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X-ray Photoelectron Spectroscopy of Nitroso Compounds: Relative Ionicity of the Closed and Open Forms

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Abstract: X-ray photoelectron spectroscopy (XPS or "ESCA") has been used to study several "open" and "closed" ("dimeric") nitroso compounds. As predicted by valence bond and molecular orbital arguments, XPS shows that the nitrogen (1s) peak in the "closed" form is shifted by about 3.4 eV to a higher binding energy relative to the "open" form, and oxygen (1s) shifts in the opposite direction by about 2 eV. A CNDO/2 charge-potential calculation and MINDO/3 "heat of formation" calculation are compared with the observed shifts. A change in nitrogen atomic charge apparently due to sterically disrupted conjugation is also seen in both calculations and spectra.

A typical equilibrium scheme (Figure 1) for the nitroso monomer $\rightleftharpoons$ dimer suggests large charge differences in the two species. It is unusual to measure substantial charge separation on adjacent atoms, and the accuracy of this view has been questioned for some time. Dramatic color variations observed among the monomeric species and an extensive practical utility in dye manufacture have contributed to an interest in nitroso compounds.[1] The closed (or dimeric) structure is invariably colorless or of a pale yellow color, while the monomeric species are usually deep green or blue. (Some of the structures we examined exist in true monomer $\rightleftharpoons$ dimer equilibria while others are always monomers which open and close. We will simply refer to "open" and "closed" structures for both types of equilibria.) By judicious manipulation of the substituent "R", this equilibrium can be shifted or it can change as a function of temperature. Such a system is ideal for study by X-ray photoelectron spectroscopy (XPS or ESCA), which gives a more realistic estimation of atomic charges than most other experimental methods available. Ultraviolet photoelectron spectroscopy studies[2] of the volatile monomers address molecular orbital variations rather than charge distribution.

XPS has been frequently used to estimate the atomic charge distribution in molecules. Since the pioneering work of Siegbahn,[3] correlations have been drawn between calculated charges and shifts in the measured core electron binding energies (E_B values). This has worked especially well for sulfur and carbon compounds. Subsequently, the effects of adjacent charges were taken into account, e.g., the charge-potential model.[4] However, it was found that the presence of unusual relaxation energy changes caused problems in certain molecules. Shirley[5] has demonstrated that a series of amines actually shows a change in binding energy, opposite to that calculated, because of relaxation energy effects. However, relaxation energy problems are generally small when molecules of similar size are considered and the same number of substituents are attached to the measured atom. In addition, the direction in which peaks shift upon adding substituents can be predicted if only relaxation changes are involved.

The nitroso alkane monomer $\rightleftharpoons$ dimer equilibrium is a particularly good system in which to determine if this atomic charge or "ionicity" determination is valid. The monomeric nitroso compound (Figure 1, structure I) is essentially a neutral species with the charge differences being primarily associated with differences in atomic electronegativity. However, the generally drawn valence bond structure for a nitroso dimer shows significant positive charges on the nitrogen and a negative charge on the oxygen.[6] This configuration should cause the dimer to have a higher binding energy for nitrogen and a significantly lower binding energy for oxygen. Some closed forms were examined in an earlier XPS study,[7] but no comparison between open and closed forms was made. Another XPS study of hexanitrosobenzene supported the existence of an unusual oxygen bridging to adjacent NO groups by demonstrating two binding energies for both N and O.[8]

Experimental Section

N,N-Dimethyl-*p*-nitrosoaniline (III) and sodium *p*-nitrosophenolate (VIII) were obtained from the Aldrich Chemical Co. and N,N-dimethyl-*p*-nitrosoaniline was obtained from Eastman Organic Chemicals. They were used as received. 3,3,4,4-Tetramethyl-1,2-diazetine 1,2-dioxide (V) was prepared by the method of Ullman and Singh.[11] 2,3-diazabicyclo[3.2.2]non-2-ene N,N′-dioxide (VII) was prepared by the method of Greene and Gilbert.[7] Benzo[*c*]cinnoline N,N′-dioxide (VI) was prepared by the method of Bellaart.[9] A sample 2,4,6-tri-*tert*-butyl-1-nitrosobenzene (IX) was kindly supplied by Professor A. Streitweiser. 2,6-Dimethyl-4-nitronitrosobenzene, mp 167 °C dec, was prepared by Caros acid oxidation[22] of 2,6-dimethyl-4-nitroaniline[23] in concentrated sulfuric acid.

