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The Study of Nitrenes by Theoretical Methods

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5.1 INTRODUCTION

Compounds containing neutral, monovalent nitrogen atoms are known as nitrenes. The parent structure, NH, is called imidogen. Because most stable compounds of neutral nitrogen have a valence of three, it is no surprise that nitrenes are typically very reactive and short lived and, hence, are intermediates.

Nitrenes are commonly generated by decomposition of organic and inorganic azides, although other precursors are known. Azides form bonds to many elements; consequently, many types of nitrenes are known or can be imagined. This review will be limited to the application of theoretical methods to only those nitrenes commonly encountered in organic chemistry.¹

Nitrenes are involved in many useful transformations in classical synthetic organic chemistry.¹ Physical organic chemists seek to understand the role of nitrenes in these reactions and how the structures of nitrenes control their reactivity.² Biochemists append azide groups to the natural ligands of biological macromolecules. Photolysis of the complex between ligand-bound azide and a biomolecule often leads to covalent attachment of the ligand to the biomolecule. This technique, invented by Singh et al.³ and adapted for use with azides by Bayley and Knowles,⁴ has come to be known as photoaffinity labeling.^{5,6} Materials chemists use nitrene chemistry to attach probes to surfaces.⁷ Finally, industrial scientists use azide photochemistry and the nitrenes thus formed in lithography as photoresists.⁸

Nitrenes have attracted the interest of spectroscopists. Spectroscopic studies of nitrenes have been performed in the gas phase, in inert gas matrices, and in solution by using time resolved methodologies.

The energy separations between ground and excited states of nitrenes are relatively small in comparison with the energy separations between these states in closed-shell molecules. This difference dramatically increases the level of complexity and the difficulty in assigning the chemistry and spectroscopy of a transient nitrene to a particular electronic state. In this regard, the proper use of theoretical methods has been invaluable.

This chapter will discuss the use of theory to calculate the minimum-energy geometries of singlet and triplet nitrenes and the energy separations between these states. We will demonstrate how theoretical methods can now routinely be utilized to simulate the vibrational and electronic spectra of nitrenes and, thus, to assign the experimental spectra to one or both of these spin states. Finally, we will review the ways in which theory has explained how the electronic structures of nitrenes controls their reactivity.

There has been recent, dramatic progress in our experimental and theoretical understanding of organic nitrenes.^{9–11} This review will attempt to highlight these developments and

to illustrate the synergism between theory and experiment, which has led to our current level of understanding of nitrenes.

5.2 ELECTRONIC STRUCTURES AND PROPERTIES OF THE SIMPLEST NITRENE, IMIDOGEN RADICAL NH

Very detailed spectroscopic, kinetic, and thermodynamic information has been reported for the simplest azide and nitrene, HN_3 and NH, respectively.^{12–20} The parent nitrene, imidogen, can be produced by photolysis,^{13,15,18–21} thermolysis,²² or multiphoton dissociation^{23,24} of hydrazoic acid (HN₃). Photodecomposition of ammonia^{12,16} or isocyanic acid²⁰ yields NH as well.

Photolysis of HN₃ with 266- and 248-nm light generates NH almost exclusively in the lowest singlet state (¹ Δ) with a quantum yield near unity.^{15,18–20} Formation of NH in different excited states was observed upon photolysis of HN₃ with light of shorter wavelengths.^{13,15,20} For instance, NH in X ³ Σ -, a¹ Δ , b¹ Σ ⁺, A³ Π , and c¹ Π states was found to be formed by UV photolysis of HN₃ at 193 nm and at 300 K with quantum yields ≤ 0.0019 , 0.4, 0.017, 0.00015, and 0.00061, respectively.²⁰

NH in its lowest singlet state $(a^{1}\Delta)$ inserts readily into paraffin CH bonds. In this electronic state the nitrene also abstracts hydrogen atoms from hydrocarbons and undergoes quenching to the ground triplet state.^{25,26} For example, the ratio of these channels is 0.6:0.1:03 in the case of the reaction of ¹NH with ethane:²⁶

$\mathrm{NH}(^{1}\Delta) + \mathrm{C}_{2}\mathrm{H}_{6}$	\rightarrow C ₂ H ₅ NH [*] ₂	(insertion, $\sim 60\%$)
	$\rightarrow {\scriptstyle \bullet C_2H_5} + {\scriptstyle \bullet NH_2}$	(abstraction, $\sim 10\%$)
	$\rightarrow \mathrm{NH}(^{3}\Sigma^{-}) + \mathrm{C}_{2}\mathrm{H}_{6}$	(quenching, $\sim 30\%$).

In the context of this review, the electronic structure and spectroscopy of the simplest nitrene, NH, are very important because they will be useful in the analysis of the more complicated nitrenes. The electronic structure of NH can be 240

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Figure 5.1 Molecular orbitals of nitrene NH. The 1σ -orbital, which is not shown, is the 1s AO on nitrogen.

understood on the basis of elementary molecular orbital (MO) considerations (Figure 5.1).

In NH, two valence MOs, corresponding to the N–H bond (2 σ) and lone pair on nitrogen (3 σ), are occupied by electron pairs. Two more valence electrons must be distributed between two degenerate, nonbonding molecular orbitals (NBMOs), π_x , and π_y , which consist of the $2p_x$ and $2p_y$ AOs on nitrogen. The three lowest electronic states of NH — $^{3}\Sigma^{-}$, $^{1}\Delta$, and $^{1}\Sigma^{+}$ — all arise from the electronic configurations in which the two electrons are distributed between these two NBMOs. The Pauli exclusion prevents electrons with the same spin from simultaneously appearing in the same region of space. Thus, the triplet has the lowest Coulombic repulsion energy of all the low-lying states; hence, it is the ground state of NH (Figure 5.2).

