

qualitatively consistent with the percent C2' endo inferred by Cheng et al.²³ However, it is not clear how consideration of some percent of O1' endo character would effect the NMR analysis.

Cohen et al.¹² found a ³¹P doublet in poly(d(AT)), poly(d(AU^{5Br})), and poly(d(IC)) and singlets in poly(d(AU)) and poly(d(GC)). One could imagine the observation of ³¹P singlets even in structures with different sugar puckers or ³¹P doublets despite uniform sugar puckers, which come from differences in other backbone angles. However, if we assume that the ³¹P pattern is related to sugar pucker differences, our calculations allow one to rationalize the surprising difference between poly(d(AU)) and the two 5-substituted polymers poly(d(AT)) and poly(d(AU^{5Br})), since we have noted the importance of the 5 substituent in the attractive thymine-phosphate interaction which stabilizes the alternating sugar geometries. The reason for the difference between poly(d(GC))·poly(d(GC)) and poly(d(IC))·poly(d(IC)) cannot be surmised without detailed calculations on poly(d(IC)) structures.

Our calculations find that dA₆·dT₆ prefers a conformation in which the thymine sugars have C3' endo puckers and adenine sugars have C2' endo puckers over the uniform sugar model (by 2 kcal/mol), over a conformation in which the adenines have C3' endo sugars and thymine C2' endo sugars (by 10 kcal/mol), and over a conformation in which both strands have alternating C2' endo-C3' endo conformations (by 7 kcal/mol). These results are consistent with the experimental observation by Raman spectroscopy of an equal amount of C2' endo and C3' endo sugar puckers in poly(dA)·poly(dT). However, the calculations are able to go further and suggest that the model with thymine sugars C3' endo and adenine sugars C2' endo is the *only* one more favorable than the uniform C2' endo models. This result is consistent with our earlier, less extensive calculations on dA₆·dT₆ and dA₁₂·dT₁₂, where we noted a tendency for thymine C2' endo → C3' endo sugar repuckering, even during unconstrained energy minimization starting with uniform C2' endo conformations. The results of our calculations are in contrast with those of Arnott et al.,¹⁹ who suggest that the conformation of poly(dA)·poly(dT) had adenines C3' endo and thymines C2' endo, based on a model building fit to fiber diffraction data. They also rejected the model in which the sugars attached to adenine and thymine bases had C2' endo and C3' endo puckers, respectively, because of short interstrand contacts between neighboring unpaired A and T bases, even though such a model was shown to give an *R* factor similar to that of the proposed model.²¹ Our investigations *have* obtained a model of the latter type which is energetically more favored than the one corresponding to fiber diffraction data. We stress that our model

is "B-DNA"-like in its properties, unlike that of ref 19, and note that the existence of C3' endo sugar within a B-DNA helix does not imply an "A-DNA"-like geometry of the rest of the helix.

In this context, a referee has suggested that we calculate the fiber diffraction patterns expected for the various dA₆·dT₆ structures presented here. We have not done so for two reasons. Firstly, the limits of fiber diffraction data would not allow a definitive establishment of geometry, whatever the result of the calculation. Secondly, the fiber diffraction study may not be relevant to the solution structure, and a definitive NMR study of a dA_n·dT_n polymer such as carried out by Cheng et al.²³ on d(CGCGCG)₂ is needed to determine unequivocally the conformation(s) of poly(dA)·poly(dT). It is intriguing that the calculations on d(ATATAT)₂ suggest sugar puckers (A-C3' endo, T-C2' endo) whereas those on dA₆·dT₆ suggest the opposite sugar puckers (A-C2' endo, T-C3' endo). We have been able to show that both results can be consistently explained by invoking a stabilizing thymine-phosphate interaction which occurs only when the sugar at the 5' side of the thymine is C3' endo rather than C2' endo. This has structural consequences, also, in that in the lowest energy conformation of dA₆·dT₆, only the two thymines on the 5' end, the last of which has no 5'-phosphate at all to interact with, are in O1' endo rather than C3' endo conformations, with the remaining thymines C3' endo.

In summary, we have noted three important factors which influence sugar puckering properties in B-DNA helices: (a) an intrinsic preference of ~0.5 kcal/mol for deoxyribose rings for C2' endo geometries, (b) greater phosphate-phosphate repulsions when a sugar is C3' endo, which we calculate to be ~2 kcal/mol but whose magnitude is likely to be exaggerated in our calculations, and (c) more attractive thymine-phosphate interactions, when the sugar on the 5' end of the thymine is C3' endo than when it is C2' endo, of 1-2 kcal/mol. Again, this latter figure is likely to be an upper bound, but we suggest that the effect is qualitatively important in understanding sequence-dependent DNA sugar puckering. A final point to be emphasized is the fact that the presence of C3' endo sugars does *not* imply an A-DNA-like helix, as illustrated in Figures 2 and 4.

