Photoelectron Spectra of Bicyclic Azo *N*-Oxides and Azo *N,N'*-Dioxides[1]

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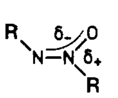
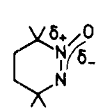
The photoelectron (PE) spectra of a series of cyclic azo *N*-oxides and azo *N,N'*-dioxides have been measured. For the former the highest lying molecular orbitals are assigned in order of decreasing energy: π(NNO) ~ n$_+$(NNO) > n$_-$(NNO). For the latter a π(ONNO) > n$_+$(OO) > n$_-$(OO) series is obtained. The assignments are based on empirical correlation including well-resolved fine structure in several cases and on semiempirical calculations involving three separate parameterizations. The molecular orbital correlation for the redox series azoalkane, azo *N*-oxide, and azo *N,N'*-dioxide is delineated.

The recent interest in the electronic structure of azo *N*-oxides and azo *N,N'*-dioxides[2-5] prompts us to present some preliminary results we have obtained in the course of our systematic investigation of the chemical,[6] thermochemical,[7] and electronic properties of acyclic, bicyclic, and polycyclic azo *N*-oxides and azo *N,N'*-dioxides. Here we report the He I photoelectron spectra of 2,3-diazabicyclo[2.2.*n*]alk-2-ene 2-oxide [**4**(*n*)], 2,3-diazabicyclo[2.2.*n*]alk-2-ene 2,3-dioxide [**7**(*n*)], and the reference compounds **1**–**3** and **5**–**6**.



1, R = CH$_3$
2, R = i-Pr



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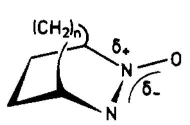
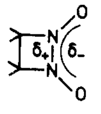


4(n), n = 1–4



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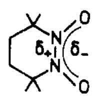

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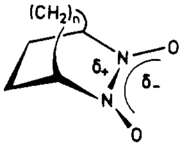

7(n), n = 1–4

The spectra are interpreted on the basis of empirical correlation and by CNDO-MO calculations for **4**(1,2), **5**, and **7**(1,2) employing several parameterizations.[8]

Experimental Section

The compounds were prepared and purified as previously described.[6] The PE spectra were recorded on a PS-18 spectrometer (Perkin-Elmer, Beaconsfield, England) and calibrated with a mixture of argon and xenon gases introduced to the target chamber *simultaneously* with the sample. The reported ionization potentials (Table I) are averages of three to six determinations. Slow scanning of the spectra with narrow slits and low vapor pressure in the target chamber enabled us to obtain well-resolved vibrational fine structure for the first bands of **6** and **8**(2). A more diffuse structure was observed for the other compounds.

Discussion

Typical spectra for the azo *N*-oxides **1** and **4**(1) are given in Figures 1 and 2, respectively. The first five experimental IP's for the compound series studied are listed in Table I.

The two highest levels are predicted by all parameterizations to be π(NNO) and n$_+$(NNO) (cf. Figure 5)[9] and to be very close in energy by CNDO/B. The former is in agreement with reported calculations for azoxymethane[10] and 3,3,4,4-tetramethyldiazetine *N,N'*-dioxide (**5**).[5] Indeed the first band in the PE spectra of compounds **1**–**3** is very intense and seems to contain two ionizations.[11] Careful scrutiny of expanded spectra of this band reveals a diffuse vibrational structure but no conclusion regarding the exact IP of each orbital can be drawn. A clearer situation is encountered in the series **4**(*n*). The PE spectrum of diazanorbornene *N*-oxide **4**(1) (Figure 2) shows two ionization bands at 9.48 and 9.72 eV (predicted splitting: 0.17 eV, CNDO/B). The energy difference between π(NNO) and n$_+$(NNO) decreases when the size of the molecule increases. We were able, however, to resolve the two bands for the other three bicycles and to estimate their respective fine structure (cf. Table I). The calculations suggest the third IP to be associated with ionization from n$_-$(NNO) consistent with the findings for pyrimidine and pyrazine *N*-oxides.[2,3]

The question as to whether the π(NNO) orbital lies above n$_+$(NNO) remains. We cannot rely exclusively on MO calculations since the energy difference is small, the calculations were performed with estimated geometries, and, further, the strict validity of Koopmans' theorem would be required in order to compare the experimental IP's with the calculated energies. Population analysis for **4**(1) and **4**(2) reveals that

Table I. First Five Experimental Vertical Ionization Potentials (IP's, eV)[a] of Some Azo *N*-Oxides