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(15) Romming, C.; Talberg, H. *Acta Chem. Scand.* **1973**, *27*, 2246-2248.

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(18) Both MINDO/3 and CNDO/2 predict substantially different charges on the two nitrogens in V. These charges in turn predict binding energies about 4 eV different by using a CNDO charge-potential model. Such a large shift is not observed since only one major peak is seen. A more rigorous MO approach is evidently needed to explain this.

(19) Bigelow, R.; Freund, H. *Chem. Phys. Lett.* **1981**, *77*, 261.

(20) Some preliminary experiments in solution using temperature-dependent NMR also suggest that a monomer–dimer equilibrium is taking place.

(21) Clark, D. T.; Dilks, A. private communication.

(22) "Organic Functional Group Preparations"; Sandler, S. R., Karo, W., Eds.; Academic Press: New York and London, 1971; Vol. II, p 409.

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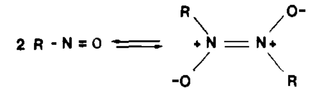


I II

Figure 1. Open (I) and closed (II) forms of nitroso compounds.

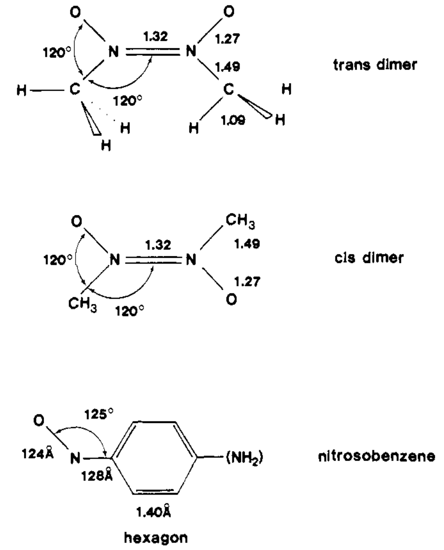


Figure 2. Model compound geometries[2] for MO calculations.

Doubled-sided adhesive tape (3M Scotch tape No. 666) was used to hold powdered samples to a metal probe which was inserted into the spectrometer. All data were collected on a Varian IEE-15 spectrometer operated in the 10^{-5} to 10^{-6} torr range or a Kratos ES-300 spectrometer operated in the 10^{-8} to 10^{-10} torr range. (Spectra of III were obtained by A. Barrie[10] on a Kratos ES-200B spectrometer. These spectra were produced by continuous evaporation of III onto a low-temperature probe during the measurement via a direct inlet shaft fitted through a second insertion lock.) Peak maxima were obtained by a least-squares computer fit of the data to a Gaussian peak shape and were reproducible to ±0.05 eV.

XPS is a surface technique for solids with only the outermost 20–70 Å being examined. Thus, for a crystal size of 0.5 mm, an impurity of less than 0.05% could effectively cover the surface so no bulk material would be seen. Hence, almost any analysis for purity (VPC, HPLC, NMR, or IR) would be essentially useless unless one were looking for a particular contaminant. In general, we have observed that slightly impure organic solids show broadened photoelectron peaks, and the surface composition deviates markedly from expected stoichiometry. The closed forms reported here gave narrow single peaks for O(1s) and N(1s) with atomic ratios of about 1:1. An exception was compound V, which gave a ratio of almost 2:1 for O/N. Since the oxygen peak was single and narrow (2.0-eV fwhh, full width at half-height), it was assumed that a small amount of an oxygen-containing organic solid with a binding energy similar to that of V was also present.

The two types of N and O present in *p*-nitronitrosobenzene (X) produced two nitrogen peaks and a broadened oxygen peak [2.7-eV fwhh vs. 2.1 eV for the other closed species with a single type of oxygen bonding (V, VI, and VIII)].