Acknowledgment. We gratefully acknowledge the support of the National Cancer Institute (Grant CA-25644) in this research and Larry Waggoner, who carried out some of the earlier calculations in this study. The use of the facilities of the UCSF Computer Graphics Lab (R. Langridge, director, and T. Ferrin, faculty manager), supported by NIH RR-1081, is also gratefully acknowledged.

Registry No. d(ATATAT), 79695-11-7; d(TATATA), 79695-10-6; d(GCGCGC), 76186-50-0; d(CGCGCG), 58927-26-7; d(A₆)·d(T₆), 80601-48-5; deoxyribose, 533-67-5.

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Ab Initio Study of the Photodissociation of Nitrosoalkanes and Nitrosamines

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Abstract: The primary step of the photodissociation in CH₃NO and NH₂NO has been investigated by ab initio SCF-CI techniques. The first singlet excited state presents a barrier along the dissociation coordinate both for CH₃NO and for the planar form of NH₂NO. However, NH₂NO prefers a twisted and pyramidalized structure in S₁, with no barrier to dissociation. These features of the S₁ surface explain the observation of a vibrational structure in the n → π* spectrum of (CH₃)₂NNO, dominate the dissociation mechanism (vibrational predissociation vs. intersystem crossing or internal conversion), and may influence the quantum yields in the condensed phase.

In this paper we present an ab initio SCF-CI study of the primary step in the photochemistry of nitroso compounds, i.e., the

dissociation of the X-NO bond. We have concentrated on two of the most important classes of nitroso compounds, nitrosoalkanes

and nitrosamines. Calculations have been run for the ground state and the first excited triplet and singlet states of the simplest representatives of each class, CH_3NO and NH_2NO .

The nature of the primary step in the photochemistry of nitrosoalkanes has been the object of contrasting interpretations in the past,¹⁻⁹ but agreement has been reached eventually. Monomeric nitrosoalkanes undergo cleavage of the C-N bond when irradiated by red light, corresponding to the $n \rightarrow \pi^*$ absorption band, both in the gas phase^{3,6} and in solution.⁷⁻⁹ The subsequent reactions of the R- and NO radicals take place in the ground state. UV irradiation brings the same products.³

The photophysics of $(\text{CH}_3)_3\text{CNO}$ has been the object of the most thorough mechanistic study. The measured fluorescence quantum yields and lifetimes and NO production rates have been interpreted as indicating a radiationless transition to T_1 , S_0 , or a hypothetical dissociative state, rather than any dissociation process taking place on the S_1 surface.¹⁰ The situation is similar for two simple, related compounds: HNO decays (via rotoelectronic coupling) to S_0 ^{11,12} and so probably does CF_3NO .¹³⁻¹⁵ This last molecule bears a close analogy with CH_3NO , as is confirmed by the values of its excitation¹⁶ and dissociation¹⁵ energies: $\nu_{0-0} = 14031.5 \text{ cm}^{-1}$ and $E_{\text{diss}} = 39.6 \text{ kcal/mol}$ (see below for CH_3NO).

The electronic spectrum of CH_3NO has been studied both experimentally¹⁷⁻¹⁹ and theoretically,^{18,20,21} mainly in order to interpret the vibrational structure of the $n \rightarrow \pi^*$ transition. We shall bring up this point in the next section.

As regards the primary step in the photolysis of nitrosamines, less is known, and the subject is still open to debate. The nitrosamines are the starting point for many photoreactions of synthetic interest; most of them employ acid catalysts, which are known to favor the cleavage of the N-N bond to produce aminium radicals.²²⁻²⁴ Nevertheless, the photolysis of nitrosamines both

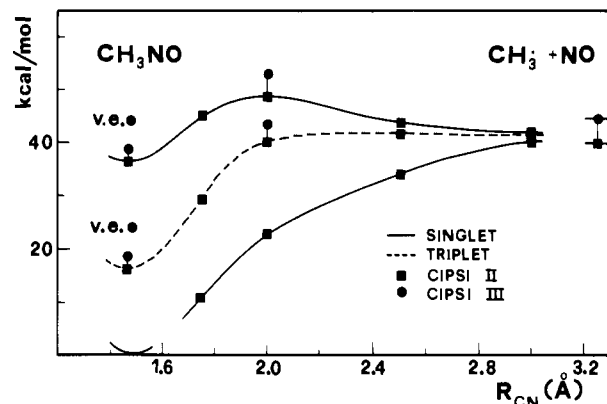


Figure 1. Potential energy curves for CH_3NO . Vertical segments link CIPSI II and III results at the same geometry: v.e. vertical excitation.