IP	1	2	3	4(1)	4(2)	4(3)	4(4)
1	10.07[b]	9.60[b]	9.13[b]	9.48 (1200)	9.30 (~1000)	9.21 (~1000)	9.13 (~1000)
2				9.72 (800)	9.42 (~1000)	9.30 (~1100)	9.24 (~1000)
3	11.06	10.33	9.88	10.75	10.28	10.09	10.00
4	13.02[c]	11.8[d]	11.4[d]	12.17	11.41	11.45	11.10
5	14.1	12.2[e]	11.8[e]	13.1	11.87	11.8[e]	11.5[d]

[a] Key: ±0.03 or ±0.1 eV. The vertical IP's are taken as the maxima of the Frank–Condon envelopes. The numbers in brackets represent the vibrational fine structure, ±50 or ±100 cm^{-1}. [b] The first two IP's interpenetrate and show diffuse vibrational structure; a precise assignment is not possible. The number indicates the maximum of the band. [c] This band exhibits a complex fine structure (~1350 and ~1000 cm^{-1}). [d] Shoulder. [e] Broad band which contains more than one IP.

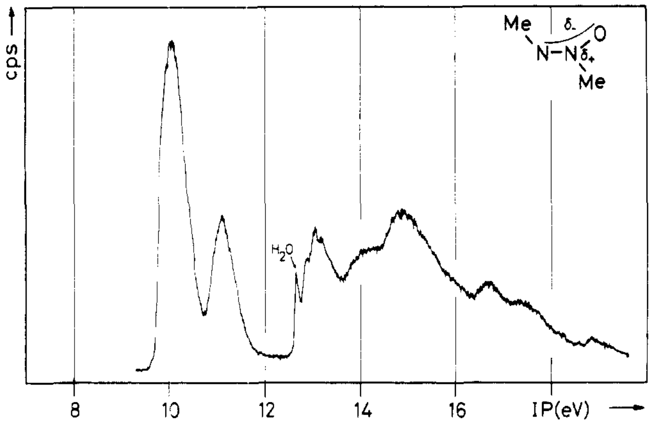

Figure 1. Photoelectron spectrum of 1.

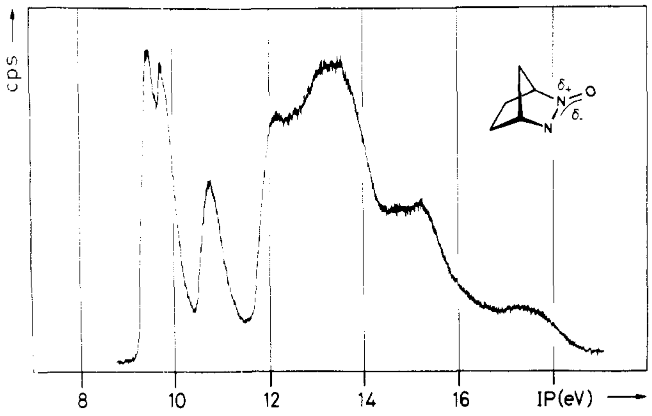

Figure 2. Photoelectron spectrum of 4(1).

Table II. First Five Experimental Vertical Ionization Potentials (IP's, eV)[a] of Some Azo *N,N'*-Dioxides

IP	5	6	7(2)	7(3)	7(4)
1	8.23 (750, 1050)	7.86 (~900)	8.04 (680)	8.04 (~800)	8.03 (~800)
2	9.45 (800)	9.33	9.44 (800)	9.48	9.46
3	10.42	9.5[b]	9.88	9.7[b]	9.7[b]
4	11.25	10.57	10.75	10.77	10.58
5	12.1	11.6[b]	11.7	11.7	11.4

[a] See Table I. [b] Shoulder.

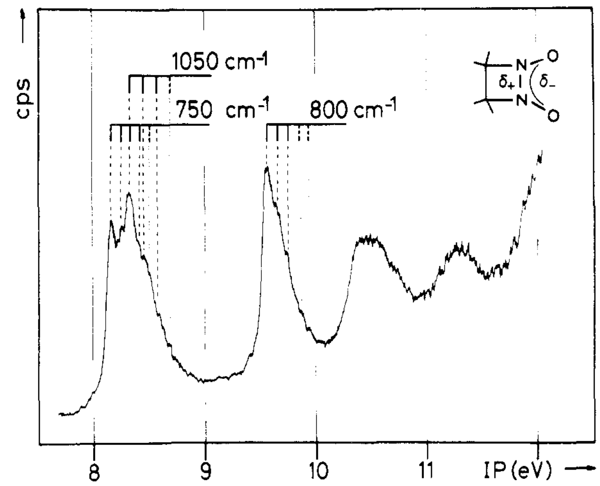

Figure 3. Photoelectron spectrum of 5 (expanded scale).