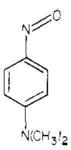
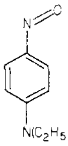
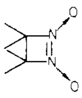
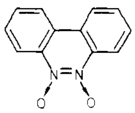
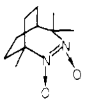
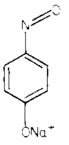
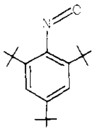
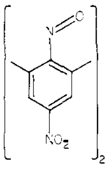
Open or monomeric materials (III, IV, VIII, and IX) were more difficult to measure because of their increased volatility and frequently nonvolatile degradation products.[1] For instance, photochemical degradation can produce radicals that would be trapped by the nitroso functionality. Samples of sodium *p*-nitrosophenolate (VIII) contained a significant amount of water that was not removed in vacuum and produced a broadened and intensified oxygen signal.

The sample of 2,4,6-tri-*tert*-butyl-1-nitrosobenzene (generously donated by Professor A. Streitwieser of the University of California at Berkeley) was small and did not cover the analyzed surface. The probe area not covered by the sample contained oxygen species in substantial amounts and gave a large background signal.

XPS measurements of closed forms are aided both by their lowered volatility (increased ionicity) and by the generation of volatile photochemical degradation products. For instance, V decomposes to C_2H_6 and NO, which are removed from the surface by the vacuum system.[11]

Molecular orbital calculations used standard programs available from the Quantum Chemistry Exchange Program (University of Indiana).

Table I. Binding Energies for the Series of Nitroso Compounds[a]

compd	$E_B(N)$	$E_B(O)$	$\Delta E_B(O\text{-}N)$
 III	400.3	534.1	133.8
 IV	399.7	533.1	133.4
 V	403.4	532.3	128.9
 VI	403.8	531.8	128.0
 VII	403.1	531.7	128.6
 VIII	400.1	(C.532)	(C.132)
 IX	401.6 (403.4)	(C.533)	(C.132)
 X	403.7, 405.5	C.532.5	128.8

[a] Binding energies (E_B) in electron volts; III–X, referenced to the largest carbon peak as 285.0 eV. Greene and Gilbert[7] discussed V and VII and included the N(1s) binding energy for V; when a calibration change is corrected for, their value agrees with the one reported here.

From X-ray data available on dimeric nitroxides,[12,13] the following geometry was used for the cis nitrosomethane dimer: $r(NO) = 1.27$ Å, $r(NC) = 1.49$ Å, $r(CH) = 1.09$ Å, angle ONC = 120°, and angle NNC = 120° (Figure 2). A monomeric model geometry for *p*-nitrosoaniline was derived from the X-ray data for *p*-nitrosoiodobenzene:[14] $r(NO) = 1.24$ Å, $r(NC) = 1.28$ Å, angle CNO = 125°, $r(NH_2\text{-}C) = 1.34$ Å. The structure of N,N-dimethyl-p-nitrosoaniline (III) has been published,[15] but the disordered structure precludes obtaining useful structural parameters from the data.

Results and Discussion

The binding energies of the nitroso compounds are collected in Table I. Four of these compounds (V, VI, VII, and X) are in the closed form, that is, the azo oxide form and four are in the open form (III, IV, VIII, and IX). The closed forms were white or slightly off-white solids, while the open forms were dark colored

Table II. Atomic Charges Calculated for the Dimer of Nitrosomethane and Nitrosobenzene[a]

	atom	CNDO	MINDO/3
		Nitrosomethane	
trans dimer	N	+0.280	
	O	−0.443	
	C	+0.100	
cis dimer	N	+0.272	+0.448
	O	−0.402	−0.524
	C	+0.084	−0.010
		Nitrosobenzene	
	N	+0.042 (+0.046)	+0.296 (+0.301)
	O	−0.179 (−0.202)	−0.422 (−0.445)
	C_1	+0.079 (+0.048)	−0.015 (−0.073)
	C_2	+0.008 (+0.031)	+0.050 (+0.101)
	C_3	+0.003 (−0.057)	+0.020 (−0.128)
	C_4	+0.025 (+0.169)	−0.061 (+0.237)
	(N_H)	(−0.200)	(−0.239)

[a] Units are fraction of an electron; values in parentheses are for *p*-nitrosoaniline; MINDO/3 results were obtained for us by F. Carrion of M. Dewar's laboratory in Austin, TX.

except for IX, which was light green.

