the experimental value is 0.086, a small A term. Since the principal optical absorption intensity and hence D_0 for this band seems to be due to a different state ($1A_2''$) than that leading to the value of A_1 ($3E'$), the experimentally determined value of $-A_1/D_0$, 0.05 μ_B, must be viewed with suspicion. The moment analysis procedure is apt to be breaking down here in a manner similar to that found for the first band in this molecule.

The third optical absorption band in cyclopropane is the most intense transition of all, $f = 0.7$. It displays a maximum at 10.3 eV, and some superimposed Rydberg structure to low frequencies. The principal transition usually has been assigned to the transition $3e' \rightarrow 1a_2'$, but all theoretical values for the energy of this state have been 2–3 eV higher than experimental values. No MCD data exist this far into the vacuum ultraviolet.

Our computations find three optically allowed states in this region, $6E'$ ($1e'' \rightarrow 2a_2''$), $2A_2''$ ($1e'' \rightarrow 4e'$), and $7E'$ ($3e' \rightarrow 1a_2'$, $1e'' \rightarrow 2e''$) at 10.56, 10.79, and 11.94 eV, respectively. The first of these is a transition to the $3p_z$ Rydberg state with a large oscillator strength ($f = 0.135$), while the second also has considerable Rydberg character and a computed oscillator strength of 0.072. The principal valence transition, $7E'$, with an oscillator strength of 0.376 is found at 11.94 eV.

Our results are thus somewhat at variance with experiment for this band, since our total computed oscillator strength in this region is 0.2 whereas the experimental value is 0.7. Our calculations lead us to assign the third band as due to transitions to the $6E'$ and $2A_2''$ states with considerable configurational mixing between the $6E'$ (Rydberg) and $7E'$ (valence) elementary configurations.

This absorption band lies at rather high energies, and it is probable that the situation is complicated by the interaction of the states mentioned with Rydberg states of higher principal qunatum number since the first ionization potential lies within the band and near to the absorption maximum. Examination of this question would require a larger Gaussian orbital basis set than that used here. Since no MCD data exist and we are in order of magnitude agreement with the experimental oscillator strength, we have not chosen to pursue the matter further. In view of this limitation, our results on the third band should be viewed as tentative; however, it does seem clear that this band cannot be assigned to the ($3e' \rightarrow 1a_2'$) transition in any simple fashion.

D. Conclusions

As described in the first section of this report, cyclopropane exhibits both a large number of degenerate electronic energy levels and an unusually high density of electronic states in the energy region between the onset of optical absorption and the first ionization potential. The D_{3h} point group of the molecule implies that only transitions from the ground state to the A_2'' and E' members of the excited electronic state manifold will be electric dipole allowed. The extensive configuration interaction calculations which we have carried out lead to the conclusion that eight states, six E' and two A_2'', are involved in the first three absorption bands.

The assignments of the absorption and MCD spectra which these calculations afford seem convincing in view of the extensive agreement with the available experimental data, particularly for the first two bands, and the extent of coincidence between experiment and the ab initio calculation of the MCD spectrum is gratifying.

Since the calculations which we present lead to an interpretation of the MCD which is strongly at variance with that afforded by moment analysis of the experimental spectrum and since cyclopropane, while complex, is not atypical of other polyatomic molecules, one is led to the conclusion that the interpretation of MCD spectra under the assumption that a single electronic state is responsible for each band is fraught with danger. States which are undetectably weak in optical absorption may lead to a strong MCD band, and situations like the interaction between the 3s and $3p_{x,y}$ ($1E'$ and $2E'$) Rydberg states in cyclopropane will often be encountered.

This danger is of course the obverse of the power of MCD spectroscopy to generate new and unique information about molecular excited states. Coupled with calculations of sufficient quality as to provide dependable guidance, MCD spectroscopy is a valuable source of information about the electronic states of polyatomic molecules. In the case of cyclopropane, we have argued that the first MCD band consists of two B terms masquerading as an A term, an interpretation which leads to the conclusion that the vertical excitation energy of the previously unobserved but much discussed 3s Rydberg state is 7.49 eV.

Finally, the perturbational configuration interaction approach which we have used in these calculations, while quite economical, would appear to be sufficiently accurate as to allow the ab initio calculations of the MCD of a molecule like cyclopropane as well as the assignment of its absorption spectrum.