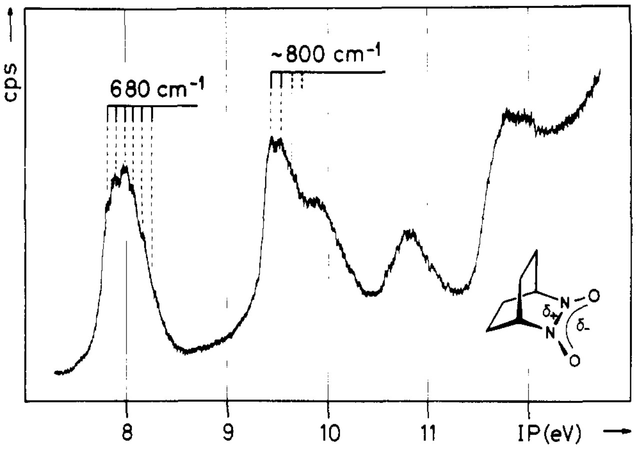

Figure 4. Photoelectron spectrum of 7(2) (expanded scale).

both π(NNO) and n_+(NNO) orbitals are NN bonding and NO antibonding. The former is quite localized on the NNO moiety whereas the latter mixes more with other MO's. It might be expected that the vibrational frequency will be reduced to a greater extent for n_+(NNO) than for π(NNO). However, the NN and NO stretches (1508 and 1200 cm^{-1}, respectively, in the neutral molecule[12]) are probably strongly coupled so that a more detailed analysis will be required in order to make a secure assignment.

The addition of a second oxygen atom to the NNO group leads to a more symmetrical moiety whose characteristic high-lying orbitals are a ONNO antibonding π orbital and two oxygen lone pair orbitals, n_+ and n_- (cf. Figure 5). Typical spectra are shown on an expanded scale for 5 and 7(2) in Figures 3 and 4, respectively. The experimental first five IP's of the compounds studied are collected in Table II.

Again the CNDO/B, CNDO/S and CNDO/2 methods used here and other work[5,10] agree that the antibonding π(ONNO) orbital is the HOMO. We thus assign the first band in all the spectra to this energy level. Although no explicit calculations were carried out for dioxide 6, the analogous assignment is supported by the similarity of observed fine structure for 6 and 7(*n*)[13] (680–900 cm^{-1}). In the case of 5 two progressions are observed, one of which (1050 cm^{-1}) could arise from the NO stretching vibration (1320 and 1450 cm^{-1} in neutral *cis*-nitroso dimers[14]). The next two bands are assigned to the symmetrical and antisymmetrical lone pair combinations, respectively. The observed splitting, $\epsilon(\Delta n) = \epsilon(n_+) - \epsilon(n_-)$, amounts to 0.96 eV for 5. According to the CNDO calculations, it is mainly through-bond dominated owing to an appreciable contribution of the cyclobutane ring orbitals to the n_+ and n_- orbitals. The situation changes in going to the six-membered ring. Through-bond and through-space interactions almost cancel each other leading to $\epsilon(\Delta n) \simeq 0.17$ eV (calculations predict it to be five times smaller than for 5). That two ionizations are contained in the second band of 6 is not very obvious; however, the situation is clear for 7(2) where the two bands are well separated. For 7(3) and 7(4) we observe only shoulders.

In summary the oxidation of an azo alkane perturbs both the lone-pair and the π system in a straightforward fashion as illustrated by the [2.2.2]-bicyclic example in Figure 5. The strong 1,2-azo lone pair interaction [$\epsilon(\Delta n) \simeq 3.0$ eV][15] is replaced by the reduced 1,3-nitrogen–oxygen interaction in the *N*-oxides [$\epsilon(\Delta n) = 0.98$ eV]. The splitting is further diminished in the *N,N'*-dioxide where the oxygen lone pairs experience a 1,4 relationship [$\epsilon(\Delta n) = 0.44$ eV]. The center of gravity of the lone pair splittings is not a simple function of the atoms involved. It arises in part from orbital mixing with framework MO's. Changes in the IP's of the π levels are understood by considering the second order perturbation of π(NN)/azo with