(A) Molecular Orbital Calculation of Charge and Binding Energies. There are at least three common ways to calculate the binding energy of a given atom in a molecule—and by implication, its atomic charge. They are Koopmans' theorem, a charge potential model, and a relaxation model. Koopmans' theorem simply equates the calculated orbital energy with the negative of the binding energy or ionization potential. It works very well for the valence band region but fails for core levels where reorganization, i.e., relaxation of electrons, is important. In addition, most semiempirical molecular orbital methods like CNDO, MINDO, and SPINDO do not calculate core orbitals.

The charge potential model uses a valence shell calculation to predict charge distribution within a molecule. This distribution is arbitrarily partitioned among atoms and is used to calculate a simple point-charge potential at a given atom by this field, that is,

$$E_{Bi} = k_i q_i + \sum_{i \neq j} (q_j / r_{ij}) + E_{B0}$$

where E_{Bi} is the binding energy of atom i; k_i is the effect of the atom's charge on the binding energy, i.e., the shift/unit charge; q_j is the charge on atom j; r_{ij} is the distance between i and j; and E_{B0} is a reference point for zero charge.

Finally, several methods are available for calculating electron-relaxation effects. The two previous methods assume that all electrons stay frozen when core ionization takes place or at least that any relaxation of the remaining shells does not vary from molecule to molecule. We have used a variation of a method developed by W. F. Jolly[16] where the next highest atom (i.e., $z + 1$) is used in a calculation of the heat of formation. Comparison of this value with that of the unaltered molecule gives the energy required to create the molecule containing this "next element". This assumes that removing the 1s electron from oxygen makes it resemble F^+.

Standard CNDO/2 and MINDO/3 calculations were made on model compounds, and the calculated atomic charges are summarized in Table II. Point-charge-potential calculations using CNDO/2 charges indicate that both the O and N peaks should change position by about 4.5 eV in going from one form to another. The usual valence bond picture predicts a significant charge separation in the nitrosobenzene dimer, in contrast to the open form. On dimerization, oxygen becomes more negative and nitrogen more positive. Since these changes are large, the small secondary potential exerted by neighboring atoms has little effect on the final value (Table III). The value for *k* in these calculations is somewhat arbitrary. For calculating CNDO/2 charges on N and O, *k* values from 18 to 31 eV/e⁻ are normally used. We chose a value of $k = 20$ eV/e⁻ for O(1s) and 21 eV/e⁻ for N(1s) as values that would be consistent with the current literature. MINDO/3 calculations generate much larger charges on the atoms, and these values have not been used to compare with experimental XPS shifts.

Table III. Point-Charge-Potential (eV) Calculation of Binding Energy Shifts Using CNDO Atomic Charges and $k_O = 20$, $k_N = 21$ eV/e⁻ [a]

	atom	α (nearest neighbor)	β (next nearest)	γ (three atoms away)	total
N			Cis Dimer		
N	5.71	−0.03	−0.11	0.01	5.58
O	−8.04	0.22	0.17	−0.06	−7.71
			Nitrosobenzene		
N	0.88	−0.08	0.01	0.01	0.82
O	−3.58	0.03	0.04	0.03	−3.48

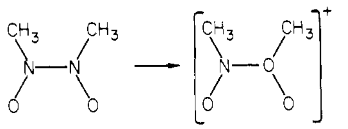
[a] Closed − open(nitrosobenzene): N, 5.58 − 0.82 = 4.76 eV (closed at higher E_B); O, −7.71 − (−3.48) = −4.23 eV (closed at lower E_B).