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Triplet Methylnitrene: An Indefinitely Stable Species in the Absence of Collisions

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Abstract: The isomerizations of triplet and singlet CH_3–N to CH_2–NH have been studied by molecular electronic structure theory. Stationary point geometrical structures have been determined and characterized (by their harmonic vibrational frequencies) at the double ζ basis set self-consistent field level of theory. At these geometries, correlation effects have been explicitly evaluated by using a basis set expanded to include polarization functions. The triplet CH_3N isomerization to methylenimine is predicted to be endothermic by 18 kcal, with an activation energy of 48 kcal. It may be concluded that ground-state methylnitrene is a relatively stable species in the absence of collisions. However, singlet $CH_2{=}NH$ lies 46 kcal below $^3A_2$ CH_3N and might be accessible if the spin–orbit coupling were substantial. There appears to be little or no barrier separating ^1E CH_3N from ground state $CH_2{=}NH$.

In many ways the reactions of nitrenes parallel those of carbenes.[1] However at present nitrenes must be considered a much less completely characterized class of free radicals. In fact, nitrene rearrangements are so rapid that it is often difficult to exclude

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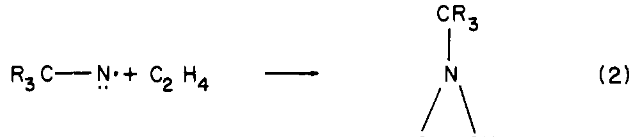
Table I. Vibrational Frequencies (cm^{-1}) for Methylnitrene, Triplet Methylenimine, and the Transition State Connecting Them

CH_3N		transitn state	CH_2NH
3290	(e), CH_3 deg stretch	3450 (a″), CH_2 asym stretch	3640 (a′), NH stretch
3290		3310 (a′), CH_2 sym stretch	3430 (a″), CH_2 asym stretch
3200	(a_1), CH_3 sym stretch	2370 (a′), NH stretch	3300 (a′), CH_2 sym stretch
1620	(e), CH_3 deg deform	1530 (a′), CH_2 scis	1570 (a′), CH_2 scis
1620		1160 (a″), CH_2 rock	1250 (a′), CNH bend + CN stretch
1570	(a_1), CH_3 sym deform	1140 (a′), CN stretch + CNH bend	1120 (a″), CH_2 rock
1090	(e), CH_3 rock	1000 (a″), C–N torsion (O/P CNH bend)	1120 (a′), CN stretch + CNH bend
1090		960 (a′), CH_2 wag	720 (a′), CH_2 wag
1070	(a_1), CN stretch	3460i (a′), reaction coordinate	720 (a″), C–N torsion (O/P CNH bend)

the possibility that a free nitrene was never present at all.[1-3] The general form of the nitrene 1,2 hydrogen shift is seen in eq 1, and

$$R_aR_b\,HC{-}\ddot{N}\cdot \longrightarrow R_aR_b\,C{=}NH \qquad (1)$$

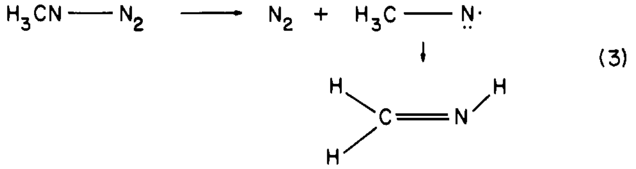
alkylnitrenes undergo this rearrangement so rapidly that the aziridine addition product (see eq 2) has never been observed



(2)

experimentally.[2,3] This has led experimentalists to the conclusion that the existence of alkylnitrenes as stable minima on potential energy surfaces is tenuous.[4,5] However, Wasserman and coworkers[6] have observed the matrix-isolated ESR spectra of several alkylnitrenes, including *n*-propylnitrene, at 4 K.

The prototype nitrene 1,2 hydrogen shift is the rearrangement of methylnitrene, typically starting from methyl azide (see eq 3).



(3)

Although the existence of methylnitrene has never been definitely established experimentally, it appears to be an important intermediate in the photolysis of methyl azide in the gas-phase or in low-temperature matrices.[4,7-10] Milligan's infrared matrix isolation study[8] was apparently the first to establish the methylenimine product of (3), thus indirectly confirming the importance of methylnitrene as an intermediate, however unstable it may be.