in the gas phase and in neutral solvents has deserved much attention. Most nitrosamines, including the simplest ones, are powerful carcinogens which may be found in foods, polluted waters, and the atmosphere, and, therefore, their photolytic degradation by sunlight is an important possibility which has been explored. For the same reason, very sensitive analytical techniques based on the photoconversion of nitrosamines to nitrites have been developed. Altogether, the photolysis of the nitrosamines has been attempted in a wide variety of conditions besides the acidic media; their behavior was found to range from complete or substantial photostability,²²⁻²⁷ possibly associated with syn-anti isomerization,^{28,29} to more or less easy photolysis.³⁰⁻⁴³ This apparent discrepancy of results has stimulated mechanistic research,⁴⁴⁻⁴⁹ showing that at least the simplest compound identified in this class, *N*-nitrosodimethylamine, undergoes photodissociation, followed by fast recombination of the amino and NO radicals, either in the liquid⁴⁴ or gas⁴⁶ phase or in solution.^{45,46}

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Theoretical investigation of the *N*-nitrosamines has been limited so far to the electronic and geometrical structure of the ground state.^{50,51} In the following section we illustrate briefly the computational techniques we have employed. In the two last sections we shall present our results concerning CH₃NO and NH₂NO and discuss their photophysical and photochemical implications.

Methods

All the SCF calculations have been performed with the PSHONDO program,⁵² taking advantage of the Nesbet effective Hamiltonian technique^{53,54} in order to adequately describe the homolytic dissociation and to ensure the degeneracy of the orbitals of NO. The occupation number of the 12th MO, which correlates with the singly occupied p orbital of CH₃ or NH₂, was set equal to 1; those of the 13th and 14th MO's, correlating with the antibonding orbitals of NO, were set equal to 0.5.

The 6-31G* basis set of Pople and co-workers⁵⁵ has been employed throughout when not otherwise specified.

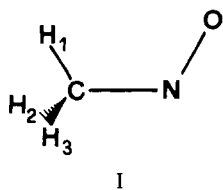
The CI calculations (18 electrons/45 MO's for CH₃NO, 18/43 for NH₂NO) have been performed with the CIPSI perturbative technique;^{56,57} two or three iterative steps (CIPSI II or III) have been run, enlarging the reference space according to the selection thresholds $\eta = 0.05$ and 0.03 for the perturbative contributions to the wave functions. We shall present both CIPSI II and III results whenever it is useful to have an estimate of the level of convergence of the CI and of the trend toward the full CI limit. The largest reference spaces were of 198 determinants, generating up to 8×10^6 single and double excitations. The Møller-Plesset baricentric partition of the Hamiltonian⁵⁶ has been employed.

The geometry optimizations made use of the Murtagh and Sargent technique,⁵⁸ with gradients calculated by finite differences. The reference CI space was kept fixed in this case, after selecting the most important configurations at a few sample geometries in the region of interest. This procedure allowed us to exploit an efficient algorithm (2-3 times faster than the original CIPSI program) implemented by us, consisting essentially in the stockage of all the labels of one- and two-electron integrals and other information needed in the perturbative CI generated only once.

Population analysis, dipole moments, and natural orbitals are based on the first-order perturbed wave functions to be entirely consistent with the second-order perturbed energies (CIPSI III).

CH₃NO

The equilibrium geometry of CH₃NO in its ground state, S₀, is known from microwave spectroscopy;^{59,60} one of the CH bonds is eclipsed with respect to NO. In our calculations we have retained the structure given in ref 60, but we have averaged the HCN bond angles in order to have a local C_{3v} symmetry for the CH₃ group: this simplifies the treatment of internal rotation.



With the parameters $R_{NO} = 1.211 \text{ \AA}$, $R_{CN} = 1.480 \text{ \AA}$, $R_{CH} = 1.094 \text{ \AA}$, $\angle CNO = 113.2^\circ$, and $\angle HCN = 108.5^\circ$, we obtain the

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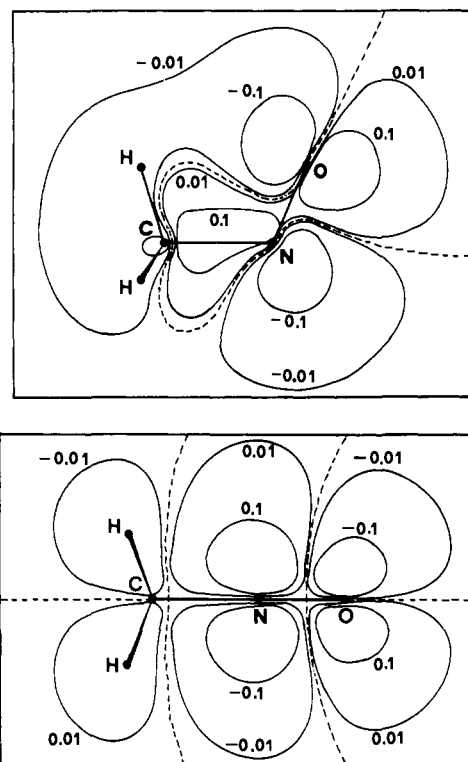


