Electronic Spectroscopy of Highly Polar Aromatics. VII. Photoelectron Spectra of Nitroanilines[1]

O. S. Khalil, J. L. Meeks, and S. P. McGlynn*

Contribution from the Coates Chemical Laboratories,
The Louisiana State University, Baton Rouge, Louisiana 70803,
and the Department of Chemistry, Cumberland College,
Williamsburg, Kentucky 40769. *Received February 23, 1973*

Abstract: The lower energy ionization potentials, $I \leq 12$ eV, of the nitroanilines can be arranged, in one-electron language, in the order of increasing energy, in C_{2v} notation, as: $b_1(\pi)$, delocalized; $a_2(\pi)$, ring; a_1, a_2, and possibly b_2, all of which are either wholly or dominantly localized on the nitro group; and b_1 "lone pair" or l, with heavy weighting on the amino nitrogen atom. Changes of relative substituent (*i.e.*, $-NO_2$ and $-NH_2$) positions on the ring, N-methylation and ring methylation, all produce large shifts of ionization potentials but no change in their relative order of occurrence. N-Methylation is akin to a simple change of electron donating ability; it produces a large energy change in ionizations which remove b_1 electrons (*i.e.*, in the lowest energy ionization and in the removal of an l electron). Ring methylation exerts a number of different influences, the dominant one of which is a large decrease of the second lowest energy ionization potential. This effect is used to identify the ionic state in question as $^2A_2(C_{2v})$. The electron-acceptor nature of the $-NO_2$ group, the electron-donor nature of the $-NH_2$ group, and the inhibition of conjugation caused by steric factors produce readily demonstrable effects in the photoelectron spectra of the nitroanilines. In particular, the "lone pair" or l orbital is usually of mixed σ,π type and may possess considerable ring-π character.

Despite considerable attention,[2] the electronic structure and spectra of aromatic nitro compounds are not well understood. In particular, the luminescence characteristics are most peculiar. The nitroanilines, for example, exhibit[3,4] a gross dependence of emission parameters on structural factors such as substituent positions and N-methylation as well as on environmental factors such as solvent polarity. Since photoelectron spectroscopy (pes) provides a means[5] of detailing ground-state characteristics of interest in molecular electronic spectroscopy, it seemed imperative to apply pes techniques to a discussion of the effects of structural factors on the lower energy ionization potentials of nitroanilines.

The photoelectron spectra of nitrobenzene, the isomeric nitroanilines, and various of their N-methyl and ring-methyl derivatives are reported here. The lower energy region of these spectra is discussed in terms of prior assignments of the pes spectra of nitrobenzene[6] and aniline,[7-9] molecules which constitute apt building blocks for a composite molecule view of the nitroanilines. The composite molecule approach is itself elaborated using CNDO/s–CI computations of the Del Bene–Jaffé variety[10] and their comparison with other computational results of different types available for nitrobenzene[6] and aniline.[11]

In the comparison of photoelectron spectra with the results of molecular orbital computations, it is usual to invoke Koopmans' theorem[12] and to assume a one-to-one correspondence between computed MO energies (as multiplied by some empirical factor which supposedly compensates for the electron reorganization which occurs during ionization)[13] and the pes bands. This, at best, is a specious procedure. Consequently, we use the MO calculational results for correlative purposes only. We accept the outer MO configuration of benzene to be[14-23] $\ldots[1a_{2u}(\pi)]^2[3e_{2g}(\sigma)]^4[1e_{1g}(\pi)]^4$, and we agree that one effect of substitution will be a splitting of the $1e_{1g}(\pi)$ MO such that, in C_{2v}, the $b_1(\pi)$ component will delocalize over the whole molecule, including the substituent, whereas the $a_2(\pi)$ component, with a 1–4 nodal plane, will remain ring localized. We also assume, granted the large $3e_{2g}$–$1e_{1g}$ energy gap,

---

[1] Research supported by contract between the United States Atomic Energy Commission–Biology Branch and The Louisiana State University.

[2] For a review up to 1969 see G. H. Wagnière, "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., Wiley, New York, N. Y., 1969, Chapter I.

