Photoelectron Spectra of Cyclic Azo *N*-Oxides and Azo *N,N'*-Dioxides

Kevin E. Gilbert

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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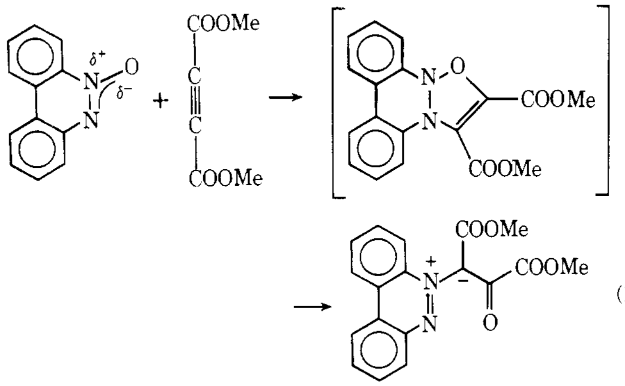
The photoelectron spectra of 3,3,4,4-tetramethyldiazetine (**1**), 3,3,4,4-tetramethyldiazetine N-oxide (**2**), 3,3,4,4-tetramethyldiazetine N,N'-dioxide (**3**), 3,3,6,6-tetramethyl-1,2-diazacyclohexene (**4**), 3,3,6,6-tetramethyl-1,2-diazacyclohexene N-oxide (**5**), and 3,3,6,6-tetramethyl-1,2-diazacyclohexene N,N'-dioxide (**6**) have been measured and the ionization potentials have been interpreted in terms of molecular orbitals with the assistance of INDO calculations. The energy of the highest occupied π orbital increases along the series azo > azo oxide > azo dioxide, a result consistent with expectations based on simple perturbation theory. The relationships between the molecular orbital energies and the chemistry of azo N-oxides and azo N,N'-dioxides are discussed.

Azo N-oxides and azo N,N'-dioxides, formally obtained by stepwise oxidation of azo compounds, have many interesting physical and chemical properties such as the valence isomerization of azo N-oxides to oxadiaziridines[1] and the dissociation/dimerization of azo dioxide/nitroso alkanes.[2] While studing these two reactions we prepared a number of cyclic azo, azo N-oxide, and azo N,N'-dioxide compounds. Herein we report the photoelectron spectra of these compounds and calculations of the electronic structures of azo N-oxides and azo N,N'-dioxides by the INDO–SCFMO method.

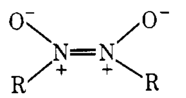
Azo N-oxides, like azomethine ylides, azomethine imines, nitrones, azimines, and nitroalkanes, are 1,3 dipoles having nitrogen as the central atom[3]. In this series of 1,3 dipoles, reactivity in cycloaddition reactions varies from very high (azomethine ylides) to undetectable (nitroalkanes), with azo N-oxides being among the less reactive compounds. Rees and co-workers have reported that the reaction of benzo[c]cinnoline N-oxide and dimethyl acetylenedicarboxylate at 190 °C gives an ylide, presumably through rearrangement of an initially formed cycloadduct (eq 1).[4] The reactivity of 1,3 dipoles in cycloaddition reactions has been correlated with the electronic structure of the 1,3 dipole,[5] as will be elaborated upon later.



(1)

Azo N-oxides are thermally more stable than the corresponding azo compounds. In cases where the rates of extrusion of N_2O and N_2 from azoxy alkanes and azo alkanes have been measured the ratio of the rate constants is on the order of $k_{\text{azoxy}}/k_{\text{azo}} = 10^{-16}$.[6] The difference in the rates of these reactions has been attributed to a symmetry-induced barrier to reaction in the azo N-oxide due to the perturbing effect of the oxygen on the MO's of the reactant.[6]

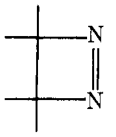
The chemistry of azo N,N'-dioxides has many aspects of interest, including the thermal dissociation of the azo dioxide to the corresponding nitroso alkane, in the formal sense cleavage of a double bond under very mild conditions (eq 2). Rates and equilibria of the reaction have been measured for a number of cyclic and acyclic systems.[2,7,8] The mechanism of the dimerization/dissociation process has been studied by Hoffmann, Mallory, and Gleiter; they suggested a non-least-motion path for the dimerization reaction, the least-motion path being symmetry forbidden.[9] Their ideas have received experimental support in the work of Greene and Gilbert on cyclic azo dioxides.[8]



$$\underset{R^{\diagup}\ +\ \ +\ ^{\diagdown}R}{\overset{O^-\ \ \ \ \ \ O^-}{N{=}N}} \rightleftharpoons 2\text{RNO} \tag{2}$$