Figure 2. Natural orbital maps for CH₃NO, S₁ state. Top: occupation number (o.n.) = 1.045, C-N-O plane. Bottom: o.n. = 1.046; left-hand side, a plane perpendicular to C-N-O, along the CN bond; right-hand side, as before but along the NO bond.

energies -169.30461 au (CIPSI II) and -169.30616 au (CIPSI III). All the other energies will be given as differences with respect to these two values (see Figure 1).

The dissociation energy of CH₃NO has been calculated relative to the fragments in their experimental equilibrium geometries: $R_{CH} = 1.079 \text{ \AA}$, D_{3h} symmetry, for CH₃ (²A₁)⁶¹ and $R_{NO} = 1.1508 \text{ \AA}$ for NO (² π).⁶² The CIPSI III calculation gives $\Delta E = 44.5 \text{ kcal/mol}$ (CIPSI II, 39.8). The zero-point energy for the CH₃ radical has been evaluated as 19.4 kcal/mol by Pople et al.,⁶³ and those of NO and CH₃NO, 2.7 and 25.8 kcal/mol, respectively, can be deduced from their IR and Raman spectra.^{62,64} Including these vibrational corrections, we obtain a dissociation energy of 40.8 kcal/mol, in agreement with the highest experimental estimates^{65,66} (40 kcal/mol) and with the trend from tertiary to primary nitrosoalkanes⁶⁶ (35 kcal/mol for *t*-Bu, 36.5 for *i*-Pr, and 38.4 for *i*-Bu).

The calculated vertical excitation energies to T₁ and S₁ ($n \rightarrow \pi^*$) are 23.9 and 44.0 kcal/mol, respectively (CIPSI III). It was already known that *t*-BuNO quenches O₂ (¹ Δ_g), accepting the relatively low energy of 23 kcal/mol; on the basis of such experimental evidence, a non-Franck-Condon energy-transfer mechanism was supposed.⁶⁷ In view of our result, it seems that a more usual kind of vertical process may take place. The ΔE for S₁ should be compared with the energy of the strongest peak

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Table I. Mulliken's Population Analysis for CH₃NO (Experimental Geometry)

	S ₀	T ₁	S ₁
C			
σ	5.24	5.22	5.21
π	1.14	1.15	1.15
tot	6.38	6.36	6.36
N			
σ	6.08	5.69	5.74
π	0.86	1.31	1.28
tot	6.93	7.01	7.02
O			
σ	7.14	6.60	6.55
π	1.15	1.68	1.71
tot	8.29	8.27	8.26
H ₁	0.80	0.78	0.79
H ₂ , H ₃	0.80	0.79	0.79
CN bond			
σ	0.21	0.21	0.21
π	0.00	-0.01	0.00
tot	0.21	0.20	0.21
μ _x ^a	-0.575	-0.700	-0.537
μ _z	-2.269	-2.457	-2.411
μ _{tot}	2.431 ^b	2.555	2.471

^a Dipole moments in debyes. The molecule lies in the *xz* plane, with the CN bond along the *z* axis. ^b Experimentally,⁶⁰ μ_{tot} = 2.32 D; unperturbed CI wave function, 2.878 D.

in the *n* → π* absorption spectrum^{17,18} at 14 830 cm⁻¹ (=42.4 kcal/mol).

The population analysis (Table I) and the natural orbital maps (Figure 2) afford a better characterization of the *n* → π* transition. The *n* orbital is mainly an out-of-phase combination of nonbonding orbitals of oxygen and nitrogen. The π*, with nodes between C and N and N and O, is mainly localized on the NO group. Altogether, the CH₃ is almost unaffected by the excitation. Nitrosomethane has been shown to prefer the staggered conformation in the S₁ state, both on theoretical^{18,21} and spectroscopical^{18,19} grounds. The experimental data alone, however, are not sufficient to assess without ambiguity even the skeletal (C–N–O) deformations involved in the electronic transition. Only for the CNO bending is there reasonable agreement between experimental estimates,^{17,18} calculations,^{18,21} and the analogy with HNO,⁶⁸ all indicating an increase of ∠CNO by 4–8°. We have, therefore, optimized the CN and NO bond lengths in the S₁ state, staggered conformation, with ∠CNO = 119.2° and all other coordinates as in S₀. Only modest variations of the two optimized coordinates have been obtained: Δ*R*_{CN} = -0.009 Å and Δ*R*_{NO} = +0.048 Å, with a stabilization of 5.6 kcal/mol of the S₁ state (CIPSI III). In the course of the optimization, the energy changes in the T₁ state parallel almost perfectly those of S₁, indicating that the equilibrium geometries for the two states are not very different: also T₁ is stabilized by 5.6 kcal/mol with respect to the vertical excitation. Larger variations of *R*_{CN} and *R*_{NO} have been obtained with a partial optimization procedure by other authors,¹⁸ 0.08 and 0.11 Å, respectively; an unrefined evaluation of Franck–Condon factors shows that our values are in better agreement with the assignment of the most intense vibronic transitions as Δ*ν*_{NO} = 0 and Δ*ν*_{CN} = 0.