Table IV. Calculated Heats of Formation (ΔH°_f, eV)[a] and Their Differences with MINDO/2 for Model Compounds[b]

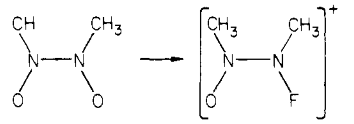
	closed (cis dimer)	open (nitrosobenzene)
(a) ground state	1.41	2.51
(b) N → O⁺	9.18	10.79
(c) O → F⁺	12.32	9.70
(d) b − a (i.e., N(1s))	10.91	7.19
(e) c − a (i.e., O(1s))	7.77	8.28

[a] 1 eV = 23 kcal. [b] Closed − open(nitrosobenzene): N, 10.91 − 7.19 = +3.73 eV; O, 7.77 − 8.28 = −0.51 eV.

The relaxation method took advantage of MINDO/3's ability to calculate heats of formation. For nitrogen ionization, the equation is



and for oxygen ionization, the equation is



The results of such calculations are collected in Table IV. Program parameters are well established for C, N, and O with MINDO/3, but less so for F. For this reason, values for the oxygen photoionization have a larger uncertainty. The derived shifts are in the same direction as calculated with the charge potential CNDO model, but about 20% smaller for nitrogen (3.7 eV) and about an order of magnitude smaller for oxygen (−0.5 eV). The same approach was used for calculations on *p*-fluoronitrosobenzene, and similar results were obtained (+3.63 eV for N and −0.49 eV for O). This molecule was also calculated since F is π-electron donating and would offer a strong σ inductive effect.

(B) Photoelectron Spectra. This series of molecules was originally chosen for XPS examination because the projected ionicity changes should produce large shifts in the binding energy values in opposite directions. Hence, calibration procedures to correct for sample charging would not be necessary, and one could simply measure the difference between the nitrogen and oxygen peaks. If the valence bond picture is valid in the closed form, the oxygen would shift to a lower binding energy and the nitrogen to a higher binding energy. Thus, the net effect would be a smaller peak separation in the closed than in the open form. Although this was observed, the presence of additional oxygen species on some sample surfaces led to an unexpected ambiguity in determining the binding energy of the oxygen. A more direct estimation of the state of

Table V. E_B Shifts (eV) Going from Open to Closed Forms

	O(1s)	N(1s)	increased separation
obsd	−2.2	+3.4	+5.6
calcd (CNDO/2)	−4.0	+4.6	+8.6
calcd (MINDO/3)	−0.5	+3.7	+4.2

the nitroso compound is therefore obtained simply from examining the binding energy of nitrogen.

The N 1s binding energies for the closed forms are 403.4 ± 0.5 eV. In contrast, the E_B values of the open forms (III, IV, and VIII) are 400.0 ± 0.5 eV. A special complication exists for the case of open form IX, which will be discussed later. These E_B values are referenced to a largest carbon peak, arbitrarily set as 285.0 eV. Since the carbons are in various environments, it is expected that this peak will not be as reproducible as the usual "contaminant carbon" standard, and some shifting is expected, although it should not contribute more than about 0.3 eV. This is probably the largest contributing factor to the variation among the E_B values for the N 1s photoelectron peaks. A method that introduced some intentional contamination and determined its position by curve fitting would avoid this shift.

Oxygen peaks (O 1s) were, in general, broader than the nitrogen peaks largely because of contamination. However, it is unambiguous that the O 1s peaks of the open forms are at a higher E_B than the closed forms.

When one compares these observed shifts with those calculated by using the molecular orbital methods, the data in Table V is obtained. The CNDO/2 model works quite well, especially for nitrogen. Slightly larger shifts are calculated than observed, but they are in the right direction. The deviation is greater for oxygen (1.8 eV) than for nitrogen (1.2 eV), and in fact, one would expect this from intermolecular interaction. Clark[17] has shown these interactions to be significant in the XPS spectra of amino acids. Since oxygen is at a terminal point of the molecule, the closed form would allow approach by the neighboring molecules and would reduce the effective negative potential. MINDO/3 calculations are qualitatively correct, but substantially underestimated the oxygen shift. This is probably due to the fact that the parameters that have been put into this model are not as well-known for F as they are for N, O, and C. However, in all cases, the direction of the shift observed is consistent with the model prediction.[18] On this basis, we assume that the calculated charges using the models are approximately correct although perhaps slightly larger than the true values. If this is so, then approximately 0.2 electron is transferred from the N to the O upon going to the closed form. Since there is no unique or nonarbitrary way to define the space around an atom that contains its assigned electrons, we do not expect a better calculated value of the shift.