[3] (a) O. S. Khalil, H. Bach, and S. P. McGlynn, *J. Mol. Spectrosc.*, **35**, 455 (1970); (b) C. J. Seliskar, O. S. Khalil, and S. P. McGlynn, "Advances in Electronic Excitation and Relaxation," E. C. Lim, Ed., Academic Press, New York, N.Y., in press.

[4] O. S. Khalil, C. J. Seliskar, and S. P. McGlynn, *J. Chem. Phys.*, **58**, 1607 (1973).

[5] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970.

[6] J. W. Rabalais, *J. Chem. Phys.*, **57**, 960 (1972).

[7] T. P. Debies and J. W. Rabalais, *J. Electron Spectrosc.*, in press.

[8] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).

[9] D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Lett.*, **17**, 90 (1972).

[10] J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968). The program used here was QCPE: CNDO 174 (The Quantum Chemistry Program Exchange, Indiana University).

[11] G. W. King and A. A. G. van Putten, *J. Mol. Spectrosc.*, **44**, 286 (1972).

[12] T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1933).

[13] W. G. Richards, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 419 (1969).

[14] L. Asbrink, O. Edqvist, and E. Lindholm, *Chem. Phys. Lett.*, **5**, 192 (1970).

[15] L. Asbrink, E. Lindholm, and O. Edqvist, *Chem. Phys. Lett.*, **5**, 609 (1970).

[16] L. Asbrink, C. Fridh, and E. Lindholm, *Chem. Phys. Lett.*, **15**, 567 (1972).

[17] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, **94**, 1451 (1972).

[18] C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Amer. Chem. Soc.*, **94**, 1466 (1972).

[19] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

[20] E. Lindholm and B.-Ö. Jonsson, *Chem. Phys. Lett.*, **1**, 501 (1967).

[21] J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **43**, 3287 (1965).

[22] P. A. Clark and J. L. Ragle, *J. Chem. Phys.*, **46**, 4235 (1967).

[23] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 88, 2353 (1966).

Table I. Vertical Ionization Energies (eV) of Nitroanilines and Related Compounds[a]

CH_3-NO_2[b]	NB[b]	NB	PNA	MNA	ONA	NMPNA	NND-MPNA	26D-MPNA	35D-MPNA	2NN-TMPNA	NMONA	Ph_2-NH_2[b]	Ionic state type (C_{2v})
						Correlated Ionizations							
	9.99	9.99	8.60	8.60	8.43	8.17	8.0	8.33	8.23	8.30	8.02	8.02	$^2B_1$, ring
	10.35	10.42	9.88	9.88	9.71	9.76	9.61	9.17	9.13	9.43	9.62	9.12	$^2A_2$, ring
11.32	(10.90)[c]	10.88	10.19	10.52	10.43	10.18	9.97	10.05	10.18	9.88	10.39		$\{^2A_1$ [d]
11.73	11.15	11.11	10.43	10.83	10.68	10.43	10.17	10.28	10.43	10.10	10.64		$^2A_2$, $-NO_2\}$
14.73	11.3	11.31	10.78	11.11	10.93	10.71	10.35	10.58	10.69	10.31	10.84		$^2B_2$
			11.46	11.43	11.47	10.87	10.60	11.06	11.17	10.55	11.28	10.78	$^2B_1$, 1, 66% $^2p_\pi(N)$
						Uncorrelated Ionization Energies							
		12.77	12.49	12.77	12.53	12.57	12.19	12.32	12.20	12.11	12.41		
		13.43	13.15	13.30	13.1	13.88	13.49	13.19	12.98	12.73	13.21		
		14.89	14.08	14.2	14.8	14.60	14.13	14.42	14.2	14.0	13.72		
		15.44	14.85	14.9	15.2	15.48	15.57	15.7	16.6	16.1	14.55		
		16.60	15.21	16.0	15.9	17.4	17.3	16.2	18.8		15.31		
		18.9	17.56	16.75	17.0	18.7	18.4				16.43		
			18.96	18.0	19.3						18.20		
				19.4									