We have calculated the energy difference between the staggered and eclipsed conformations, both with the experimental geometry of S₀ and with the optimized geometry of S₁. We obtain, respectively, 829 and 432 cm⁻¹ for T₁ and 831 and 413 cm⁻¹ for S₁ (CIPSI II); experimentally¹⁹ we have Δ*E*(S₁) = 475 ± 50 cm⁻¹. Probably, the magnitude of the torsional barrier is particularly sensitive to variations in the CNO angle, which determines the distance between the oxygen lone pair and the H atom in the eclipsed position. This observation explains why the fittings of spectral data, based on the hypothesis of a constant barrier height, are hardly ever perfectly satisfactory^{18,19} and immediately suggests an improvement of such models.

Both T₁ and S₁ dissociate to the same fragment states as S₀. We have defined a reasonable reaction coordinate leading to virtual dissociation: *R*_{CH}, *R*_{NO}, and the pyramidalization angle of CH₃ are polynomially interpolated between their values at the minimum in S₁ and those experimentally known for the fragments as *R*_{CN} goes from 1.471 to 4. Å; the CNO angle is kept constant. In S₁ a barrier of 11.5 kcal/mol (CIPSI II) with respect to the minimum is found for *R*_{CN} ≈ 2 Å (see Figure 1): this should be considered as an upper limit to the true value, since no optimization has been carried out in this case. Along the same dissociation path there is no barrier in T₁; the minimum in this state has a depth of 26.2 kcal/mol.

The vibrational structure of the *n* → π* band extends over an energy range approximately corresponding to the height of the barrier in S₁,^{17–19} partly below and partly above the dissociation limit according to our results. The existence of quasi-bound vibronic levels in the range of dissociative energies is certainly accounted for by the presence of the barrier, but our results do not exclude that some of these levels lie above or close to the top of the barrier. Classical^{69,70} and quantum dynamical⁷⁰ model studies on two- and three-dimensional wells have demonstrated that very long-lived vibrational states may exist above the dissociation threshold and that their lifetimes are not monotonically decreasing with energy. These results are in contrast with the formulations which assume complete randomization of the energy distribution among vibrational modes,⁷¹ and, therefore, they cast some doubts on the application of RRKM theory to the cases of (CH₃)₃CNO¹⁰ and CF₃NO,¹³ when this is made in order to rule out the vibrational predissociation mechanism. Of course, also the model calculations quoted above^{69,70} are far from conclusive for our case: apart from quantitative differences, the higher dimensionality of the problem and the possibility of tunneling under the barrier may alter the results significantly. As a matter of fact, no transitions with Δ*ν* ≠ 0 have been observed for the CN stretching mode:^{18,19} therefore, the excitation of this vibration, a necessary condition for dissociation in S₁, must follow an energy transfer from other modes.

According to Reiser et al.,¹⁰ the most probable predissociation mechanism for (CH₃)₃CNO is intersystem crossing to T₁ or internal conversion to S₀ (but in the latter case, their analysis indicates that the unimolecular dissociation rate in S₀ should be much faster than is allowed by RRKM theory). Our preceding remarks are not necessarily in contrast with their conclusions: even in the hypothesis that long-lived vibronic states should be found at energies above the barrier in S₁, their vibrational and electronic relaxations are competing processes whose relative rates are largely unknown and certainly depend on the specific compound and state considered.

Finally, we can rule out another mechanism proposed as a less probable alternative by the same authors,¹⁰ i.e., the crossing from S₁ to a dissociative surface. Indeed, our calculations show that T₁ is not a dissociative state, and no other electronic states lie between S₀ and S₁.

NH₂NO

The NH₂NO molecule has never been detected as such, although it is probably the primary product of the observed gas-phase reaction of NH₂ with NO.⁷²

For the NNO group we have assumed the geometry determined by electron diffraction for (CH₃)₂NNO:⁷³ *R*_{NN} = 1.3440 Å, *R*_{NO} = 1.2345 Å, and ∠NNO = 113.57°. *R*_{NH} = 1.005 was taken by analogy from nitramine,⁷⁴ and standard HNN bond angles of 120° have been assumed. All the atoms lie on the same plane.^{73,75,76}

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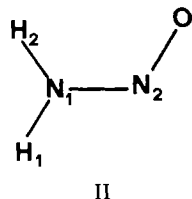
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For the ground state we calculate a total electronic energy of -185.34550 au (CIPSI III) or -185.34982 au (CIPSI II). A comparison of the population analysis for CH_3NO and for NH_2NO (Table II) shows the π -electron donor and σ -acceptor properties of the NH_2 group.