In those azo dioxides which do not dissociate, the chemistry of the azo dioxide functional group can be observed. Azo dioxides can be reduced to azo N-oxides and azo compounds, but they are resistant to further oxidation.[8] Azo dioxides react photochemically to give nitroxyls (loss of NO).[8,10] In a thermal reaction, 3,3,4,4-tetramethyldiazetine N,N'-dioxide (**3**) gives 2,3-dimethyl-2-butene and NO.[11] Overall, azo dioxides are a relatively inert functional group.

Herein we report the photoelectron spectra of a series of cyclic azo, azo N-oxide and azo N,N'-dioxide compounds and molecular orbital calculations on the electronic structures of these molecules. The reactivity of azo N-oxides in 1,3-dipolar cycloaddition reactions and the oxidation–reduction chemistry of azo N,N'-dioxides have received particular attention as we are interested in relationships between molecular orbital theory, photoelectron spectroscopy, and chemical reactivity.



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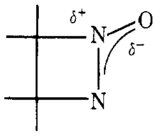

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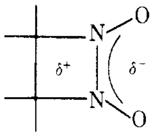

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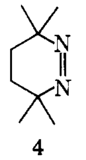

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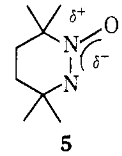

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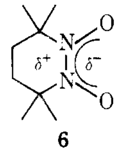

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Experimental Section

The spectra were run on a PS-18 spectrometer (Perkin-Elmer) with a standard inlet for liquid and solid samples. The spectra were calibrated with argon as an internal standard. The ionization potentials reported in Table I are the average values from three or more spectra; single values were reproducible to ±0.05 eV. All compounds were prepared as previously reported.[8] For the solid samples the probe was heated to increase the count rate: 36 °C for **2**, 65 °C for **3**, 50 °C for **5**, and 80 °C for **6**, all ±5 °C.

PE Spectra. The PE spectra of the four-membered ring series 3,3,4,4-tetramethyldiazetine (**1**), 3,3,4,4-tetramethyldiazetine N-oxide (**2**), and 3,3,4,4-tetramethyldiazetine N,N'-dioxide (**3**) are presented in Figure 1. The PE spectra of the six-membered ring series 3,3,6,6-tetramethyl-1,2-diazacyclohexene (**4**), 3,3,6,6-tetramethyl-1,2-di-

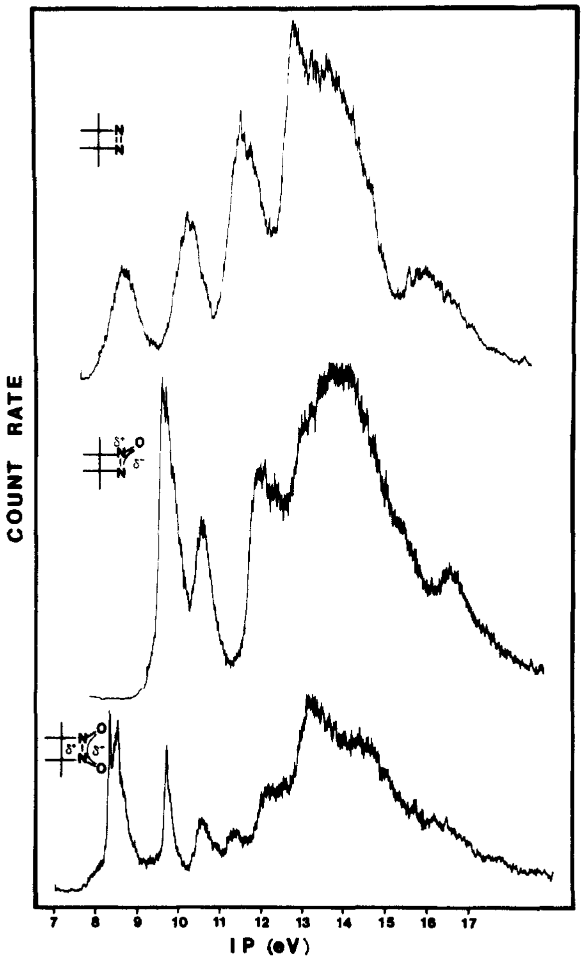


Figure 1. Photoelectron spectra of four-membered ring series (1, 2, and 3).

