carbonyl compounds by H atom donors may be of the same order.

The chemistry of the triplet state of *sym*-triazine has been studied[34] and was found to be similar to that of the diazabenzenes examined in this work.

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Photoelectron Spectroscopy and Quantum Chemical Analysis of Some *N*-Nitrosamines

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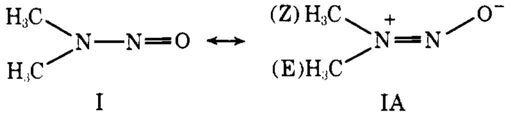
Abstract: Photoelectron (PES) and electronic absorption spectra of a series of *N*-nitrosamines have been obtained and compared with the results of CNDO/2 and CNDO/S calculations; all observable PES and electronic absorption bands have been assigned. The highest occupied molecular orbital is a π orbital, and the subjacent occupied orbital is an n orbital localized on the nitroso oxygen. Bond orders, charge densities, and dipole moments determined by the calculations are presented and discussed. The calculated π charge densities indicate that the amino nitrogen is electron deficient; however, the calculated total charge densities indicate that amino nitrogen is slightly electron rich. Barriers to syn-anti isomerization of dimethylnitrosamine by means of both rotation around the N-N bond and inversion at the nitroso nitrogen have been calculated by means of the CNDO/2 method. The inversional barrier is four times greater than the rotational barrier. The calculated rotational barrier, 18.2 kcal/mol, has the same magnitude as that of the experimentally determined barrier, 23 kcal/mol. Conformational analyses of methylphenylnitrosamine and of diisopropylnitrosamine have been made by means of the CNDO/2 method and have been compared with the analyses of previous investigations.

Introduction

The NMR spectrum of dimethylnitrosamine (I) consists of two singlets.[1] The nonequivalence of the two methyl groups is postulated to be the result of partial double bond character between the two nitrogen atoms; one methyl group is syn (*Z*) and the other is anti (*E*) to the nitroso oxygen.[1,2,3] NMR coalescence studies have given the energy of activation for reorientation of the methyl groups in dimethylnitrosamine (I) to be 23 kcal/mol.[1] The observation of two separate methyl resonances implied a planar or nearly planar configuration for all atoms but hydrogens in dimethylnitrosamine.



I IA

X-Ray diffraction studies[4] on dimethylnitrosaminecopper(II) chloride $(CH_3)_2N\text{-}NOCuCl_2$ and electron diffraction studies on dimethylnitrosamine[5,6] have indicated that the C_2N_2O atoms in both compounds lie in a single plane. A comparison of the bond lengths of gaseous dimethylnitrosamine and of the copper(II) chloride complex reveals that both have the same C-N bond length but the N-N and N-O bond lengths in the complexed molecule are shorter by 0.08 and 0.02 Å, respectively,[6] than the corresponding bond lengths in the gaseous one. The greater shortening of the N-N bond distance in the complex indicates that complexation increases the N-N bond order more than it increases the N-O bond order.

In order to establish the energetic ordering of the molecular orbitals we have studied the photoelectron spectra of some *N*-nitrosamines. Quantum chemical calculations of the CNDO/2 and CNDO/S type have been performed to obtain orbital energies and transition energies of com-

Table I

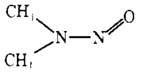
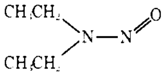
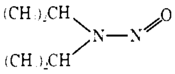
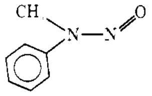
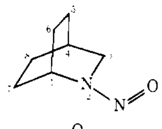
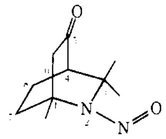
Compd	Structure	Name
I		*N*-Nitrosodimethylamine
II		*N*-Nitrosodiethylamine
III		*N*-Nitrosodiisopropylamine
IV		*N*-Methyl-*N*-nitrosoaniline
V		*N*-Nitroso-2-azabicyclo-[2.2.2]octane
VI		*N*-Nitroso-1,3,3-trimethyl-2-azabicyclo[2.2.2]octan-5-one

Table II

Bond	Length, Å Electron diffraction	This study
N-O	1.235	1.20
N-N	1.344	1.31
$C-N_{syn}$	1.461	1.41
$C-N_{anti}$	1.461	1.41
C-H	1.129	1.12
	Angle, deg	
NNO	113.6	115.0
CNN_{syn}	120.4	121.0
CNN_{anti}	116.4	120.0
CNC	123.2	119.0
NCH	109.6	109.5 (assumed)

pounds I-VI (Table I), and we have used these calculations in the interpretation of the photoelectron spectra. Koopmans' approximation,[7] which sets the negative of the appropriate eigenvalues of the molecular orbitals equal to the experimental ionization potentials, was utilized. Ionization potentials based on the use of this approximation are usually too large because electron reorganization during ionization[8] is neglected; in the customary manner their magnitudes were reduced empirically in order to make comparison with experimental results easier. Our studies indicate that the occupied orbital of highest energy is the π orbital and that the second highest occupied orbital is an n orbital localized mostly on the nitroso oxygen.

The result of our calculation of the rotational barrier is in good agreement with the experimentally determined value. We have calculated the barrier to inversion (a planar dilacement of the oxygen from one side to the other through a linear transition state N-N-O) to be four times greater than the barrier to rotation. The calculated charge densities and bond orders are in good agreement with the results of a previous Pariser-Parr-Pople calculation.[5a] Lehn has previously indicated[5b] that heteroatoms attached to the N atom can bring the barrier to rotation below the carrier to inversion. We believe that the resonance form IA is an insufficient representation of the actual charge distribution in spite of its ability to account for the nonequivalence of the two methyl groups that is revealed by the NMR spectrum.