The dissociation energy, with NH_2 ($^2\text{B}_1$)⁷⁷ and NO^{62} at their experimental geometries ($R_{\text{NH}} = 1.024$ Å, $\angle\text{HNH} = 103.3^\circ$), is 56.2 kcal/mol (CIPSI III) or 54.8 kcal/mol (CIPSI II). The zero-point energy of NH_2NO has been evaluated in the SCF approximation, using the 4-31G basis set,⁷⁸ as 22.7 kcal/mol; combined with the experimental vibrational frequencies of NH_2 , quoted by Buenker et al.,⁷⁹ and of NO ,⁶² this brings our prediction of ΔE_{diss} to 47.7 kcal/mol. The fact that NH_2NO is more stable than CH_3NO with respect to dissociation may be related to the partial double bond character of the N–N bond. The difference between the dissociation energy of NH_2NO and that of the simplest compound identified in this class, nitrosodimethylamine (NDM), can be evaluated around 8–12 kcal/mol, by analogy with other pairs of compounds: $\text{NH}_2\text{-NH}_2$ and $\text{NH}_2\text{-N}(\text{CH}_3)_2$,⁸⁰ $\text{Ph-CH}_2\text{-NH}_2$, and $\text{Ph-CH}_2\text{-N}(\text{CH}_3)_2$.⁸¹ This would bring our result in substantial agreement with the value of 40.5 kcal/mol for NDM, based on a collection of thermochemical data and appearance potentials,⁶⁵ which, to our knowledge, is the only experimental estimate of ΔE_{diss} for a nitrosamine.

The calculated vertical excitation energy to T_1 is 62.1 kcal/mol (CIPSI III) or 63.3 kcal/mol (CIPSI II). Sensitization experiments conducted on *N*-nitrosopiperidine allowed $\Delta E(S_0-T_1)$ for that compound to be placed around 59 kcal/mol.⁸²

For S_1 , still at the same geometry, we find $\Delta E = 81.1$ kcal/mol (CIPSI III) or 81.9 kcal/mol (CIPSI II). The population analysis (Table II) and the natural orbital maps (Figure 3) show that the nature of the $n \rightarrow \pi^*$ transition of NH_2NO closely resembles that of CH_3NO ; the main difference is that the π^* orbital of NH_2NO is somewhat delocalized also on the N_1 atom. The change in sign of the π overlap population in going from S_0 to T_1 or S_1 and the node in the π^* natural orbital indicate a weakening of the interactions which favor the planar form of this molecule. The $n \rightarrow \pi^*$ gas-phase spectrum of NDM⁴⁸ shows a coarse vibrational structure with spacings of about 1000 cm^{-1} and the most intense peak at 363.5 nm ($\Delta E = 79$ kcal/mol). Calculations at different R_{NN} bond lengths ($R_{\text{NN}} = 1.50, 1.65, 1.80, 2.00, \text{ and } 2.20$ Å), with all other geometrical parameters kept constant, show that a barrier exists in the S_1 state, around $R_{\text{NN}} = 2.0$ Å (see Figure 4). The minimum takes place at $R_{\text{NN}} = 1.40$ Å, with an elongation of 0.05–0.06 Å with respect to the ground state. At the top of the barrier we find an energy 20 kcal/mol above the minimum in S_1 (CIPSI III) and 100 kcal/mol above the ground state. Even though the latter value may be slightly overestimated for a lack of optimization at the saddle point, this dissociation channel is apparently closed for excitation wavelengths longer than $\lambda = 320\text{--}330$ nm, that is, for probably the whole range of the n

Table II. Mulliken's Population Analysis for NH_2NO (Experimental Geometry)

	S_0	T_1	S_1
N_1			
σ	5.91	5.84	5.84
π	1.76	1.88	1.87
tot	7.67	7.72	7.72
N_2			
σ	5.84	5.52	5.57
π	0.94	1.30	1.27
tot	6.78	6.82	6.85
O			
σ	7.06	6.48	6.42
π	1.30	1.82	1.85
tot	8.37	8.30	8.27
H_1	0.58	0.58	0.58
H_2, H_3	0.60	0.58	0.59
NN bond			
σ	0.11	0.20	0.20
π	0.06	-0.05	-0.05
tot	0.17	0.14	0.15
μ_x^a	-0.917	-0.806	-0.537
μ_z	-3.383	-2.994	-3.002
μ_{tot}	3.505 ^b	3.100	3.050

^a Dipole moments in Debyes. The molecule lies in the xz plane, with the NN bond along the z axis. ^b Experimentally,⁷⁵ for $(\text{CH}_3)_2\text{NNO}$, $\mu_{\text{tot}} = 4.22$ D; unperturbed CI wave function, 3.734 D.