Table I. Ionization Potentials (eV) of Compounds 1–6[a]

Compd	1st	2nd	3rd
1	8.77	10.24	11.5
2		9.82[b]	10.8
3	8.52	9.73	10.6
4	7.85	10.7[c]	
5		9.20[b]	10.1
6	8.19	9.58	10.7

[a] The spectra were calibrated with argon as a single internal standard (see Experimental Section). As a referee has pointed out, care must be taken when using this technique that the linearity of the spectral range not change with time; otherwise ionization potentials in the 8-eV region will be inaccurate. The reproducibility of our results suggests that we have not encountered this problem. (For a comparison, see ref 29, Table I). [b] The first two bands overlap and a precise assignment is not possible; see text for discussion. [c] Broad, diffuse band, assignment accurate to only ±0.1 eV.

azacyclohexene *N*-oxide (**5**), and 3,3,6,6-tetramethyl-1,2-diazacyclohexene *N*,*N*′-dioxide (**6**) are presented in Figure 2. The corresponding vertical ionization potentials of compounds **1**–**6** are given in Table I. These potentials refer to the positions of the corresponding maxima of the Frank–Condon envelopes.

Results and Discussion

INDO Calculations. Calculations of the electronic structures of azo *N*-oxides and azo *N*,*N*′-dioxides by the INDO–SCFMO[12] method were investigated to aid interpretation of the photoelectron spectra.[13] Initially we sought a model system which would reproduce the significant trends in the photoelectron spectra. Calculations were performed on diimide (**7**), diimide *N*-oxide (**8**), and diimide *N*,*N*′-dioxide (**9**) with the HNNH angle fixed to reproduce either the four-membered ring series (95°) or the six-membered ring series (120°). The calculations on this model system were checked against similar calculations on the four-membered ring series compounds **1**, **2**, and **3** (methyl groups included): for **1**, **2**, and **3** standard bond lengths and angles (except within the ring) were used and the total energy was minimized with respect to the NN bond length for **1** and with respect to the NN and NO bond lengths for **2** and **3**.[14] The results are summarized in Table II. Since the model system reproduces the geometries

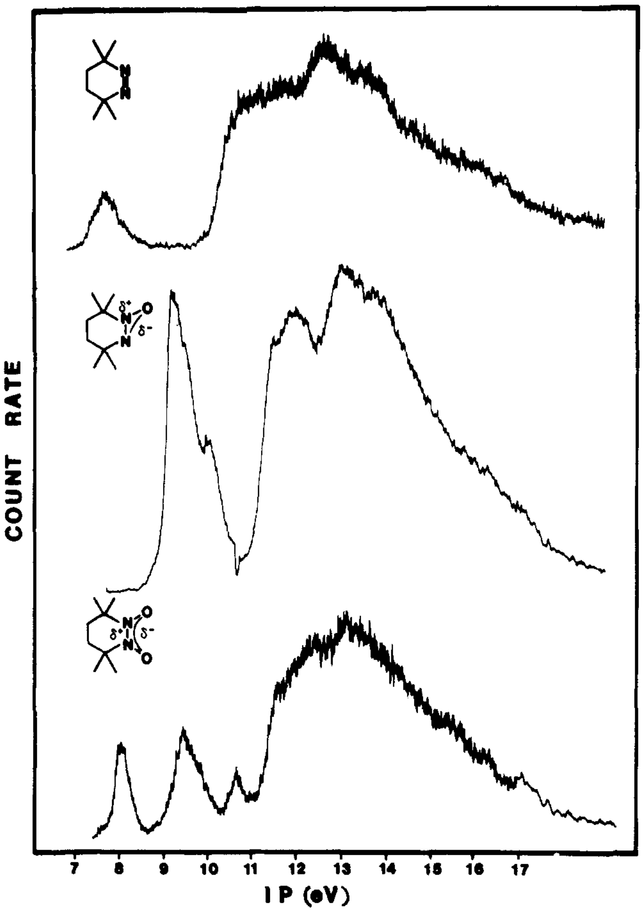


Figure 2. Photoelectron spectra of six-membered ring series (4, 5, and 6).