By means of our calculational methods we have examined the preferred conformations of diisopropylnitrosamine and methylphenylnitrosamine. The preferred conformations agree with those suggested by the NMR data.[3]

Experimental Section

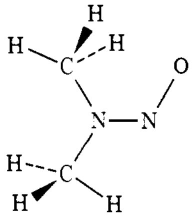
The *N*-nitrosamines listed in Table I were prepared and purified by means of conventional methods. Compound VI is a new compound, and its preparation is described in another paper.[18]

PES spectra were recorded by means of a Perkin-Elmer Model PS-18 photoelectron spectrometer equipped with a 10-cm radius cylindrical electrostatic field deflection analyzer. The He I resonance line at 584 Å (21.22 eV) was used as the ionization source. Solid samples (compounds V and VI) were allowed to sublime in a probe heated to a temperature between 50 and 80°. The liquids I-IV were introduced into the target chamber at 0.1 Torr. The $^2P_{1/2}$ and $^2P_{3/2}$ lines of argon were used to determine resolution; the resolution range of all spectra was between 18 and 25 meV.

The ultraviolet spectra were recorded by means of a Cary Model 14 spectrophotometer in the double beam mode. EPA (by volume 5 parts ethyl ether, 5 parts isopentane, and 2 parts ethanol) was a solvent for all compounds; a 3-methylpentane solution of compound IV was also used.

Quantum Chemical Calculations. The CNDO/2 and CNDO/S calculations were carried out for the series of nitrosamines, I-VI, by means of an IBM 360/65 digital computer. The CNDO/2 program written by Pople and Dobosh[9] was used. The CNDO/S method was originally developed by Del Bene and Jaffe;[10] their later reparameterization[11] was used in this work. The Fock matrix averaging technique suggested by King[12] was employed to accelerate convergence.

The CNDO/2 program was used to calculate the minimum energy bond lengths and bond angles of the >N—N=O group of dimethylnitrosamine, and the equilibrium geometry determined by means of this calculation was usually considered to be the geometry of the same group in the other nitrosamines in the series; the exceptions are described later. Since the C_2N_2O atoms of dimethylnitrosamine have been shown by X-ray and electron diffraction to have a planar geometry,[4,5,6] we used a planar model of the C_2N_2O framework of the molecule. We further assumed that (a) the bond angles in the methyl group are tetrahedral, (b) all of the C-H bond lengths are the same, (c) the two C-N bond lengths are identical, and (d) the methyl hydrogens are oriented in the manner shown in IA'.



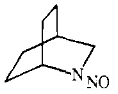
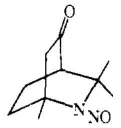
IA'

With these assumptions, the calculations gave the energy-minimized bond lengths and bond angles of dimethylnitrosamine that are presented in Table II; this table includes the experimental bond lengths and bond angles based upon electron diffraction results. The agreement between calculations and experiment is quite good; the calculated bond lengths are slightly shorter than the experimental ones.

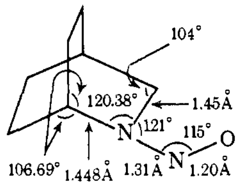
Bond lengths and bond angles within the ethyl and isopropyl groups of II and III were taken to be those given by Pople and Beveridge.[13] Within the phenyl group of IV, the carbon-carbon bond lengths were taken to be 1.395 Å, the carbon-hydrogen bond lengths to be 1.084 Å, and all carbon-carbon-carbon bond angles to be 120°. The energy-minimized bond length of the phenyl-nitrogen bond was found to be 1.41 Å for both a completely planar molecule and for several conformations that have various angles of twist between the planar phenyl and planar NNO groups.

Compounds V and VI were assumed to have standard C-C and C-H bond lengths of 1.54 and 1.07 Å, respectively.[13] All C-C-C and C-C-H bond angles in the methyl groups and in the bicyclic ring structures were assumed to be tetrahedral. The geometry of

Table III. Ionization Potentials

Compd	Type orbital	CNDO/2 Calcd (−3.0 eV)	CNDO/S Calcd (−2.0 eV)	Obsd, eV
I $(CH_3)_2NNO$	π_1	8.99	9.21	9.09
	n	10.23	10.35	9.69
	π_2	15.39	13.54	11.54
	σ	13.48	12.84	12.90
II $(CH_3CH_2)_2NNO$	π_1	8.69	8.93	8.76
	n	9.92	10.21	9.39
	π_2	13.81	12.53	11.61
	σ	12.34	11.15	12.30
III $(i\text{-}Pr)_2NNO$	π_1	8.29	8.60	8.58
	n	9.65	9.85	9.18
	π_2	13.74	12.30	
	σ	11.65	11.11	11.60
IV $PhCH_3NNO$ (planar conformation)	π	8.24	7.59	9.01
	π_{Ph}		8.19	
	n	10.03	10.05	9.66
	π_{Ph_2}	11.28	10.22	10.76
	σ	11.30	10.60	11.50
V 	π_1	8.40	8.70	8.72
	n	9.62	10.01	9.15
	π_2	11.32	10.42	10.97
	σ	10.72	10.32	11.37
VI 	π_1	8.20	8.57	8.63
	n	9.07 (NNO)	8.98 (C=O)	9.29
	n	9.55 (C=O)	9.40 (NNO)	9.49
	σ	10.94	10.57	10.80