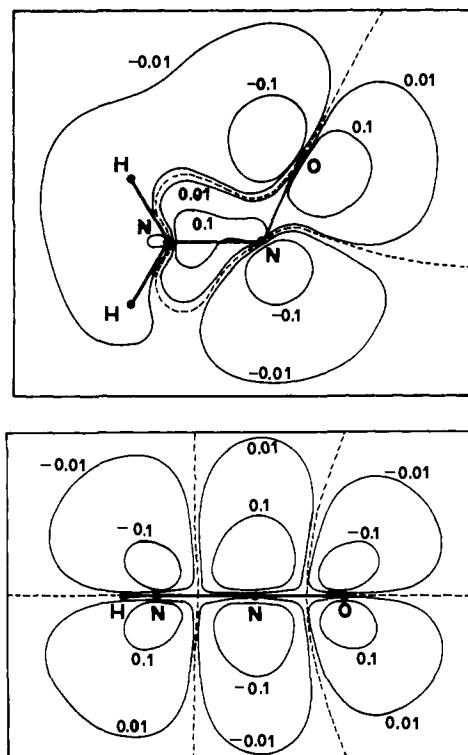
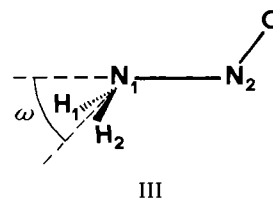


Figure 3. Natural orbital maps for NH_2NO , S_1 state. Top: occupation number = 1.026, N–N–O plane. Bottom: o.n. = 1.025; left-hand side, a plane perpendicular to N–N–O, along the NN bond; right-hand side, as before but along the NO bond.

$\rightarrow \pi^*$ band. However, a series of exploratory calculations has indicated that another kind of geometrical relaxation can take place in S_1 . The preferred structure in the S_1 state is twisted and pyramidalized, as shown below. Making use of the 4-31G basis



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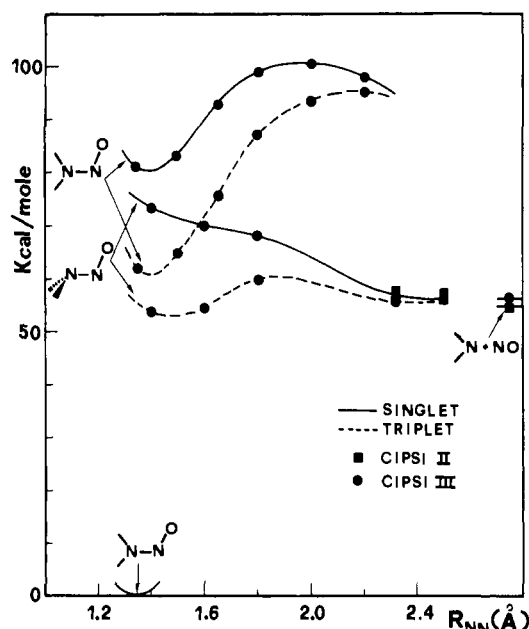


Figure 4. Potential energy curves for NH_2NO .