[a] Notation is as follows: NB, nitrobenzene; PNA, *p*-nitroaniline; MNA, *m*-nitroaniline; ONA, *o*-nitroaniline; NMPNA, *N*-methyl-*p*-nitroaniline; NNDMPNA, *N*,*N*-dimethyl-*p*-nitroaniline; 26DMPNA, 2,6-dimethyl-*p*-nitroaniline; 35DMPNA, 3,5-dimethyl-*p*-nitroaniline; 2NNTMPNA, 2,*N*,*N*-trimethyl-*p*-nitroaniline; NMONA, *N*-methyl-*o*-nitroaniline; $PhNH_2$, aniline. [b] From Rabalais, ref 6 of text. [c] Inferred from Rabalais' spectrum (*cf.* footnote *b* above). The possibility that this shoulder is a resolved vibrational structure accompanying a lower energy or higher energy ionization act is quite high. All ionization potentials to the right of this footnoted entry in the third row are arguable; they are the numbers corresponding to the correlation lines of Figures 1, 3, and 5 which are denoted with a "?". [d] Diagrams of the vacant MO's produced in the generation of these states are given in Figure 5 of Rabalais, ref 6 of text. The enclosure of these states in braces implies our unwillingness to specify their relative order with regard to energy, or even the number of them which occur in the ~11 eV band of nitrobenzene and the correlated band of the nitroanilines.

that substituent orbitals will intrude in this energy range and be followed at higher binding energies by the split $3e_{2g}$ MO components and, finally, by the $1a_{2u}$ MO.

Finally, a word of caution. When dealing with complex molecules such as the nitroanilines, the amount of useful information which can be extracted from photoelectron spectra drops quickly, over-interpretation tends to set in, and the fallibility of investigators who attempt to work their way around poor signal/noise ratios and crowded spectra (in which electronic structure is not always readily distinguishable from vibronic activity) undergoes a rapid increase. It is probable that this work suffers from all or some of these tendencies.

Experimental Section

Pes spectra were recorded on a Perkin-Elmer Model PS-18 photoelectron spectrometer with a 10-cm radius cylindrical electrostatic field deflection analyzer. The HeI resonance line at 584 Å (21.22 eV) was used as an ionization source. Solid samples were allowed to sublime in a heated probe, the temperature of which was adjusted for maximum count rate. The range of temperatures for solid samples was 30 to 120°. Nitrobenzene vapor was introduced at a pressure of 0.1 Torr. The spectra were calibrated with the $^2P_{1/2}$ and $^2P_{3/2}$ lines of xenon. The $^2P_{1/2}$ and $^2P_{3/2}$ lines of argon were used to determine resolution, which always lay between 18 and 22 meV, prior to the recording of any given spectrum.

Nitrobenzene was a Mallinkrodt "reagent grade" and was used without further purification. The nitroanilines were Eastman Kodak products and were recrystallized from dilute ethanol solutions and/or vacuum sublimed. The sterically hindered nitroanilines were kindly provided by Dr. B. M. Wepster (Technical University of Delft, Holland) and were used as received.

Results and Discussion

The observed vertical ionization potentials are tabulated and correlated in Table I. The arguments leading to the correlation of the various ionization energies and their identification in molecular orbital terms are given below.

(i) Nitrobenzene. The photoelectron spectrum of nitrobenzene is shown in Figure 1a and is identical with that of Rabalais.[6] The two lowest energy bands (at 9.99 and 10.36 eV, respectively) are assigned, with Rabalais,[6] as the $b_1(\pi)$ and $a_2(\pi)$ ionizations which result from the increased binding and degeneracy splitting of the 9.24 eV, $e_{1g}(\pi)$ ionization of benzene.

The ionization band of nitrobenzene in the 11–12 eV region exhibits two peaks, 11.15 and 11.3 eV, respectively, and one shoulder at 10.88 eV. The two peaks have been assigned,[6] on the basis of INDO-MO computations and similarities to the corresponding spectrum of CH_3NO_2, as $a_1(\sigma)$ and $a_2(\pi)$ ionizations which involve electrons wholly or dominantly localized on the $-NO_2$ group; the existence of the shoulder at 10.88 eV has been disregarded,[6] presumably because it could equally well be associated with the resolution of some vibrational structure.