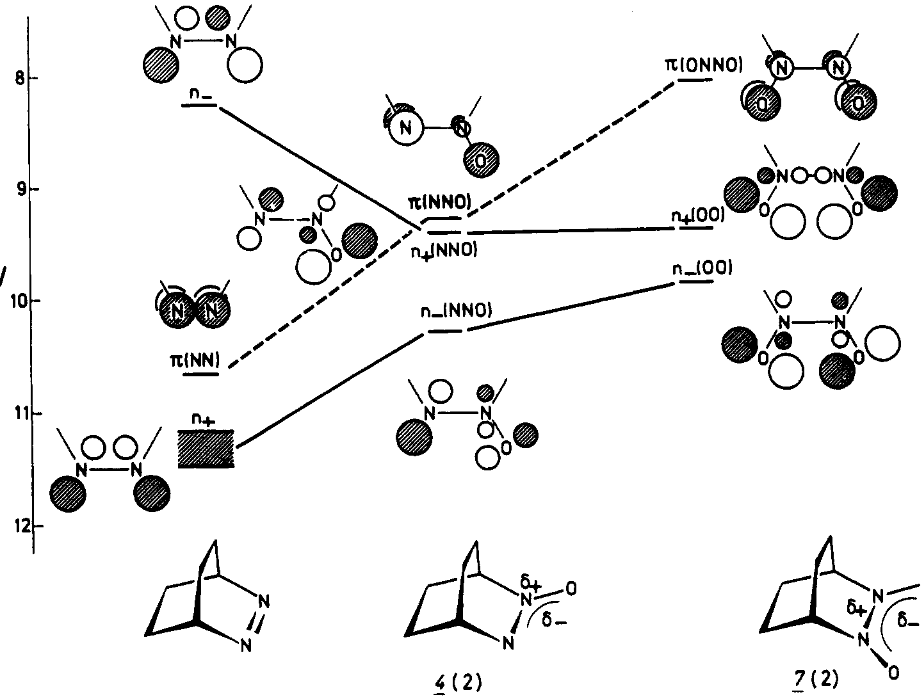

Figure 5. Correlation diagram for the high-lying MO's of azoalkanes, azo *N*-oxides, and azo *N,N'*-dioxides as represented by the experimental IP's for 2,3-diazabicyclo[2.2.2]oct-2-ene,[15] 4(2), and 7(2). The assignment π(NNO) < n_+(NNO) is speculative and is based on semiempirical calculations.[8]

π(pO). The former is raised in energy and the resulting π(NNO) contains a node between N and O. Addition of a second π(pO) by oxidation to the *N,N'*-dioxide lifts the π orbital still further [π(ONNO)].

Efforts are underway to determine unambiguously the sequence for the azo *N*-oxide π(NNO) and n_+(NNO) orbitals. When this has been accomplished, our MO calculations will be described in detail and the implications of the relationships shown in Figure 5 for the relative chemical behavior of azo alkanes, azoxy alkanes, and azo *N,N'*-dioxides will be discussed.

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Registry No.—**1**, 54168-20-6; **2**, 35216-94-5; **3**, 54143-34-9; **4**(1), 22509-00-8; **4**(2), 25926-96-9; **4**(3), 26081-83-4; **4**(4), 25926-97-0; **5**, 34493-89-5; **6**, 54143-35-0; **7**(2), 36479-80-8; **7**(3), 54143-30-5; **7**(4), 54143-31-6.

References and Notes

(1) (a) *cis*-Azoxy Alkanes. 7. For part 6, see (b) J. P. Snyder, M. L. Heyman, and E. M. Suciu, *J. Org. Chem.*, **40**, 1395 (1975).
(2) J. P. Maier, J.-F. Müller, and T. Kubota, *Helv. Chim. Acta*, **58**, 1634 (1975).
(3) J. P. Maier, J.-F. Müller, T. Kubota, and M. Yamakawa, *Helv. Chim. Acta*, **58**, 1641 (1975).
(4) M. B. Robin in "The Chemistry of the Hydrazo, Azo and Azoxy Groups", Part 2, S. Patai, Ed., Wiley, New York, N.Y., 1975, Chapter 1.
(5) K. E. Gilbert, *J. Org. Chem.*, preceding paper in this issue.
(6) H. Olsen and J. P. Snyder, *J. Am. Chem. Soc.*, **96**, 7839 (1974); ref 1b and preceding papers.
(7) J. P. Snyder, J. F. M. Oth, and H. Olsen, to be published.
(8) CNDO/B: R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 73 (1972). CNDO/S: J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968); R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, **26**, 131 (1972). CNDO/2: J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
(9) The group theoretical designation of the symmetrical analogue of this orbital is n_+ for cis compounds and n_- for trans compounds; cf. R. Hoffmann, *Acc. Chem. Research*, **4**, 1 (1971).
(10) J. Kuhn, W. Hug, R. Geiger, and G. Wagnière, *Helv. Chim. Acta*, **54**, 2260 (1971).
(11) Intensity arguments have to be used with great care since photon absorption cross sections may be very different for different orbitals.
(12) N. B. Colthup, C. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, N.Y., 1964, pp 288-289.
(13) The PE spectrum of 7(1) could not be obtained. The compound decomposes thermally in the heated probe.
(14) Cf. B. G. Gowenlock and W. Lüttke, *Q. Rev., Chem. Soc.*, **12**, 321 (1958).
(15) R. J. Boyd, J. C. Bünzli, J. P. Snyder, and M. L. Heyman, *J. Am. Chem. Soc.*, **95**, 6478 (1973); R. J. Boyd, J. C. Bünzli, and J. P. Snyder, *ibid.*, **98**, 2398 (1976).