_- in all cases.

* The first band of the p-NH_2 derivative shows a marked decrease in intensity with respect to the second one on going from HeI to HeII (see Figure 1). Considering the relative n/π cross sections [21], this behaviour confirms the nature of the first orbital of this compound. No information was obtained from the HeII spectra of other derivatives since the first two bands overlap.

Table 1. Ionization energy data for p-*trans*-azobenzenes and IE_1 of benzene (eV)[a].

X		IE_1	IE_2	$IE_n - E_{1/2}$[c]	IE_1 benzene
NH_2	exp.	7.67	8.25	9.85	8.02 [12]
	theor.	10.78	11.47		
OCH_3	exp.	8.0	8.3	9.83	8.39 [13]
	theor.	11.14	11.58		
OH	exp.	8.2	8.5		8.67 [14]
	theor.	11.15	11.59		
CH_3	exp.	(8.3)[b]	(8.4_5)	9.87	8.82 [15]
	theor.	11.20	11.53		
H	exp.	8.5	8.8	9.87	9.24 [16]
	theor.	11.60	11.56		
Cl	exp.	8.5_5	8.8	9.85	9.31 [16]
	theor.	11.86	11.58		
COOH	exp.	(8.7_5)	(8.9_5)	9.99[d]	9.48 this work
	theor.	11.81	11.63		
NO_2	exp.	9.0_5 9.6	9.0_5 9.6	10.02[e]	9.99 [17]
	theor.	12.19	12.18		

[a] UPS spectra were recorded with a Perkin-Elmer PS 18 spectrometer. Reproducibility was better than ±0.05 eV. The estimated error is ±0.05 or ±0.1 eV according to the degree of overlap of the two bands. The products were commercially available or prepared according to the literature.

[b] Values in parentheses are estimated (see spectra).

[c] $E_{1/2}$ from [3]; to calculate this difference the assumption was made that IE_n corresponds to the first band when X = H, Cl, COOH, NO_2, and to the second one in the other cases.

[d] $E_{1/2}$ calculated from the $E_{1/2}$-σ relationship [3].

[e] $E_{1/2}$ from [18].

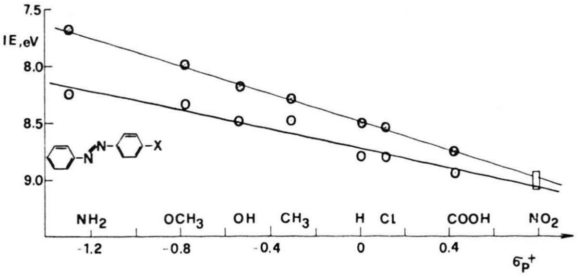

Fig. 2. Plot of the two outermost ionization energies for para-substituted trans-azobeneznes vs. $\sigma_p{}^+$.

4) The first column of Table 1 gives the differences between the IE of the n_- orbital and the $E_{1/2}$ polarographic reduction potential [3], assuming the π/n inversion for X = H or a withdrawing group. Such values are almost constant along the series. This behaviour would seem to a) rationalize the fact that the energy of the n-π^* transition is not very sensitive to the substituent [2] (the two levels are almost equally influenced by the substituent); b) support the π/n inversion hypothesis.

However, this would be true only under the assumption that the J and K integrals do not appreciably change along the series and that the excited state be described by a single configuration [22]. INDO/S calculations, parametrized as reported in [23], show that in the azobenzenes considered here the first low energy low-intensity band is mainly an n-π^* transition. The C.I. coefficients for this transition are 0.90—0.93 for all the compounds except the nitro derivative whose C.I. coefficient is 0.77. Also the calculated $(-J+2K)$ sum is not strictly constant, the corresponding figures being as follows: p-NH_2-*trans*-azobenzene $= -5.33$ eV; p-$OCH_3 = -5.34$ eV; p-$CH_3 = -5.34$ eV; H $= -5.36$ eV; p-COOH $= -5.10$ eV; p-$NO_2 = 4.11$ eV. On the other hand, if no π/n inversion is assumed, the $IE_n - E_{1/2}$ difference shows a break at the hydrogen point, the corresponding figures being: H = 10.17 eV; Cl = 10.10 eV; COOH = 10.19 eV; NO_2 = 10.02 (10.57 if $IE_n = 9.60$ eV).