CNDO/s computational results for CH_3NO_2 and $C_6H_5NO_2$ are shown in Figure 2. These computations indicate that the nonbonding $1a_2(\pi)$ MO of the nitro group in CH_3NO_2 evolves to the highest energy filled MO of nitrobenzene, still heavily localized on the $-NO_2$ group. The $5a_1(\sigma)$ and $4b_2(\sigma)$ MO's of nitromethane evolve toward nitrobenzene MO's which remain wholly localized on the $-NO_2$ group. In contrast to the INDO computations,[6] however, the CNDO/s results do not discriminate between the presence of two

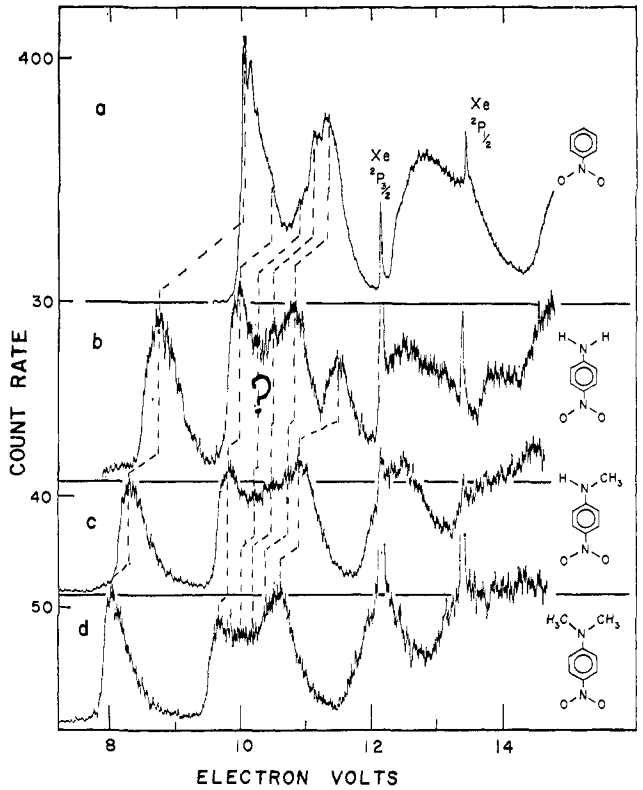

Figure 1. Photoelectron spectra of: (a) nitrobenzene; (b) *p*-nitroaniline; (c) *N*-methyl-*p*-nitroaniline; and (d) *N*,*N*-dimethy-*p*-nitroaniline. The dashed lines join ionization regions of similar orbital nature. The third ionization region, denoted by a question mark, may represent vibrational structure associated with regions 2 or 4; it is discussed in the text.