the NNO group was kept the same as that in the energy-minimized structure of dimethylnitrosamine. However, the bond angles and bond lengths associated with the CNC position of the molecule were varied in order to find the minimum energy geometry. The resultant geometry has angles at the carbons α to the ring nitrogen which are slightly smaller than the normal tetrahedral angles of the ring structure, C-N bond lengths that are greater than the 1.41 Å energy-minimized value for dimethylnitrosamine, and a C-N-C bond angle near 120°. The compressed ring angles at the α carbons and the C-N bond distances, lengthened with respect to those of dimethylnitrosamine, are the structural features that were adjusted to accommodate the nitrosamine group into the bicyclic ring system. The energy-minimized geometry of compound V is shown in VA. The geometry of the bicyclic ring of compound VI was the same as that of compound V except that the $C^4C^5C^6$ angle (see Table I, compound VI) was increased slightly from tetrahedral to a value approaching 120° and the C^4-C^5 and C^5-C^6 bond lengths were decreased from 1.54 to 1. 52 Å. These changes were made to lessen the strain in the C_α-C(=O)-C_α group. The C=O bond length was assumed to be 1.22 Å.



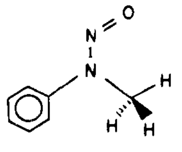
VA

Results and Discussion

Ionization Potentials. Table III presents the four highest occupied molecular orbitals and the orbital energies produced by both CNDO/2 and CNDO/S calculations for compounds I-VI. In each case the occupied molecular orbital with the highest energy is predicted to be a π orbital that is denoted π_1 and is essentially localized on the nitroso group. The orbital is quite similar to the highest occupied π orbital of allyl anion and has large electron density on the oxygen and the amino nitrogen. There is practically a node on the nitrogen bound to oxygen. In each case except that of IV, the next subjacent occupied molecular orbital is predicted to be an in-plane orbital which has major electron density on the oxygen atom and some delocalization onto both nitrogens. This orbital has been designated to be an n orbital because most of its electron density is on the oxygen atom. Both of these occupied orbitals become more energetic and consequently less stable as the alkyl groups attached to N become more complex.

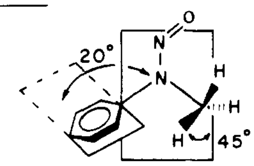
Table IV. Orbital Energies and Assignments

CNDO/2



IV a

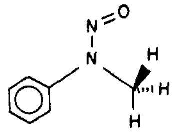
Energy (eV)	Orbital
-11.24	π_1
-13.03	n_{NNO}
-14 28	π_ϕ
-14.30	σ
-14.62	σ
-15.29	π_{mixed}



IV b

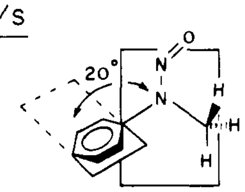
Energy(eV)	Orbital
-11.26	π_1
-13.03	n_{NNO}
-14.26	σ
-14.29	π_ϕ
-14.60	σ
-15.22	π_{mixed}

CNDO/S



IV c

Energy(eV)	Orbital
-9.59	π_1
-10.19	π_ϕ
-12 05	n_{NNO}
-12.22	π_{mixed}
-12.60	σ
-13. 12	σ



IV d

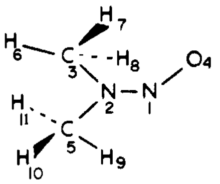
Energy (eV)	Orbital
-9 58	π_1
-10 20	π_ϕ
-12 02	π_{mixed}
-12 29	n_{NNO}
-12.67	σ
-13. 16	σ

The energetic order of the remaining occupied orbitals varies from molecule to molecule, and CNDO/2 and CNDO/S methods give different relative and absolute values. In the cases of the nitrosamines I, II, III, and V, that contain only carbon-hydrogen substituents, the calculations indicate that there are one or two σ orbitals at lower energy than that of the n orbital. Only the more energetic σ is given in Table III. A nitroso π orbital, π_2, occurs at lower energy than does the first σ orbital in the cases of I, II, III, and V. The π_2 orbital has major electron density on the nitrogen and the oxygen of the nitroso group but does not have a node on the nitrosamino group. In the case of VI the CNDO/2 and CNDO/S methods yield opposite orders for the energies of the two n orbitals below the most energetic occupied orbital; the CNDO/2 calculation places the NNO n orbital at higher energy, but the CNDO/S calculation places the CO n orbital at higher energy.

The ordering of the occupied orbitals of methylphenylnitrosamine (IV) depends upon both the conformation chosen and the calculational method used. The results of the CNDO/2 and CNDO/S calculations on two representative conformations are shown in Table IV.

The CNDO/2 method predicts the two highest molecular orbitals to be the nitroso π orbital, π_1, and the nitroso n orbital. The energetic order of these two orbitals does not change upon twisting the phenyl group or rotation of the methyl hydrogens. However, the phenyl localized π orbital,

Table V. Bond Orders and Charge Densities for Dimethylnitrosamine



Bond	π Bond Order CNDO/2	π Bond Order CNDO/S
N-O	0.773	0.752
N-N	0.198	0.217

Atom	π Charge Densities CNDO/2	π Charge Densities CNDO/S
N_1	+0.126	+0.133
N_2	+0.253	+0.202
O_4	-0.312	-0.335

Atom	Overall Charge Densities CNDO/2	Overall Charge Densities CNDO/S
N_1	+0.154	+0.137
N_2	-0.078	-0.109
C_3	+0.094	+0.021
O_4	-0.238	-0.321
C_5	+0.097	-0.028
H_6	-0.001	+0.039
H_7	-0.010	+0.039
H_8	-0.010	+0.039
H_9	-0.005	+0.030
H_{10}	-0.002	+0.048
H_{11}	-0.002	+0.048

π_{Ph}, becomes less energetic in the twisted models than in the planar model.