set, we have optimized at the CI level, with the procedure described in the Methods section, four independent coordinates: R_{NN} , R_{NO} , $\angle\text{NNO}$, and the pyramidalization angle ω , while the HNH bond angle was linearly interpolated as a function of $\cos \omega$ between the ideal sp^2 and sp^3 situations. The minimum in S_1 was found for $R_{\text{NN}} = 2.323 \text{ \AA}$, $R_{\text{NO}} = 1.223 \text{ \AA}$, $\angle\text{NNO} = 110.6^\circ$, and $\omega = 57.7^\circ$; the energy decreased from 66.9 kcal/mol (vertical transition energy in the 4-31G basis) to 40.1 kcal/mol, with $\Delta E = -26.8$ kcal/mol. In the same basis, the ground-state dissociation energy, without zero-point correction, is 47.7 kcal/mol. A CIPSI III calculation with the more complete 6-31G* basis set at the optimized geometry confirmed the remarkable energy lowering with respect to vertical excitation ($\Delta E = -24.3$ kcal/mol) but also showed that the supposed minimum in S_1 lies at an energy very close to that of dissociation. When the R_{NN} distance is increased, the S_1 energy remains almost constant; that is, the minimum does not exist or is very shallow to the best of our knowledge. It should be noted also that the minimum found with the 4-31G basis is shallow and occurs at a very stretched R_{NN} distance: therefore, the difference between the two sets of 4-31G and 6-31G* results, although not negligible, remains within acceptable quantitative limits. For shorter R_{NN} bond lengths, with all other parameters kept constant, the S_1 energy rises gradually, still remaining below that of the planar form (see Figure 4). On the contrary, the T_1 potential surface exhibits a minimum and a barrier also in the twisted form, with $E_{\text{min}} = 53$ kcal/mol above the ground state at $R_{\text{NN}} \approx 1.5 \text{ \AA}$ (unoptimized geometry); this finding should be related to the failure to cause dissociation in *N*-nitrosopiperidine by triplet sensitization.⁸² We have also performed a limited exploration of the interconversion pathways between the planar and twisted-pyramidalized forms: starting from the minimum in S_1 ($R_{\text{NN}} = 1.400 \text{ \AA}$, about 80 kcal/mol above the ground state) and keeping all the A' coordinates fixed, we have on one hand twisted the NN bond by 90° , and, on the other hand, pyramidalized the NH_2 group by 20° . In the first case, at the CIPSI III level, the energy goes up (S_1 , 82.7 kcal/mol; T_1 , 61.2), but the torsional barrier is much lower than in the ground state where $E^* = 21.1$ kcal/mol for NDM in the gas phase;⁸³ in the second case the energy goes

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down (S_1 , 77.5 kcal/mol; T_1 , 58.9), indicating that probably the molecule can rearrange to the twisted-pyramidalized form without passing over any potential barrier.

Summarizing, we have shown that a direct photodissociation channel is open for NH_2NO , even at the lowest excitation energies, but a major geometrical rearrangement of the NNO group is required to avoid the barrier in the S_1 surface. No true minimum exists in that surface for coplanar nuclear arrangements, nor, probably, for the twisted form; this is likely to hold also for all other nitrosamines, which have lower dissociation limits. In spite of this, a vibrational progression is observed in the $n \rightarrow \pi^*$ spectrum of NDM, indicating the presence of quasi bound vibronic states trapped by the potential barrier. The coupling of such states with the dissociative continuum requires the activation of an antisymmetrical coordinate, wagging and twisting of the NH_2 group. The N-N stretching itself is a good candidate for the vibrational progression observed, according to the shape of the potential curve in S_1 .

In conclusion, the quasi-bound states of NH_2NO differ from their hypothetical analogues of CH_3NO for two qualitative aspects: first, the "escape" coordinate is antisymmetrical; second, the potential well is replaced by a saddle point. Here again, internal conversion or intersystem crossing may compete with vibrational predissociation. Which process actually prevails is not without consequence for the photochemistry of the nitrosamines. In the gas phase at low pressures, the molecule eventually dissociates, by whatever mechanism (no fluorescence has been reported for excited nitrosamines, and the fluorescence quantum yields of the analogous nitrosalkanes are very low).^{10,13} In solution, on the contrary, the extra vibrational energy can be dispersed in the medium, after a radiationless transition to the ground state or even to T_1 ; therefore, the dissociation quantum yields may differ significantly from 1, but only if some kind of electronic deexcitation competes efficiently with vibrational predissociation. In the condensed as well as in the gas phase, the very efficient recombination of amino and NO radicals makes it difficult to measure or even to detect the photodissociation rate.^{39,44-48}

A deformation of the potential surface of S_1 , caused by substituents or solvent effect, can easily produce a shallow minimum at rather large R_{NN} distances, and indeed this seems to be the case for *N*-nitrosodiphenylamine.⁴⁹ If such a biradical exists, our calculations indicate that it should be twisted and pyramidalized as in III. Its decay channels should include reaction with other species⁴⁹ and conversion to the ground state, indifferently in the syn or anti planar forms: therefore it constitutes a possible intermediate in the photoisomerization processes^{28,29} as already proposed by Chow.²⁷

Conclusions

In this work we have investigated the geometry changes induced by the $n \rightarrow \pi^*$ transition in the molecules CH_3NO and NH_2NO . We have shown that the nitrosamine undergoes an important structural rearrangement in passing from S_0 to S_1 , whereas the deformation of CH_3NO is modest. The shape of the S_1 potential energy surface of NH_2NO is only consistent with the existence of quasi-bound, not of truly, bound vibrational states. As to CH_3NO , it is questionable whether all the vibrational states observed in the $n \rightarrow \pi^*$ spectrum are bound, even disregarding a tunnel effect. In both cases, vibrational predissociation should compete with transitions to lower electronic states (S_0 or T_1). The balance of such competition can influence the quantum yield of nitrosamine photodissociation in a condensed phase.

Registry No. CH_3NO , 865-40-7; NH_2NO , 35576-91-1.