Table II. Geometries of 1–3 and the Models for 1–6 Calculated by the INDO Method

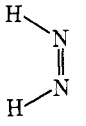
Compd	<CNN, deg[a]	<HNN, deg	R_{NN}, Å	R_{NO}, Å
1	95		1.26	
7		95	1.26	
7		120	1.22	
2	95		1.29	1.23
8		95	1.29	1.23
8		120	1.26	1.23
3[b]	95		1.32	1.24
9		95	1.32	1.24
9		120	1.29	1.24

[a] These CNN angles were found by minimizing the total energy with respect to the NN bond length for **1**, and with respect to the NN and NO bond lengths for **2**. These values were then used for <HNN in the calculations on **7**–**9**. [b] Calculations for **3** were not carried to the full energy minimization.

Table III. Orbital Coefficients in the Azo *N*-Oxides

Compd	π_2 O	π_2 N_1	π_2 N_2	n_+ O	n_+ N_2	n_- O	n_- N_2
2	−0.67	0.13	0.66	0.39	0.43	−0.66	0.29
8 (95°)	−0.73	0.11	0.68	0.66	0.23	−0.52	0.60
8 (120°)	−0.75	0.09	0.66	0.62	0.32	−0.55	0.63

of **1**, **2**, and **3**, we assume that this model system will delineate the significant trends in shape, electron density, and energy of the molecular orbitals of compounds **1–6**. One limitation of calculations based on the protio models **7–9** is that they cannot assess the effects of the carbon skeleton on the MO trends. Comparison of the calculations on the four-membered ring compounds **1–3** and the protio models **7–9** revealed no significant differences in the trends we were interested in—the ordering of the molecular orbitals and the prediction of ionization potentials. The ionization potentials calculated, based on these model compounds and Koopmann's theorem,[15] will not correspond to the observed ionization potentials in absolute value, but significant trends in the ordering of the molecular orbitals and in relative energy differences between orbitals should be preserved.



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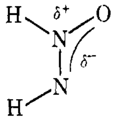

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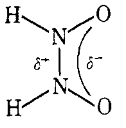

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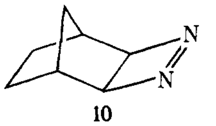

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Azo Compounds 1 and 4. The PE spectra of azo compounds have been extensively studied and the assignments of the first three ionization potentials to ionization from the antisymmetric (n_-) and symmetric (n_+) combinations of lone pair orbitals on the nitrogens and to the π orbital are well established.[16] The first three bands in the PE spectrum of **1** (Figure 1) at 8.77, 10.24, and 11.5 eV are accordingly assigned to the n_-, n_+, and π orbitals, respectively. The observed ionization potentials and assignments are in excellent agreement with the results of Heilbronner, Lemal, et al., for 3,4-diazatricyclo[4.2.1.0^{2,5}]non-3-ene (**10**).[17] The splitting between the π orbital and the σ levels is much greater in **1** than in **10** and allows a more precise assignment of the ionization for the π level in the four-membered-ring azo compounds.

The PE spectrum of azo compound **4** has recently been reported by Houk, Engle, and Chang[18] and our results are identical with theirs. The first ionization potential, at 7.85 eV, is broad and structureless and has been assigned to ionization from the n_- orbital. The second band was not well defined and has been assigned an ionization potential of 10.7 ± 0.1 eV.

Azo *N*-Oxides 2 and 5. Oxidation of an azo group to an azo *N*-oxide changes the ethylenic π system of the azo group to an allyl π system in the azo *N*-oxide, and changes the lone pair interaction from a 1,2 interaction of orbitals of equal energy (azo) to a 1,3 interaction of orbitals of unequal energy (azo *N*-oxide: O_p and N_p). All 1,3 dipoles have a three-atomic-orbital system containing four electrons, and thus π_1 and π_2 are filled in the azo *N*-oxides (see Figure 3).[3] The point of interest for interpreting the PE spectra is the relative ordering of π_2 and the two lone pair orbitals. It is difficult to assess the effect of the difference in energy of the oxygen and nitrogen p orbitals on the relative ordering of the three orbitals of interest. INDO calculations on **2** and **8** were studied as a function of both the CNN or HNN angles and the NNO angle. With the HNN angle of **8** fixed at either 95° or 120°, the ordering of the molecular orbitals was π_2, n_+, and n_- for an NNO angle of 120°. The energy of the π_2 orbital was insensitive to the NNO angle while the relative energies of the lone pair orbitals were calculated to cross at an NNO angle of 115°. The π_2 orbital had most of the electron density on the two end atoms with a node between O and N_1. The lone pair orbitals are shown below and the orbital coefficients are given in Table III.