The CNDO/S method predicts the highest occupied orbital of the planar form to be the nitroso π orbital, π_1. However, in contrast to the CNDO/2 method, the subjacent occupied molecular orbital is predicted to be π_{Ph}. The two remaining orbitals to lie above the highest occupied σ orbitals are the nitroso n orbital and a π orbital which is delocalized over the entire molecule, π_{mixed}. When the phenyl group is twisted out of the plane the two most energetic occupied orbitals retain the same ordering. The π_{mixed} orbital, however, becomes more energetic than the nitroso n orbital. The CNDO/2 calculation indicates that this π_{mixed} orbital is at lower energy than that of either of the two σ orbitals.

Charge Densities, Bond Orders, Dipole Moments. These CNDO/2 and CNDO/S calculations also produced charge densities, bond orders, and, in the case of the CNDO/2 calculations, dipole moments. Bond orders have been defined to be the square of the density matrix element for the out-of-plane p orbitals on the two atoms between which the bond is made.[17] Since the phenyl and carbonyl groups in compounds IV and VI did not appreciably change the bond orders and charge densities for the nitrosamino group of compounds I-VI, only the results from the calculations of these quantities for the nitrosamino group of compound I will be given. Table V presents the π bond orders, π charge densities (relative to the formal structure >N—N=O), and overall charge densities of dimethylnitrosamine. Note the similarity between the CNDO/2 and CNDO/S results. The N-O π bond order is slightly less than one, the N-N π bond order is about 0.2, and the π charge densities give two electron-deficient nitrogens and an electron-rich oxygen. However, the overall charge densities predict an alternating distribution of charge in which the oxygen is electronegative, the nitroso nitrogen electropositive, the amino nitrogen electronegative, and the methyl carbons electropositive. This predicted alternating charge distribution for polar molecules has been pointed out by Pople and Beveridge.[14]

Table VI. π Bond Orders of *N*-Methyl-*N*-nitrosoaniline

Bond	CNDO/2	CNDO/S
N–N	0.1871	0.2014
N–O	0.7804	0.7616
N–C_{Ph}	0.0788	0.0574

The experimental dipole moments of compounds I and IV are 3.98 and 3.62 D, respectively.[15] The dipole moments calculated for these compounds by means of the CNDO/2 method are 2.99 D for I and 2.72 D for IV and are smaller than the observed values. However, the calculated values fall in the same order as the observed ones and little significance should be attributed to the quantitative results because neither CNDO method is parameterized to give good dipole moments. Nevertheless, the calculations may be underestimating the charge separation and contributions of canonical forms such as IA.

The π bond orders for the planar CN_2O portion of compound IV are shown in Table VI. Note that the N-C_{Ph} π bond order is very small, and thus only a small amount of formal conjugation between the phenyl group and the nitrosamino group is predicted. In the case of compound VI, the overall charge density (CNDO/2) of the carbonyl oxygen and carbon are −0.271 and +0.253, respectively. One interesting result in the case of compound VI is that C-3, the methylene carbon α to the carbonyl, is predicted to carry a slight negative charge and its attached hydrogens are predicted to be significantly electropositive.

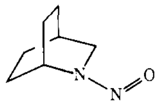
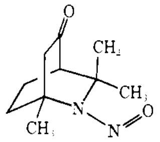
This charge results from the reinforcement of the negative charge on C-3 by the alternating charge distributions from both the carbonyl oxygen and the nitroso oxygen. Because of the predicted electropositive character and the expected enolizable nature of these hydrogens we anticipated easy exchange with dilute NaOD/D_2O. Indeed, both of these hydrogens undergo replacement by deuterium under mild conditions.

Electronic Spectra. The CNDO/S method was also used to calculate electronic transition energies and oscillator strengths. Configuration interaction with 30 single-electron-excitation CI states was used. Table VII gives the predicted lowest energy singlet-singlet transition energies and the oscillator strengths for compounds I-VI. The general result for compounds I-III and V is a weak low-energy n → π* transition and a strong higher energy π → π* transition. Increasing the complexity of the alkyl group (I → III) results in a predicted red shift in both transitions. The n → π* transitions of V are predicted to occur to the blue of the n → π* transitions of I → III, and its π → π* transition is predicted to be between those of I and II.

Calculations for compounds IV and VI likewise show the low-energy n → π* and strong high-energy π → π* transitions. In addition, both compounds have a predicted intermediate transition. In the case of IV, the intermediate transition is a π → π* transition that is primarily localized on the phenyl group and has an intermediate intensity; the position of the band is influenced by the nitroso group. It is predicted to occur near the position of the lowest energy π → π* transition of benzene. In the case of the twisted conformations of IV the predicted n → π* transition is red shifted from that of the planar form, and the nitroso π → π* transition remains at practically the same position.

In the case of VI, the predicted intermediate transition is an n → π* transition of the carbonyl group and has a low intensity. It is predicted to occur to the red of the n → π* transition of acetone.