Despite experimental skepticism concerning the existence of alkylnitrenes as relative minima on their CNR_3 potential energy surfaces, theory suggests otherwise. First, the triplet 1,2 hydrogen shifts of the related vinylidenes and carbenes occur only with large activation energies,[11-13] of the order of 50 kcal/mol. Second,

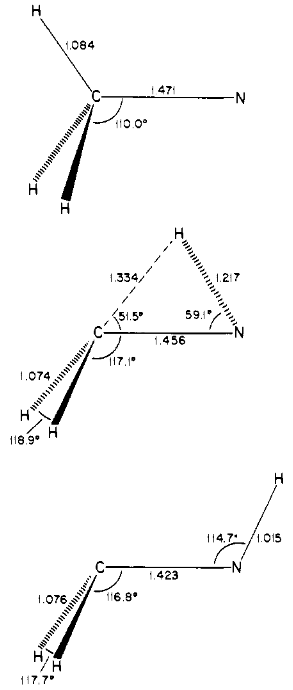
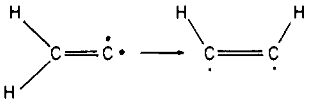


Figure 1. Predicted stationary point geometrical structures for the triplet methylnitrene isomerization.

alkylnitrenes have triplet electronic ground states.[14] For these reasons we have suspected for some time that ground-state alkylnitrenes might be quite stable in the absence of collisions.

Here we support the above hypothesis with a detailed theoretical examination of the potential surface for the triplet methylnitrene → methylenimine rearrangement. Geometrical structures were fully optimized[15] at the self-consistent field (SCF) level of theory[16] by using a standard double-ζ basis set[17] C,N(9s5p/4s2p) and H(4s/2s). For the $^3A_2$ CH_3N isomerization, this procedure leads to the results shown in Figure 1. The $^3A_2$ CH_3N structure is essentially the same as that reported earlier by Yarkony.[14] However, the transition state is more interesting inasmuch as it maintains a plane of symmetry, the only element of symmetry which could reasonably exist. This result is qualitatively different from that obtained previously[12] (by comparable theoretical methods) for the related triplet isomerization. For the vinylidene



(4)

triplet 1,2 hydrogen shift, a plane of symmetry was expected for

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Table II. Summary of Predicted Energies Pertinent to the Methylnitrene → Methylenimine Rearrangement

	triplet			singlet	
	CH_3N	transitn state	CH_2NH	^1E CH_3N	$H_2C=NH$
		Abslolute Energies (hartrees)			
DZ SCF	−93.97912	−93.85227	−93.93575	−93.91360	−93.99555
DZ CI	−94.16313	−94.06168	−94.12915	−94.09590	−94.21922
DZ + P SCF	−94.01673	−93.90666	−93.98081	−93.95249	−94.05143
DZ + P CI	−94.28057	−94.19236	−94.25073	−94.21886	−94.34877
above plus Davidson cor	−94.30311	−94.21931	−94.27417	−94.24161	−94.37685
		Relative Energies (kcal/mol)			
DZ SCF	0.0	79.6	27.2	41.1	−10.3
DZ CI	0.0	63.6	21.3	42.2	−35.2
DZ + P SCF	0.0	69.1	22.5	40.3	−21.8
DZ + P CI	0.0	55.4	18.7	38.7	−42.8
above plus Davidson cor	0.0	52.6	18.2	38.6	−46.3

the transition state, but in fact relaxation to a nonplanar structure was found. The structure of the lowest triplet state of methylenimine is also interesting since it is both twisted (as is triplet ethylene) and pyramidalized.[18] It must be noted that this prediction does not agree with the minimum basis lowest triplet CH_2NH structure of Osamura et al.[19] They propose a planar H_2CN arrangement with the N–H axis rotated 42° out of this plane.