In addition to the shifts measured for simple open ⇌ closed equilibria, there are several anomalies observed in the spectra of III and IX that bear comment. Even the spectra of vacuum-deposited III show a small N 1s peak at a higher E_B in addition to the major N 1s peak. This is shown in Figure 3. The small peak at 403.7 eV varies in intensity depending upon conditions of the deposition. Since the position of this small peak coincides almost exactly with that of the closed form, we assume that this peak is due to the dimerization of the solid material in the surface region. There is also a chance that this is the result of an unusual shake-up structure which has been reported in *p*-nitroaniline,[19] a related compound. The O 1s peak is broader and the shift is somewhat smaller, so that if the dimerization did take place, it would not be as noticeable but might cause a slight asymmetry. In fact, such an asymmetry is observed, and it appears that a small shoulder is present at a lower binding energy on the O 1s peak.[20]

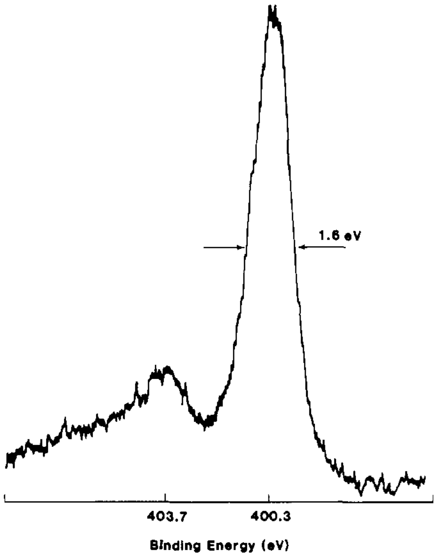


Figure 3. N(1s) region for III (cf. Table I).

Another unusual aspect of this peak concerns the calculated N(1s) E_B for the dimethylamino group. Although not of direct concern in this study of the nitroso group, the shift calculated is greatly different from that observed. Two widely different values are predicted by CNDO/2 for III, but only one main peak is observed. We have not tried more sophisticated MO methods to reproduce this effect; however, it has also been noted by Clark and Dilks.[21]

Finally, the unusual value of 401.6 eV observed for the N 1s of compound IX may be an example of a conformational effect on the charge density. Dimerization is inhibited by both the large *tert*-butyl groups and the electron-donating substituents. However, this material is pale green in color instead of the usual deep green. It is likely that the O of the nitroso group is out of the plane of the benzene ring because of steric interaction. This would decrease the possibility of conjugation and change the chromophoric character, and thus the color, resulting in the binding energy value of 401.6, substantially different from the usual 400-eV value observed for monomeric species. We made several CNDO/2 calculations to determine if a change in charge occurred when this moiety was twisted out of conjugation. The charge on N approximately doubles (from 0.45 to 0.80) on going to a 90° out-of-the-plane twisted conformation, while that on the O remains the same at 0.20. This configuration would cause a shift in the expected direction, although the magnitude of the shift is larger than one would expect. However, using the same *k* factor one calculates an E_B shift of 0.74 eV and measured one of 1.2 eV, i.e., within the experimental range. Hence, we feel that this is one of the rare cases where XPS actually responds to a conformational change in a molecule.

Registry No. I (R = Ph), 586-96-9; *cis*-II (R = Me), 17606-84-7; *trans*-II (R = Me), 37765-15-4; III, 138-89-6; IV, 120-22-9; V, 34493-89-5; VI, 7052-12-2; VII, 34122-40-2; VIII, 823-87-0; IX, 24973-59-9; X, 62272-80-4.