Table VII. Transition Energies (Vertical)

	Exptl		Theor		Type of transition	Oscillator strength
	λ, nm	$\bar{\nu}$, cm^{-1a}	λ, nm	$\bar{\nu}$, cm^{-1}		
I $(CH_3)_2NNO$	358	27,930 w	566	17,660	$n \to \pi^*$	2.0×10^{-6}
	230	43,480 s	200	50,110	$\pi \to \pi^*$	0.149
II $(CH_3CH_2)_2NNO$	363	27,550 w	571	17,520	$n \to \pi^*$	1×10^{-6}
	232	43,100 s	205	48,790	$\pi \to \pi^*$	0.148
III $(i\text{-}Pr_2)NNO$	370	27,027 w	582	17,190	$n \to \pi^*$	0
	233	42,919 s	211	47,320	$\pi \to \pi^*$	0.159
IV CH_3PhNNO	381	26,247 w	552	18,097	$n \to \pi^*_{NNO}$	0
	273	36,630 s	267	37,391	$\pi \to \pi^*_{Ph}$	3.8×10^{-3}
	218	45,872 s	247	40,405	$\pi \to \pi^*_{NNO}$	0.223
V 	347	28,820 w	557	17,970	$n \to \pi^*$	3×10^{-6}
	233	42,920 s	203	49,320	$\pi \to \pi^*$	0.169
VI 	376	26,600 w	532	18,790	$n \to \pi^*_{NNO}$	2.1×10^{-4}
	307	32,570 w	324	30,850	$n \to \pi^*_{C=O}$	2.3×10^{-4}
	235	42,550 s	209	47,920	$\pi \to \pi^*_{NNO}$	0.140

[a] w = weak; s = strong.

The spectra of compounds I-VI included a weak absorption in the 340-400 nm region which showed vibrational structure, and in the case of all compounds except V and VI a vibrational spacing of about 750 cm^{-1} was noted; see Figure 1 and Table VII. When a more polar solvent is used, there was observed a blue shift of the band of IV in this region; this shift is indicative of an $n \to \pi^*$ transition. All compounds also have a strong structureless band in the 215-235 nm region. A change to a more polar solvent caused the band of IV in this region to red shift, and this shift indicates that this band is a $\pi \to \pi^*$ band. Thus, the weak band in the 340-400 nm region is an $n \to \pi^*$ band of the nitroso group while the strong absorption in the 215-235 nm region is a $\pi \to \pi^*$ band. Our calculated results agree qualitatively with these conclusions. It is normal for CNDO/S calculations to predict $n \to \pi^*$ transitions well to the red of the observed positions.

Both IV and VI showed a band intermediate between these two bands. In IV this intermediate band is a broad, relatively intense band that has only a hint of structure. The band of IV is only slightly red shifted in a more polar solvent but the shift does indicate a $\pi \to \pi^*$ transition. Its location is approximately that of the $^1A \to {}^1L_b$ transition in benzene. The calculations predicted in this wavelength range a band for IV which is primarily located on the phenyl group. Therefore, we conclude that this band is a $^1A \to {}^1L_b$ transition perturbed by the nitrosamino group.

In the case of VI there is a weak transition in the 320 nm region which shows structure that has a vibrational progression of approximately 1200 cm^{-1}. This value is approximately that which would be expected for an excited carbonyl stretching vibration. The location of this band is red shifted from the position of a typical carbonyl $n \to \pi^*$ transition. The calculation predicted a weak C=O $n \to \pi^*$ transition in this region; thus, this band is interpreted to be a perturbed $n \to \pi^*$ transition of the carbonyl group in the molecule.

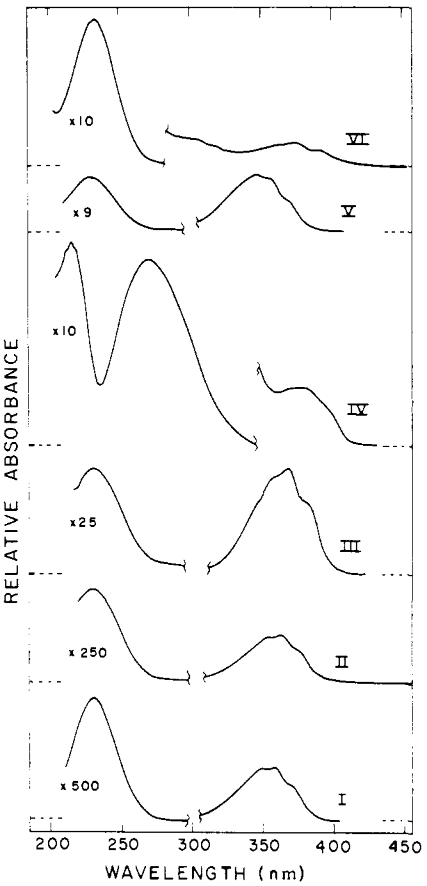


Figure 1. Electronic absorption spectra of the *N*-nitrosamines I → VI

Barriers to Rotation and Inversion. The CNDO/2 method was used to calculate the barrier to rotation around the N-N bond and the barrier to inversion of the nitroso group of dimethylnitrosamine. Two transition states were employed. (a) One was a 90° rotated form in which the N-N-O plane is perpendicular to the C-N-N plane; this transition state is the one for rotation about the N-N bond. (b) The other was a N-N-O linear transition state; this transition state is the one for inversion at the nitroso nitrogen. In each case the approximate barrier was calculated to be the difference between the binding energy of the transition state and the binding energy of the planar form. In the case of the rotational transition, N-O and N-N distances and the NNO angle were energy minimized. For this conformation, both NNC angles were assumed to be 120°, and all C-H bond lengths were taken to be 1.10 Å. The energy-minimized parameters were calculated to be: N-O, 1.18 Å; N-N, 1.34 Å; and ∠NNO, 115°. Note (see Table II) that the N-O distance is predicted to be shorter and the N-N