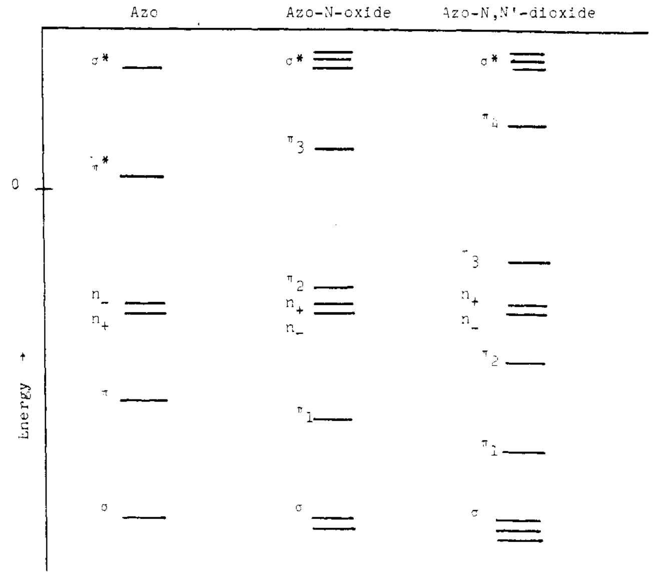
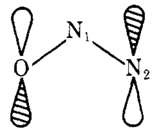
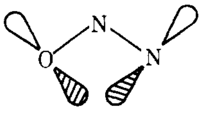


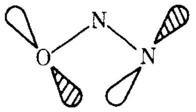
Figure 3. Schematic diagram of the orbital levels in the azo, azo *N*-oxide, and azo *N,N'*-dioxide compounds based on INDO calculations.



π_2



n_+



n_-

In all the calculations on azo *N*-oxides with the NNO angle fixed at 120° the ordering of the MO's was π_2, n_+, and n_-. The difference in energy between the π and n_+ orbitals was calculated to be 1.3 eV for **8** with an HNN angle of 95°, 1.5 eV for an HNN angle of 120°, and 0.6 eV for **2**. These results are based on Koopman's theorem.[14] We also have calculated the total energy of the radical cation formed by loss of an electron from a specified orbital in the ground state molecule, and from this calculated total energy we subtracted the calculated total energy of the ground state molecule; in this way we have taken some account of electron reorganization which must occur during ionization and thus have circumvented some of the problems inherent in Koopman's theorem.[19,20] With this method the calculated energy differences between the π_2 and n_+ MO's in **8** were 0.4 eV for HNN = 95° and 0.3 eV for HNN = 120°; convergence problems complicated calculations on **2**. We expect to see two closely spaced bands in the PE spectra of azo *N*-oxides corresponding to ionization from the π_2 and n_+ orbitals with the n_- orbital coming at higher energy.

The PE spectrum of **2** showed a broad, intense first band capped by two sharp spikes. Whether the two sharp peaks at 9.75 and 9.9 eV should be assigned to separate ionization potentials or to vibrational fine structure is not clear from the spectrum. Further work at higher resolution than we have obtained, or on more tractable analogous compounds (such as the perfluoro derivatives), would be required to resolve this