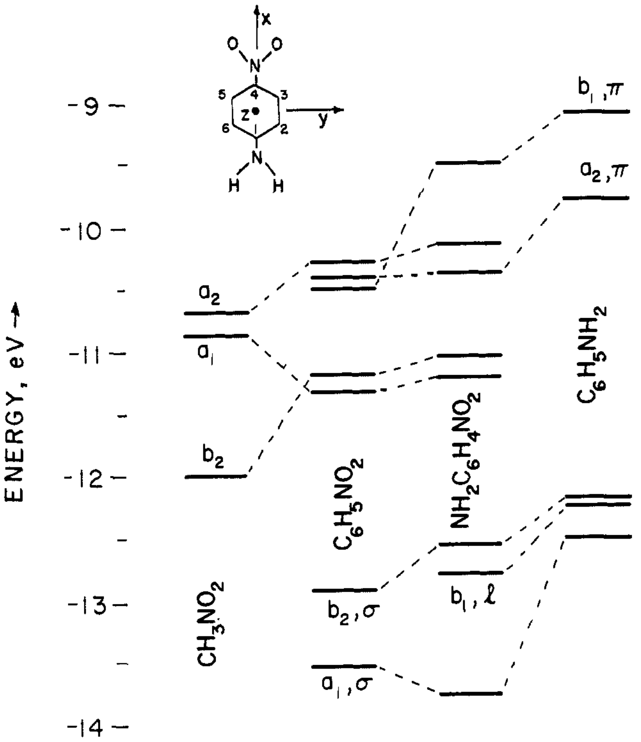

Figure 2. Correlation of various calculated molecular orbitals in nitromethane (C_{2v}), nitrobenzene (C_{2v}), *p*-nitroaniline (C_{2v}), and "planar" aniline (C_{2v}). Nitromethane possesses an actual C_s symmetry but is assumed here to have a gross symmetry of C_{2v} for comparative purposes. The aniline C_{2v} molecular orbitals are taken from King and van Putten.[11] The coordnate system used is shown as an insert. The $1a_2$, $5a_1$, and $4b_2$ MO's of CH_3NO_2 are localized on the $-NO_2$ group and remain wholly or largely so in nitrobenzene and *p*-nitroaniline. The -10.4 eV, $a_2(\pi)$ MO of nitrobenzene is dominantly localized on the ring and remains so in *p*-nitroaniline and aniline. The -9.99 eV, $b_1(\pi)$ MO of nitrobenzene is ring localized but extends over the aniline part in *p*-nitroaniline and aniline. The -12.8 eV, b_2 and -13.5 eV, a_1 MO's of nitrobenzene are σ MO's with complete and heavy ring character, respectively; they remain so in *p*-nitroaniline and aniline. The -12.8 eV, $b_1(\pi)$ MO of *p*-nitroaniline is the l MO; it possesses 66% nitrogen $^2p_\pi$ character and is more or less identical in both *p*-nitroaniline and planar aniline.

or three ionizations in the 11–12 eV ionization band. Consequently, while we agree with Rabalais[6] that the 11–12 eV band involves ionization of "nitro-group" electrons, we find it difficult to specify which, or even how many, ionic states are involved. Hence, the origin of the correlation line of Figure 1 which is denoted by a question mark.

(ii) ***p*-Nitroanilines.** The photoelectron spectrum of *p*-nitroaniline is shown in Figure 1b. The lowest energy ionization band at 8.60 eV resembles the lowest energy 8.02 eV ionization band of aniline,[7–9] and, as also in aniline,[8] N-methylation lowers the ionization energy to 8.17 eV in *N*-methyl-*p*-nitroaniline and to 8.02 eV in *N*,*N*-dimethyl-*p*-nitroaniline. CNDO/s computations predict the highest energy filled MO to be of $b_1(\pi)$ type with most amplitude on the aniline fragment; it is analogous to the $b_1(\pi)$ MO of aniline[11] and, to a less extent, the $b_1(\pi)$ MO of nitrobenzene. Consequently, the 8.60-eV ionization is surely connected with removal of a $b_1(\pi)$ electron. It can be supposed to be that of aniline shifted to higher energy by the electron-acceptor nature of the $-NO_2$ group or that of nitrobenzene shifted to lower energy by the electron-donor effect of the amino group.

The second ionization potential of *p*-nitroaniline lies at 9.88 eV and is not very sensitive to N-methylation, shifting to 9.76 eV in *N*-methyl-*p*-nitroaniline and to 9.61 eV in *N*,*N*-dimethyl-*p*-nitroaniline. In this regard, it is quite similar to the 9.15-eV ionization potential of aniline[8] and may be similarly assigned: removal of an $a_2(\pi)$ ring-localized electron. It also corresponds to the 10.42-eV ionization of nitrobenzene and correlates with the third lowest energy computed ionization potential of *p*-nitroaniline (see Figure 2). The insensitivity to N-methylation is then associated with the presence of a 1–4 nodal plane running through the substituent positions.

The ionization peaks at 10.2, 10.41, and 10.71 eV have no analogs in the aniline spectrum. Consequently, they may be related to the ionizations at 10.88 (?), 11.2, and 11.31 eV for nitrobenzene. These ionizations are relatively insensitive to N-methylation, in accord with expectation for nitro-group localized electrons.

A well-defined ionization peak occurs at 11.46 eV in *p*-nitroaniline. It has no obvious analog in the nitrobenzene spectrum. It shifts to 10.83 eV in *N*-methyl-*p*-nitroaniline and to 10.60 eV in *N*,*N*-dimethyl-*p*-nitroaniline, where it overlaps the ionizations associable with the nitro-group electrons. A somewhat similar band appears in aniline[7–9] at 10.78 eV, undergoes similar shifts, to 10.24 and 9.79 eV, upon successive N-methylation,[18] and has been assigned[7,8] to ionization of the amino-nitrogen "lone-pair" or "nonbonding" electrons.