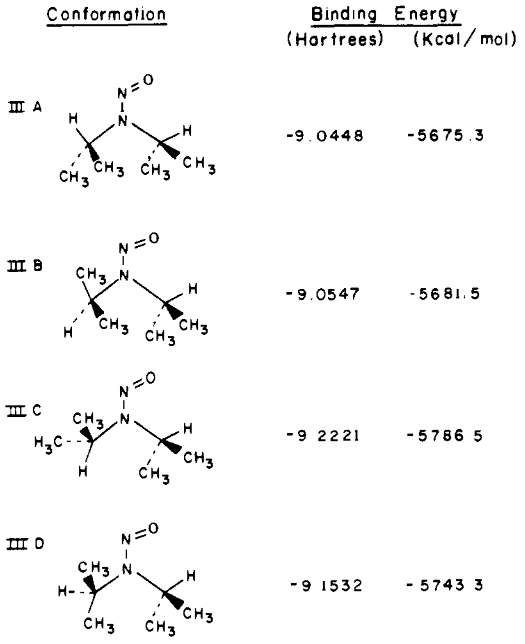


Figure 2. Binding energies of various conformers of diisopropylnitrosamine

distance to be larger than their corresponding values in the planar form. These facts are consistent with the idea that rotation destroys the N-N partial π bond. In the case of the linear transition state, the same assumptions concerning the NNC angle and the C-H distances were made. The N-N and N-O distances were energy minimized, and the resultant values were 1.29 and 1.16 Å, respectively. Note (see Table II) that both of these distances are shorter than the corresponding distances in the planar form. The calculated energy barriers to rotation and inversion are 18.2 and 73.3 kcal/mol, respectively.

The CNDO/2 program was also employed to predict the preferred conformations of molecules III and IV. In the case of IV the parameter of interest is the angle between the phenyl group plane and the nitrosamino group plane.

Binding energies were calculated for the stable conformer of methylphenylnitrosamine (O syn to methyl). The dihedral angle between the C_2NNO plane and the planar phenyl ring was varied from 0 to 90°. However, it was found that the spatial orientation of the methyl hydrogens greatly influenced the binding energy of conformers having various angles of phenyl twist. Steric repulsions between a methyl hydrogen and an ortho hydrogen on the phenyl group caused greater destabilization than steric interaction between a methyl hydrogen and the nitroso oxygen. Therefore, a representative number of methyl conformations were averaged to give a representative binding energy for each angle of phenyl twist. The averaging formula employed was

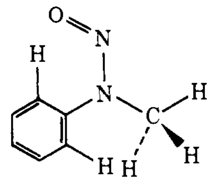
$$\text{binding energy} = \sum_i B_i e^{-(B_i - E_0)/RT} / \sum_i e^{-(B_i - E_0)/RT}$$

B_i is the binding energy for one particular methyl conformation, E_0 is the binding energy of the most stable methyl group conformation for a given phenyl angle of twist, T is room temperature, and the sum extends over all methyl conformations which were calculated for each angle of twist. Note that the formula weights each contributing methyl conformation by a Boltzman factor which gives its relative importance in the overall distribution of conformers. Table VIII presents the binding energy as a function of the dihedral angle between the phenyl group and the nitrosamine group after the averaging has been done.

Table VIII. Binding Energy as a Function of Dihedral Angle

Phenyl angle, deg	Binding energy, hartrees
0	-9.14567
10	-9.14568
20	-9.14532
30	-9.14458
40	-9.14345
50	-9.14207
60	-9.14069
70	-9.13956
80	-9.13884
90	-9.13859

Note that the most stable conformation has a value of the phenyl-nitrosamine angle of about 10°. The binding energy of the unstable conformer of methylphenylnitrosamine shown below was calculated. The difference in binding energy between IVe and the more stable IVa is approximately 7.8 kcal/mol. The steric interaction of the ortho phenylhydrogen with the nitroso oxygen in IVe causes IVa to be the only observed conformer.



IVe

Conformational Analysis. The few conformations of diisopropylnitrosamine that were considered are shown in Figure 2 along with their binding energies. In each of the four conformations interactions between methyl group hydrogens syn and anti to oxygen were minimized. The isopropyl group syn to oxygen was maintained in the same spatial arrangement in each of the four conformers because NMR evidence indicates that α-methine hydrogens resonate at lower fields when they are syn than when they are anti to the oxygen. This arrangement requires the methine hydrogen to be in the plane or very nearly in the plane of the nitroso group. By comparison of the NMR chemical shift of the anti methine resonance in methylisopropylnitrosamine and diisopropylnitrosamine Karabatsos and Taller[3] showed that the anti methine in the latter compound must spend more time in the shielding zone of the nitroso group than does that in the former compound. Thus, these workers assigned the preferred conformation of diisopropylnitrosamine to conformer IIIB of Figure 2. However, conformer IIIB is calculated to be only 6.2 kcal/mol more stable than the most strained conformational possibility, conformer IIIA. Conformer IIID is calculated to be about 62 kcal/mol more stable than IIIB. The most stable conformer is IIIC, and its stability may be attributed to the minimization of hydrogen-hydrogen interactions between the isopropyl group syn to oxygen and the one anti to oxygen. However, IIIC does not account for the observed NMR absorptions. Conformer IIID does account for the observed NMR chemical shifts, and the calculations demonstrate it is energetically more stable than conformer IIIB. Figure 3 shows that the two conformations (IIIB and IIIA) considered by Karabatsos and Taller[3] are predicted by means of the CNDO/2 calculation to be the least stable ones. Thus, the present work elucidates the effects of the hydrogen-hydrogen interactions between the two isopropyl groups on the conformational preference of diisopropylnitrosamine.