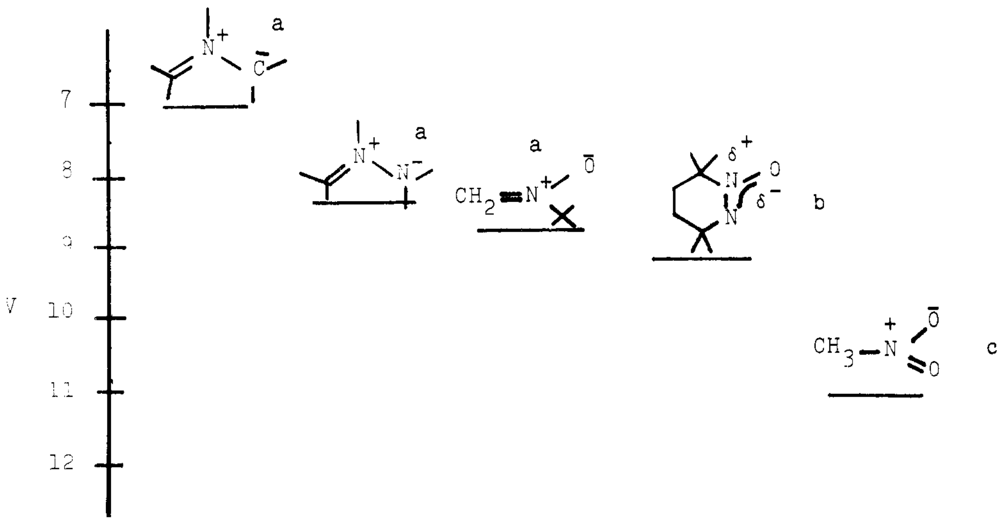


Figure 4. HOMO energies of the series of nitrogen-centered 1,3 dipoles taken from (a) ref 5, (b) this work, and (c) M. J. S. Dewar, M. Shanshal, and S. D. Worley, *J. Am. Chem. Soc.*, **91**, 3590 (1969).

uncertainty. Tentatively, we would assign the π_2 and n_+ molecular orbitals to the first band based upon the calculations and upon the high intensity of the band. The third band in the spectrum at 10.8 eV was assigned to the n_- orbital.

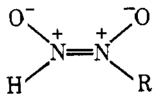
The PE spectrum of **5** shows a broad first band which could not be resolved into separate peaks. This was not unexpected since the energy differences predicted were smaller in this system, and because increasing the size of a molecule usually results in less well defined peaks. We have assigned two ionization potentials, π_2 and n_+, to this first band for the same reasons given for the four membered ring compound **2**. The band at 10.1 eV was assigned to the n_- MO.

The effect of oxidizing an azo system is to raise the energy of the π orbital and to interchange the energy of the n_- and n_+ orbitals.[22]

Houk and co-workers have correlated the energies of the highest occupied π orbitals with reactivity in 1,3-dipolar cycloaddition reactions for a series of 1,3 dipoles.[5] Application of perturbation theory to 1,3-dipolar cycloaddition reactions led them to conclude that reactivity in 1,3-dipolar cycloadditions would increase as the dipole LU was lowered and the dipole HO increased.[5] Since the changes in the HO level are larger than changes in the LU level, they proposed that reactivity would correlate with the HOMO level.[5] Their work did not include azo *N*-oxides, probably owing to lack of information.

In Figure 4 we have plotted the HOMO energies of several 1,3 dipoles. Along the series azomethine ylide, azomethine imine, nitrone, azo *N*-oxide, and nitroalkane the reactivity in 1,3-dipolar cycloaddition reactions decreases. The ionization potential of azo *N*-oxides, measured here, would suggest very little reactivity in cycloaddition reactions for the azo *N*-oxides, as has been observed experimentally.[4,8] The only reported case is that of Rees and co-workers referred to above.[4] This type of negative evidence is not conclusive, but it is consistent with the ideas of Houk et al.[5]

Azo *N,N'*-Dioxides 3 and 6. Oxidation of an azo *N*-oxide to an azo *N,N'*-dioxide changes the allyl π system of the monooxide to a butadiene-like π system in the dioxide, and the 1,3 lone pair interaction into a 1,4 lone pair interaction between orbitals of equal energy. Previous SCF calculations on azo dioxides have emphasized that the major contributor to the electronic structure of azo dioxides is I, with some contribution from structure II to reduce the positive charge on the adjacent nitrogens.[24,25] Our results suggest that this simple type of valence bond picture may not be a good representation for azo dioxides and that a MO picture might be more accurate.