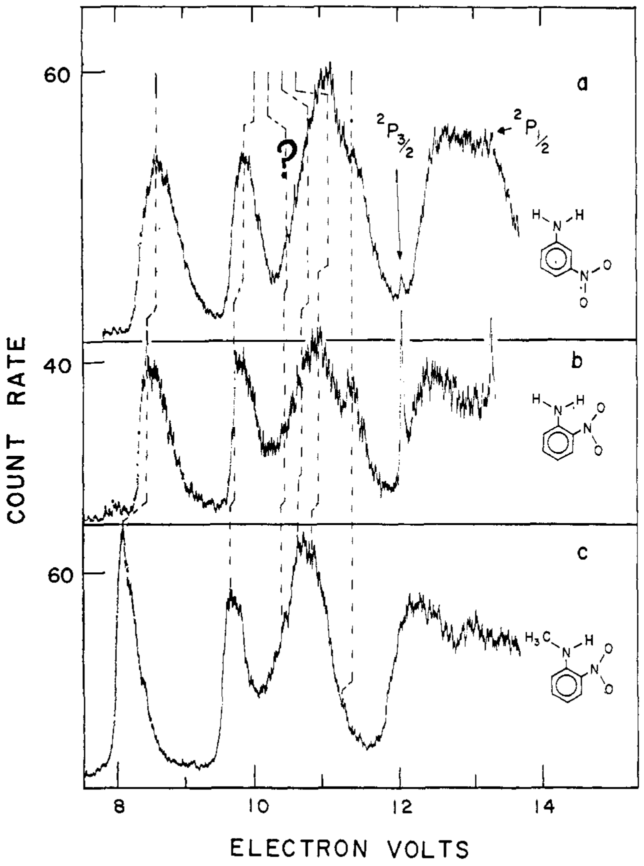

Figure 3. Photoelectron spectra of: (a) *m*-nitroaniline; (b) *o*-nitroaniline; and (c) *N*-methyl-*o*-nitroaniline. The solid vertical bars at the top of the diagram are the experimental ionization potentials of *p*-nitroaniline. The third ionization region, denoted by a question mark, is discussed in the caption to Figure 1 and in the text.

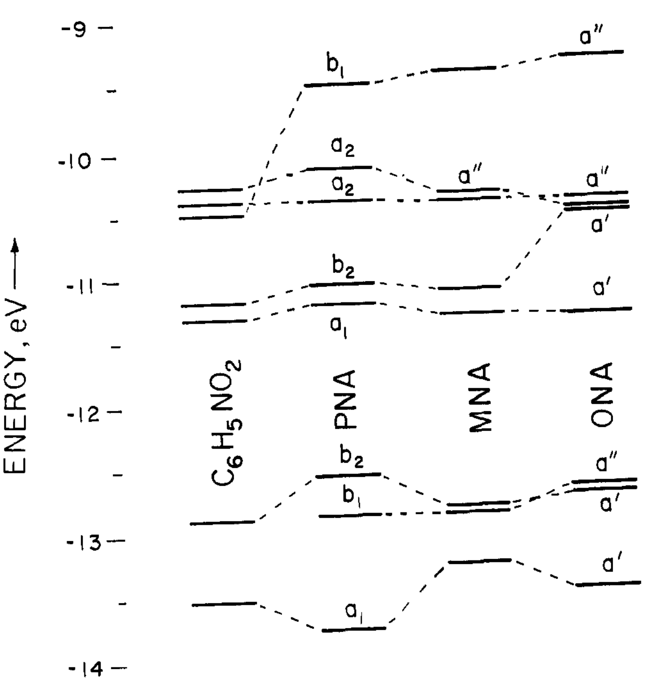

Figure 4. Correlation of molecular orbitals of nitrobenzene (C_{2v}), *p*-nitroaniline (C_{2v}), *m*-nitroaniline (C_s), and *o*-nitroaniline (C_s) as computed by CNDO/s means. The nature of the MO's is described in the caption to Figure 2.