Photoelectron Spectroscopy. The photoelectron spectra of compounds I-VI are shown in Figure 4. The shapes of the bands in the spectra of the series are similar; the first band is a broad low intensity band, but the second band is

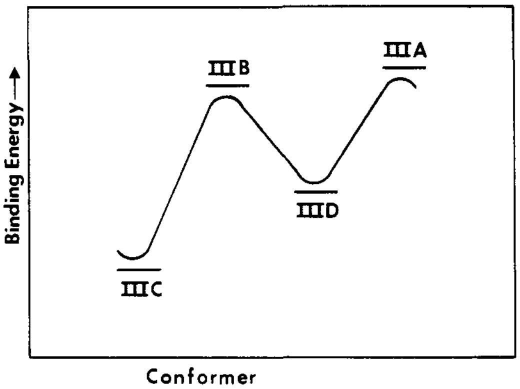
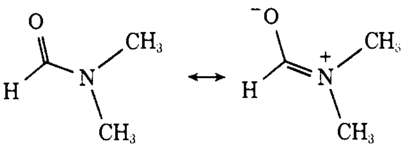


Figure 3. Binding energies of diisopropylnitrosamine conformers. IIIA, -B, -C, and -D are illustrated in Figure 2. Curve is approximate because only the maxima and minima were calculated.

much sharper and is more intense. Table III lists the observed and predicted ionization potentials and also includes the molecular orbital assignment of each ionization potential.

The assignment of molecular orbitals to certain ionization potentials is based on the CNDO/2 and CNDO/S predictions and also on the assignment of molecular orbitals in dimethylformamide (VII).[16] This compound is not only isoelectronic with dimethylnitrosamine, but it also exhibits



VII VIIA

dimethylformamide

hindered rotation around the C-N partial double bond. Thus its electron distribution should be similar to that of dimethylnitrosamine (I → IA).

In dimethylformamide the occupied orbital that has the highest energy is a π orbital and has an ionization potential of 9.25 eV. The subjacent occupied molecular orbital is an n orbital that has an ionization potential of 9.77 eV. The corresponding bands in the photoelectron spectrum of dimethylnitrosamine (I) occur at 9.09 and 9.69 eV, respectively. Further, the separations between the two bands are in good agreement; the value is 0.52 eV in the case of dimethylformamide and 0.60 eV in the case of dimethynitrosamine.

The next greatest ionization potential that is observed is indicated by a band at 11.54 eV in the case of I and at 11.61 eV in the case of II. These ionization potentials have been tentatively assigned to the π_2 N-N-O orbital that was previously described in the results of the calculations. Although the calculations consistently place the ionization potential related to a σ orbital below that of π_2, we assign the lower value to π_2 because the bands are in all cases sharper than those usually associated with σ orbitals and because it is well known that CNDO calculations generally associate σ orbitals with ionization potentials that are too small relative to those associated with π orbitals. The ionization potential of III that we would assign to the π_2 orbital could not be observed with certainty probably because the bands related to σ and π orbitals overlap. The observed unexpected trend of the movement of the π_2 band from 11.54 eV in I to 11.61 eV in II to greater than 11.61 eV in III is consistent with the assignments and the overlap hypothesis.

The results of the CNDO/2 and CNDO/S calculations compare very well with the observed ionization potentials when their values are reduced by 3.0 and 2.0 eV, respectively.[8] The calculations display the same trend in orbital stability as that observed experimentally. That is, as the α substituents become more complex, Me < Et < *i*-Pr, the π and n orbitals become more energetic.