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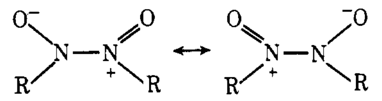

II

Calculations by the INDO method on **3** and on **9** predict the NO bond length to be shorter than the NN bond length as has been observed by DeBoer and Turley.[26] The calculated charges on the nitrogens of diimide *N,N'*-dioxide were +0.29 and on the oxygens −0.35. For comparison the calculated charge on the nitrogen of nitromethane was +0.615. A simple valence model predicts a charge of ±0.5 to +1.0 for the nitrogens of an azo dioxide. The lower value predicted by INDO calculations is supported by the ESCA results, which have been interpreted as a measure of the charge on an atom.[8,27] Calculations based on the MO picture correctly reproduce the geometry of the azo *N,N'*-dioxides and the trends in the ESCA results.[8]

INDO calculations predict the HOMO to be a π orbital similar to χ_3 of butadiene with a node between the oxygens and nitrogens, and of low energy (IP = 8–8.5 eV). The χ_3 orbital of butadiene is antibonding. Replacing the carbons of butadiene with nitrogen and oxygen to give the azo dioxide should stabilize this orbital due to the higher core charges of nitrogen and oxygen. The PE spectrum of 3,3,4,4-tetramethyldiazetine *N,N'*-dioxide (**3**) has a first band at 8.37 eV. The first band in the PE spectrum of 3,3,6,6-tetramethyl-1,2-diazacyclohexene *N,N'*-dioxide (**6**) was at 8.19 eV. Both azo dioxides have a first ionization potential at low energy, much lower than the first ionization potentials of either azo or azoxy compounds, and well in accord with the calculations.

The energies of the lone pair orbitals will be determined by the magnitude of the 1,4-through bond interaction. The lone pair orbitals on the oxygens combine to form a symmetric and an antisymmetric orbital of approximately equal energy. However, these lone pair orbitals can interact with the NN σ and σ^* orbitals and this will give rise to the characteristic through bond interaction (see Figure 5).[28] The symmetric lone pair orbital mixes into the NN σ orbital, of the same symmetry, in an antibonding fashion and goes to higher energy. The antisymmetric lone pair orbital mixes into the NN σ^* orbital in a bonding fashion and goes to lower energy. The calculated

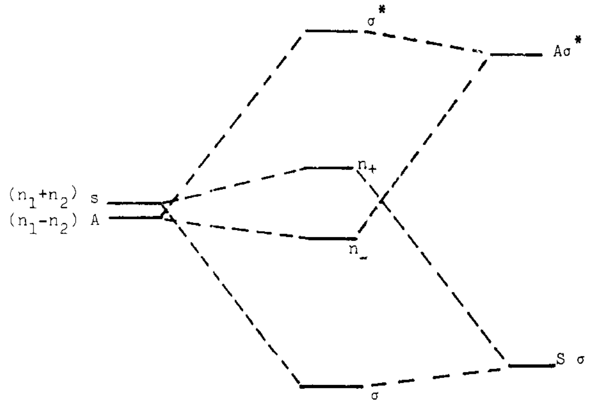

Figure 5. 1,4-Through bond interaction of oxygen lone pairs with the σ and σ* NN bonds in the azo dioxides.

splitting between the lone pair orbitals is 1.75 eV for **9** (95°) and 1.2 eV for **9** (120°). The observed splittings were 1.1 eV for **3** and 0.9 eV for **6**. Thus, the MO picture successfully reproduces the major features of the photoelectron spectra of azo dioxides.

In summary the photoelectron spectrum of azo dioxide **3** was assigned as π orbital 8.37, n_+ 9.73, and n_- 10.6 eV; and the spectrum of **6** was π 8.19, n_+ 9.58, and n_- 10.7 eV.

The general features of the molecular orbital structure of azo dioxides do not account for the known oxidation–reduction chemistry of azo dioxides. The low ionization potential of the π orbital suggests that it would readily give up an electron and be oxidized, while the high energy of the LUMO would argue against further reduction. Compound **6** has been reduced with Si_2Cl_6 and $LiAlH_4$, but it was not oxidized by a variety of reagents, including $KMnO_4$.[8]

The correlation of chemical reactivity and photoelectron spectral data is in the early stages of exploration, and definitive results are not yet available. The correlation of cycloaddition reactivity with the HOMO energy in the nitrogen-centered 1,3 dipoles suggests that PE data may be useful in the design of organic syntheses. The greater understanding of molecular properties, such as oxidation and reduction potentials, which can be obtained with PE data is another area that will be useful to all organic chemists.

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Registry No.—**1**, 54166-22-2; **2**, 40543-89-3; **3**, 34493-89-5; **4**, 19403-24-8; **5**, 54143-34-9; **6**, 54143-35-0.

References and Notes

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