The concept of "lone-pair" or l electrons on the amino group requires comment. The l ionization potential increases in the series $NH_3 \rightarrow C_6H_5NH_2 \rightarrow$ *p*-nitroaniline. This increase may be attributed to a change of hybridization since the geometry undergoes variation from pyramidal (NH_3), to bent (46° twist[24] in aniline), to planar[25] (*p*-nitroaniline). In this vein, the increase[7,8] of l ionization potential in proceeding from methylamine to ammonia or from aniline to $C_6F_5NH_2$ (*i.e.*, the "perfluoro effect") indicates that the l orbital possesses considerable σ character. The fact that the "perfluoro effect" is somewhat smaller than that normally found for σ electrons was attributed to the highly localized nature of the l orbital. An equally valid rational would attribute mixed σ,π nature to the l orbital and would rationalize the stabilization found in the series $NH_3 \rightarrow C_6H_5NH_2 \rightarrow$ *p*-nitroaniline as due to increased π delocalization. This supposition is certainly in accord with computations on "bent" and "planar" anilines[21] and with the stabilization, as shown in Figure 2, of the l MO which occurs on proceeding from "planar" aniline to *p*-nitroaniline.

(iii) **Positional Isomers of Nitroaniline.** The photoelectron spectra of *o*-, *m*-, and *p*-nitroaniline are shown in Figure 3 and are virtually identical. The lowest energy ionization potential and the l ionization potential shift to lower energies in *N*-methyl-*o*-nitroaniline, as seen in Figure 3c. These shifts parallel those of the first $b_1(\pi)$ and l ionization potentials of *p*-nitroaniline.

The results of CNDO/s computations are shown in Figure 4. The computations predict an MO serialization which is virtually the same for all three isomers.

(iv) **Ring-Methylated *p*-Nitroanilines.** The photoelectron spectra of 2,6-dimethyl-*p*-nitroaniline, 3,5-dimethyl-*p*-nitroaniline, and 2,*N*,*N*-trimethyl-*p*-nitroaniline are shown in Figure 5. The spectra are characterized by the presences of two low-energy, well-defined ionization bands, of identical shape and energy, at ~8.3 and 9.1 eV, respectively, followed by a broad band at ~11 eV which closely resembles the ionization band for the nitro-group orbitals of *p*-nitroaniline. Finally, the "lone-pair" ionization band is identifiable in 2,6-dimethyl-*p*-nitroaniline and does not seem to change energy in the 3,5-dimethyl derivative. The bands at ~8.3 and ~9.1 eV are very similar to the first two ionization bands of aniline and, to a less extent, *p*-nitroaniline.

Based on the assumption that the two highest filled MO's have the same order as those of *p*-nitroaniline, we may summarize the effects of ring methylation. (1) The ionization potentials of the highest energy filled MO, which is of $b_1(\pi)$ parentage in *p*-nitroaniline and which possesses a nodal plane perpendicular to the 1–4 substituent axis, is shifted to slightly lower energies. (2) The second highest energy filled MO, which is of $a_2(\pi)$ parentage in *p*-nitroaniline and which possesses a nodal plane through the 1–4 substituent axis, undergoes considerably larger shifts to lower energies. (3) The "lone-pair" orbitals are shifted to lower energies. (4) These three effects occur whether the ring-methyl groups are in the 2,6 or 3,5 positions. On the other hand, the ionization potentials of the nitro-group

---

(24) J. C. D. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectrosc.*, **20**, 359 (1966).

(25) K. N. Trueblood, E. Goldfish, and J. Donohue, *Acta Crystallogr.*, **14**, 1009 (1961).