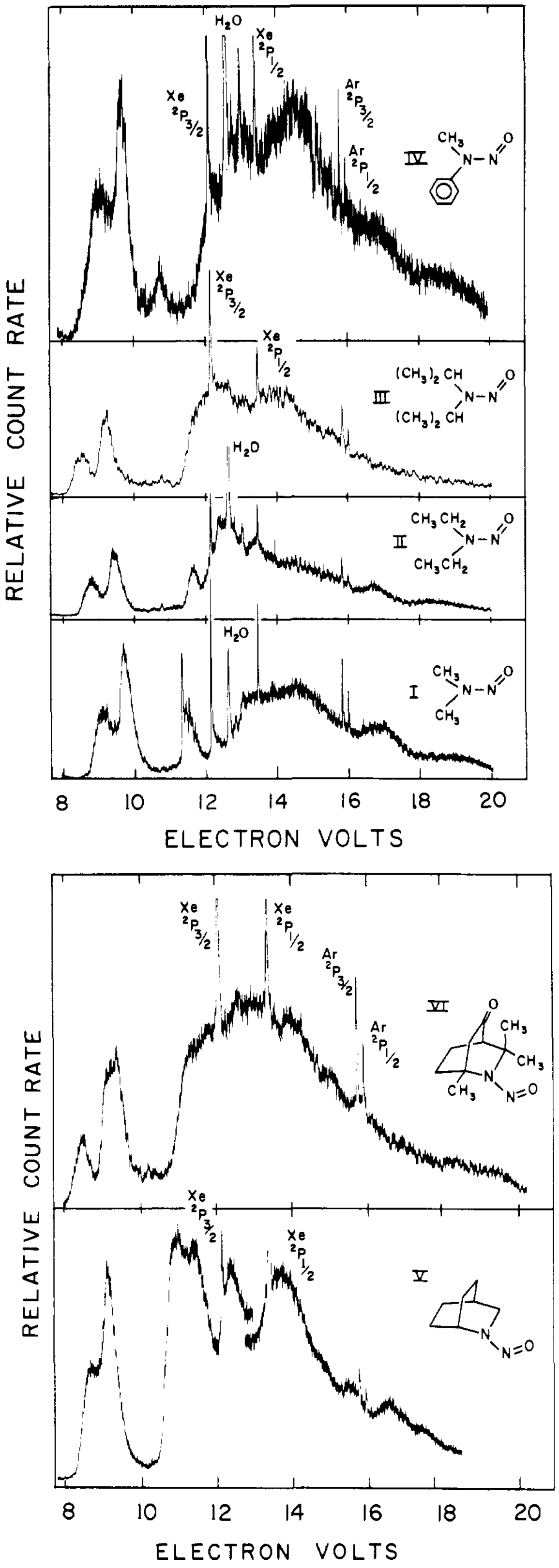


Figure 4. Photoelectron spectra of a series of *N*-nitrosamines.

In the case of methylphenylnitrosamine (IV) the CNDO/S calculations predicted two π orbitals very close in energy to be the most energetic and second most energetic occupied orbitals. Analysis of the PES spectrum shows that the first broad band which has been assigned to the π_1 orbital is at half-height twice as broad as the π_1 band for any of the other *N*-nitrosamines. The n band has approximately the same width at half-height as those of the other nitrosamines. This breadth indicates that the two bands predicted by the calculations to originate from two π orbitals may appear as one broad band in the observed spectrum.

We showed the two limiting resonance forms for dimethylnitrosamine (I and IA). Resonance form IA accounts nicely for the N-N partial double bond character, and it indicates a positive charge on the amino nitrogen and a negative charge on the oxygen. The π charge densities calculated by both CNDO/2 and CNDO/S methods that are shown in Table V agree with this picture. However, the overall charge densities calculated by both methods predict that the amino nitrogen is slightly negative, the nitroso nitrogen slightly positive, and the oxygen very negative. These results lead us to point out that (a) resonance form IA is limited to representation of the charge distribution in the π system and (b) that the σ system readjusts the electron distribution of the nitroso group largely by removing electron density from the α carbons.

Summary

The PES spectra and both calculational methods indicate that the π molecular orbital is higher in energy than the n molecular orbital in all the *N*-nitrosamines studied. As the substituents on the α carbons of the simple dialkylnitrosamines I-III become more complex, both π and n orbitals become more energetic. Both CNDO/2 and CNDO/S calculations show this same trend.

The electronic absorption spectra and the CNDO/S calculations indicate that the *N*-nitrosamines have a weak $n \rightarrow \pi^*$ transition in the 340-400 nm region. The methylphenylnitrosamine (IV) has in addition a transition near 270 nm that is intermediate in both position and intensity and is interpreted to be a transition analogous to the $^1A \rightarrow {}^1L_b$ transition of benzene that has been perturbed by the nitrosamine group. Compound VI has a weak band near 300 nm that is assigned to an $n \rightarrow \pi^*$ transition of the carbonyl group.

The charge densities obtained from the CNDO/2 and CNDO/S calculations require a clarification of the interpretation of the standard resonance form that is usually drawn for *N*-nitrosamines. Note that the π charge densities in Table V indicate an electronegative oxygen and two electropositive nitrogens; the amino nitrogen is the more electropositive. However, the overall charge densities obtained by means of the calculations show an electronegative oxygen, an electropositive nitroso nitrogen, and a slightly electronegative amino nitrogen. These charge densities present a perplexing problem in the interpretation of the significance of the resonance form. A full double bond between the two nitrogens would require a positive charge on the amino nitrogen; a partial double bond between the two nitrogens would involve the redistribution of the lone pair of electrons on the amino nitrogen toward the mitroso nitrogen, and a deficiency of electron density on the amino nitrogen would then occur. Thus, the standard resonance form would appear to be satisfactory. However, the molecule's σ electrons may redistribute themselves and indeed the electropositive character of the α carbon atoms indicates that this redistribution has taken place. Therefore, the standard resonance form should be classified as the limiting case for the π electron system.

The calculated energy barrier, 18.2 kcal/mol, for rotation around the N-N partial double bond agrees well with the experimentally determined barrier E_a = 23 kcal/mol. Because the calculated barrier for inversion of the nitroso nitrogen, 73.3 kcal/mol, is about four times larger than the calculated barrier for rotation, the inversion process for making the two methyl groups of dimethylnitrosamine equivalent may be ruled out.

This work demonstrates the successful application of CNDO/S and CNDO/2 calculational methods for predicting physical and structural properties of *N*-nitrosamines. The use of the CNDO/2 method for determining the preferred conformations of some newly synthesized bicyclic *N*-nitrosamines is the subject of research that is underway.

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