Cartesian force constants were obtained for all three structures and the force constant matrices diagonalized to yield vibrational frequencies to confirm the nature of the stationary points seen in Figure 1.[20] These vibration frequencies are given in Table I and confirm that $^3A_2$ CH_3N and $^3A''$ H_2CNH are genuine relative minima and that the central structure in Figure 1 is a true transition state. Table I also shows that the reaction coordinate (imaginary vibrational frequency) is composed primarily of C–H and N–H stretching contributions. The large magnitude of this frequency (3460i cm^{-1}) and absence of a third real high-frequency (≥ 3000 cm^{-1}) normal mode confirm this. It should also be noted here that experience suggests that these theoretical vibration frequencies are probably of the order of 10% higher than the true vibrational frequencies.[21] Such a correction, however, still leaves us with a large imaginary vibrational frequency (3110i cm^{-1}), suggesting that quantum mechanical tunneling could be very important for relative energies 30 kcal or higher.

For meaningful energetic predictions it was thought necessary to augment this basis set with d functions on carbon ($\alpha = 0.75$) and nitrogen ($\alpha = 0.80$) and p functions on hydrogen ($\alpha = 1.0$). For each of the three DZ SCF stationary points, then, single-configuration SCF energies obtained with this double-ζ plus polarization (DZ + P) basis set are reported in Table II. Furthermore, configuration interaction (CI)[22] was carried out including all single and double excitations relative to the Hartree–Fock reference configuration. With the double-ζ basis set and with use of C_s point group symmetry, there are a total of 7365 configurations of $^3A''$ symmetry for CH_3N, transition state, and CH_2NH. With the larger DZ + P basis set it was necessary to hold the lowest two SCF molecular orbitals (which are 1s or corelike) doubly occupied in all configurations. Even with these restrictions, there are a total of 16 696 configurations of $^3A''$ symmetry in the largest CI treatments reported here. Final estimates of the energy differences of interest were obtained via Davidson's correction[23] for unlinked clusters, the most important subset of quadruple excitations.

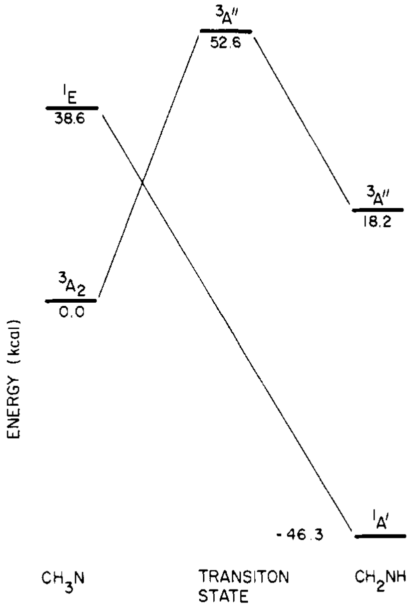

Figure 2. Relative energies, labeled in kilocalories per mole, for the singlet and triplet methylnitrene → methylenimine rearrangements.

The relative energies seen in Table II show clearly that the triplet isomerization of methylnitrene is endothermic. However, polarization functions and correlation effects both lessen the magnitude of this endothermicity, the final prediction being $\Delta H = +18.2$ kcal. Moreover, the triplet barrier height is large, 52.6 kcal, so triplet CH_3N is indeed seen to be a very stable entity in the absence of collisions. By considering zero point energies (obtained from the harmonic vibrational frequencies in Table I), we can predict an activation energy (in the sense of transition state theory) of 48.4 kcal. Consistent with the suggestion in our introduction, the barrier predicted here lies within a few kilocalories of that reported earlier for the vinylidene–acetylene triplet rearrangement.[12]

The rearrangement of singlet CH_3N was also considered by using two-configuration SCF wave functions constructed from the DZ basis set. Starting from the constrained C_{3v} SCF equilibrium geometry appropriate to the ^1E state [$r_e(CH) = 1.086$ Å, $r_e(CN) = 1.458$ Å, $\theta_e(HCH) = 108.6$], no barrier was found for the isomerization to singlet $H_2C = NH$. [The DZ SCF planar equilibrium geometry of the $^1A'$ ground state of $CH_2{=}NH$ was found to be trans $r_e(CH) = 1.075$ Å, cis $r_e(CH) = 1.082$ Å, $r_e(CN) = 1.272$ Å, $r_e(NH) = 1.009$ Å, $\theta_e(C = NH) = 116.0°$, trans