All of this shows that this approach also does not give a conclusive answer on the assignment of the first two UPS bands for *trans*-azobenzene and its derivatives containing an electron-withdrawing group.

5) Help in determining the ordering of the highest MO's of azobenzene might come from the UPS spectrum of the *cis*-isomer, where a larger splitting between the n_- and π orbitals is expected. This should be in agreement with observations on the *cis*- and *trans*-azoisopropene isomers [24]. However we could not obtain the UPS spectrum of the *cis*-isomer, since it rapidly isomerized in the gas phase to the corresponding *trans*-isomer. It is to be noted that for the same reason no electron diffraction study of *cis*-azobenzene was possible [25]. The failure of the above approaches in giving a clear answer as to the ordering of the last two orbitals in azobenzene with X = H or an electron-withdrawing group, shows that this is still an open problem.

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[1] H. Rao, Angew. Chem. Intern. Ed. **12**, 225 (1973).
[2] H. H. Jaffe', S. Yeh, and R. W. Gardner, J. Mol. Spectr. **2**, 120 (1975).
[3] S. Millefiori and G. Favini, Z. Phys. Chem. N.F. **75**, 23 (1971).
[4] R. Egdell, J. C. Green, and C. N. R. Rao, Chem. Phys. Letters **33**, 600 (1975).
[5] C. N. R. Rao, Tetrahedron **32**, 1561 (1976).
[6] J. Kroner, W. Schneid, N. Wiberg, B. Wrackmeyer, and G. Ziegleder, Trans. Faraday Soc. 1909 (1978) and references therein.
[7] E. Haselbach and E. Heilbronner, Helv. Chim. Acta **53**, 684 (1970).
[8] J. Kroner, N. Wiberg, and H. Bayer, Angew. Chem. Intern. Ed. **14**, 178 (1975).
[9] P. Bischof, R. Gleiter, D. Dach, D. Enders, and D. Seebach, Tetrahedron **31**, 1415 (1975).
[10] T. Kobayashi, K. Yokota, and S. Nagakura, J. Electr. Spectr. **6**, 167 (1975).
[11] J. J. Delange, J. M. Robertson, and I. Woodward, Proc. Roy. Soc. London **A 171**, 398 (1939); C. J. Brown, Acta Cryst. **21**, 146 ,153 (1966).
[12] T. P. Debies and J. W. Rabalais, J. Electr. Spectr. **1**, 335 (1972/73).
[13] T. P. Debies and J. W. Rabalais, J. Electr. Spectr. **6**, 421 (1975).
[14] J. P. Mayer and D. W. Turner, J. Chem. Soc. Faraday II **521** (1973).
[15] T. Koenig, M. Tuttle, and R. A. Wielesek, Tetrahedron Letters **1974**, 2537.
[16] A. D. Baker, D. P. May, and D. W. Turner, J. Chem. Soc. B, **1968**, 22.
[17] J. W. Rabalais, J. Chem. Phys. **57**, 960 (1972).
[18] K. Boto and F. G. Thomas, Austr. J. Chem. **24**, 975 (1971).
[19] J. A. Pople and D. L. Beverigde, Approximate Molecular Orbital Calculations, McGraw-Hill, New York 1972. For the geometrical parameters used see [20].
[20] A. Millefiori, G. Favini, and S. Millefiori, Z. Phys. Chem. N.F. **94**, 167 (1975).
[21a] A. Schweig and W. Thiel, J. Electr. Spectr. **3**, 27 (1974).
[21b] J. W. Rabalais, Principles of Ultraviolet Photoelectron Spectroscopy, John Wiley, New York 1976.
[22] E. Haselbach and A. Schmalzer, Helv. Chim. Acta **54**, 1575 (1971).
[23] V. Galasso and G. C. Pappalardo, J. C. S. Perkin II, 574 (1976).
[24] K. N. Houk, Yan-Min Chang, and P. S. Engel, J. Amer. Chem. Soc. **97**, 1824 (1975).
[25] M. Traetteberg, I. Hilmo, and K. Hagen, J. Mol. Struct. **39**, 231 (1977).