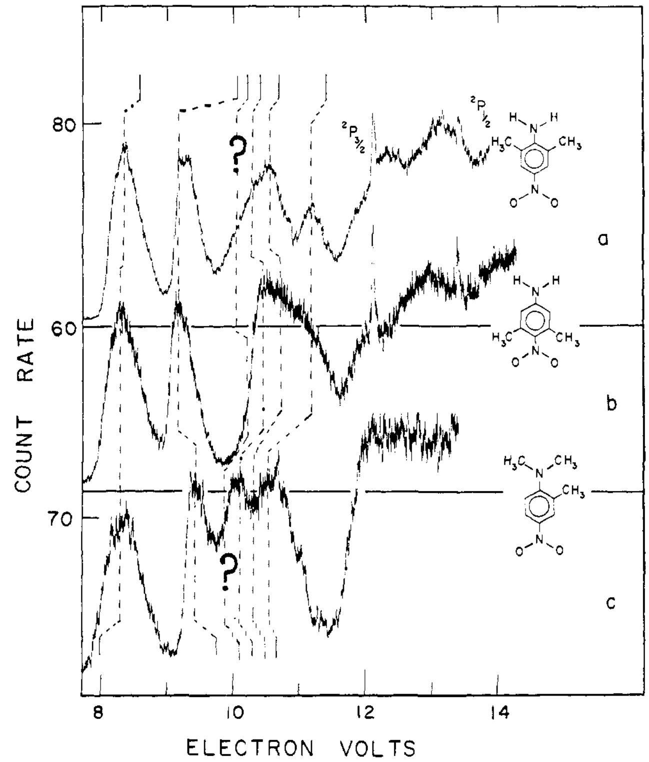

Figure 5. Photoelectron spectra of: (a) 2,6-dimethyl-*p*-nitroaniline; (b) 3,5-dimethyl-*p*-nitroaniline; and (c) 2,*N*,*N*-trimethyl-*p*-nitroaniline. The solid vertical bars at the top of the diagram are the experimental ionization potentials of *p*-nitroaniline and those at the bottom of the diagram represent the experimental ionization potentials of *N*,*N*-dimethyl-*p*-nitroaniline. For comments on the third ionization region, see captions to Figures 1 and 3 and text.

orbitals shift to lower energies in the 2,6 derivative and to higher energies in the 3,5 derivative.

Ring methylation should affect the highest energy filled MO's in either one or all of the following ways. (a) A twist of either the amino or nitro groups out of the molecular plane should decrease conjugation or, as it is said,[26] produce a "steric inhibition of resonance." (b) Substitution to either side of the 1–4 nodal plane should exert maximum effect on the $a_2(\pi)$ MO's. (c) The "inductive perturbation" of the methyl groups should produce a decrease of all ionization energies.

The large decrease of the second ionization caused by 2,6 or 3,5 substitution (*i.e.*, by either nitro-group or amino-group twisting) indicates that mechanism b is the dominant effect and, at the same time, provides cogent reason for identifying the second ionization potential with the removal of an $a_2(\pi)$ electron. Thus, the nature and ordering of the two top most filled MO's appears to be the same in all the nitroanilines considered here. The apparent decrease of the 1 ionization energy, if real, can be attributed to mechanism a and the small change of the first ionization potential may imply both mechanisms a and c. The shifts of the nitro-group orbitals to lower energies in 2,6-dimethyl-*p*-nitroaniline and to higher energies in 3,5-dimethyl-*p*-nitroaniline, although small, do not find any ready interpretation along lines a, b, or c.

The first ionization potential of 2,*N*,*N*-trimethyl-*p*-nitroaniline lies higher than that of *N*,*N*-dimethyl-*p*-nitroaniline but lower than that of *p*-nitroaniline. Since the *N*,*N*-dimethylamino group is much bulkier than the amino group, substitution in the 2 position of the ring should exert a large steric effect in the former case. Thus, the shift to higher energy in this instance indicates the dominance of mechanism a and the sensitivity of the orbital involved in this ionization act to electron-donating ability of group positions 1 and 4 of the ring. By contrast, the second ionization shifts to lower energies, indicating the dominance of mechanism b and the sensitivity of the orbital involved in this ionization to substitution off the 1–4 substituent axis. Therefore, the assertion of an $a_2(\pi)$ orbital parentage for the second ionization potential, and a $b_1(\pi)$ for the first, acquires validation. The decrease of the 1 ionization potential which seems to occur in 2,*N*,*N*-trimethyl-*p*-nitroaniline can be interpreted along the lines of mechanism a.

Acknowledgment. The authors wish to express their gratitude to Professors Wepster (Delft, Holland) and Rabalais (Pittsburgh) for donations of chemicals and discussion time.

[26] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1970, p 368.