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$\theta_e(HC=N)$ = 118.8°, and cis $\theta_e(HC=N)$ = 124.6°.[24] Thus it seems clear that the singlet electronic state is the species responsible for the widely recognized extreme reactivity[1-4] of methylnitrene. In this sense it appears that singlet alkylnitrenes are even more susceptible to 1,2 hydrogen shifts that the comparable alkylcarbenes, which have small but finite barriers to isomerization.[13]

More complete levels of theory were also applied to ^1E CH_3N and ground state $CH_2{=}NH$, and the results are summarized in Table II. The singlet predictions, at the unlinked cluster corrected DZ + P CI level of theory, are included with the triplet results in Figure 2, an electronic state energy level diagram. Figure 2 illustrates particularly clearly the crossing of the triplet and singlet potential surfaces during the CH_3N isomerization. Should the $^3A''$ and $^1A'$ states be connected sufficiently strongly by spin–orbit coupling or some other interaction, a crossing from the triplet to singlet potential energy surface might occur.

Among recent experimental studies[25-30] designed to test whether alkylnitrenes exist as discrete intermediates, one aspect of the widely cited[2,3] work of Moriarty and Reardon[25] stands in contradiction to the present theoretical predictions. Examining the products of photolysis of ten alkyl azides including the *n*-butyl compound, Moriarty and Reardon concluded that migration of the α substituent occurs synchronously with the departure of molecular nitrogen. The seemingly inexplicable result of their experiments is that the triplet photosensitized process, designed to generate a triplet nitrene intermediate, yielded the same product distribution as the direct photolytic decomposition. In spite of the above experimental data, it seems extremely unlikely to us that the room-temperature triplet 1,2 hydrogen shift of *n*-butyl nitrene could occur with the rate constant suggested,[25] namely, 10^6 s^{-1}.

This apparent conflict with the experiments of Moriarty and Reardon[25] might be explained if the triplet decomposition of the alkyl azide is concerted or if the "triplet" sensitization actually involves energy transfer from a singlet, which is not an impossible occurrence with polycyclic aromatic sensitizers. Moriarty and Reardon (page 1384, ref 25) note that the triplet photosensitizer chrysene may actually yield the singlet state of the azide.

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Ab Initio Self-Consistent Field Calculations on Some Small Amino Acids

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Abstract: Ab initio self-consistent field calculations have been performed on five small amino acids: glycine, alanine, serine, cysteine, and threonine. SCF energies are reported for the nonionic and zwitterionic forms of the molecules using a split-valence 6-31G Gaussian basis set. The ionization potential, proton affinity, and dipole moment were computed for each amino acid. The gaseous zwitterion of each amino acid was calculated to be 34–43 kcal/mol less stable than the neutral form. The difference in energy between the neutral and zwitterionic forms of the amino acids was used to determine the energy difference between the gaseous zwitterion and its solid and solvated states. The calculated properties of the neutral amino acids varied slightly among the five studied: the average ionization potential was 8.3 ± 0.6 eV and the average proton affinity was 222 ± 4 kcal/mol. The individual differences are consistent with the inductive effects of the amino acid side chains. Comparison between other computational and experimental results is also given.

Introduction

Ab initio self-consistent field (SCF) calculations have frequently been performed on atoms and small molecules, but only in recent years have these calculations been extended to larger polyatomic molecules. This is due in large part to advances made in the speed and capacity of computers and increased efficiency in software. A class of molecules now feasible to study at the ab initio theoretical level are those of biological interest; amino acids, $NH_2CHRCOOH$, for example, are ideally suited for this purpose.

Glycine (R = H), the smallest amino acid, has been the subject of several ab initio calculations. The conformation, relative energetics, and SCF energies of glycine and its zwitterion have been computed using a 4-31G Gaussian basis set.[1,2] Ryan and Whitten have studied the nature of the bonding in the glycine zwitterion and in the simplest dipeptide, glycylglycine, using both SCF and limited CI techniques.[3] Semiempirical molecular orbital theory has also been used to study glycine: Oegerle and Sabin have performed CNDO calculations to determine the conformation and molecular properties of this amino acid,[4] while Chung et al. employed the INDO method to study the protonation of glycine.[5] Examples of other theoretical calculations on glycine include extended Hückel molecular orbital theory[6] and the ab initio

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