The "closed-shell" component of ${}^{1}\Delta$ is a linear combination (with a minus sign) of two configurations in which the two nonbonding electrons occupy the same 2p orbital, whereas in the "open-shell" component one electron occupies each of the 2p AOs. The two components of a ${}^{1}\Delta$ state (Figure 5.3) may appear different, but symmetry shows that they are degenerate. If the x and y axes are rotated by 45° and the new 2p_x and 2p_y orbitals are expressed as the sum and the difference of the old 2p_x and 2p_y orbitals, the closed-shell singlet in the





Figure 5.2 Schematic depiction of one of the three spin components of the lowest triplet states of NH.



Figure 5.3 Schematic depictions of the (a) closed-shell and (b) open-shell components of the lowest singlet state $(^{1}\Delta)$ of imidogen, NH.

old coordinate system turns into the open-shell singlet and vice versa.

The third of the lowest lying electronic states of NH, ${}^{1}\Sigma^{+}$, would be schematically depicted like the closed-shell singlet in Figure 5.3a. However, the two configurations, which are mixed with a minus sign in the closed-shell component of ${}^{1}\Delta$, are combined with a plus sign in the ${}^{1}\Sigma^{+}$ state. The motions of the nonbonding electrons are "anticorrelated" in the ${}^{1}\Sigma^{+}$ state, so they have a higher Coulombic repulsion energy than in ${}^{1}\Delta$. This is why ${}^{1}\Sigma^{+}$ is a higher-energy electronic state than ${}^{1}\Delta$.

Figure 5.4 presents the state level diagram of NH, constructed on the basis of spectroscopic data.^{12,13,15–21} A value of 1.561 eV (36 kcal/mol) for the singlet-triplet splitting (ΔE_{ST}) in NH was obtained very accurately from spectro-







Figure 5.4 Energy level diagram of imidogen, NH, constructed on the basis of the spectroscopic data.^{12,13,15–21}

scopic data.¹⁶ A series of bands was observed in the absorption and emission spectra of the HN_3 and NH_3 photolysis products, which were assigned to the transitions between different NH states (Figure 5.4). The experimental absorption spectra of NH in the lowest triplet ($X^{3}\Sigma^{-}$) and singlet ($a^{1}\Delta$) states have similar bands in the near UV region with maxima at 336 and 324 nm, respectively.^{12,13,16}

The electronic absorption spectra of NH in the lowest singlet and triplet states were calculated^{26a} using the CASSCF(6,5)/CASPT2 procedure with a large atomic natural orbital (ANO-L) basis set at the experimental bond distances.²⁷ The active space consisted of the three σ -orbitals and two π -orbitals (Figure 5.1) and the six electrons in them. The allowed long-wavelength transitions of singlet and triplet NH (Table 5.1) were predicted at 340 and 308 nm^{26a}, in good agreement with experiment (Figure 5.4). Both transitions are associated with electron promotion from a 3σ (lone pair) orbital to a non-bonding orbital (Figure 5.1). The next transitions in the observed spectra of triplet and singlet NH are associated with electron promotion from a π -orbital to σ^* orbital and are in the vacuum UV region at 143 and 166 nm, respectively. The calculated value of ΔE_{ST} is equal to 45.5 kcal/mol at the complete active space self-consistent field (CASSCF) level and 38.1 kcal/mol when dynamic electron corrolation is added using second-order perturbation theory (CASPT2). The latter value is within about 2 kcal/mol of the experimental value.

5.3 PHOTOCHEMISTRY OF ALKYL AZIDES AND PROPERTIES OF ALKYLNITRENES

5.3.1 Experimental Studies

The first experimental evidence for the existence of alkylnitrenes was provided by Evectron Spin Resonance (ESR) spectroscopy in 1964.²⁸ Wasserman et al.²⁸ detected the ESR spectra of triplet n-propyl, 2-octyl, cyclohexyl, cyclopentyl, α -carbethoxybenzyl and *tert*-butylnitrenes, which were characterized by *D* values in the range of 1.575 to 1.659 cm⁻¹. Two years earlier the same authors were unable to detect the ESR spectrum of cyclohexylnitrene.²⁹ In every case the ESR signals were very weak, and sensitized photolysis of alkyl azides was found to be the most appropriate procedure to generate triplet alkylnitrenes.³⁰ Some triplet alkylnitrenes have subsequently been generated by intramolecular sensitization.^{31,32}

The photolysis of alkyl azides at room temperature cleanly forms imines as products.³³ For example, Kyba and



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nglet ($R_{\rm NH}$ = 1.034 Å) and Triplet ($R_{\rm NH}$ = 1.0362 Å) NH	Procedure
l Vertical Excitation Energies of Si	d Using the CASSCF(6,5)/CASPT2
TABLE 5.1	Calculated

$\pi_{ m x}, \pi_{ m y} ightarrow 4\sigma^{*} 97.2\%$	$4.3 imes 10^{-2}$	166	0.95	7.46	7.18	$2^{1}\Pi$
$3\sigma ightarrow \pi_{ m x}, \pi_{ m y}$ 98.6%	$9.9 imes 10^{-3}$	308	0.93	4.03	5.04	$1^{1}\Pi$
	0	1178	0.96	1.05	0.87	$^{1}\Sigma^{+}$
		I	0.96	0.0	0.0	∇^1
97.3%						
$\pi_{ m x}, \pi_{ m y} ightarrow 4 \sigma^*$	$2.2 imes 10^{-2}$	143	0.96	8.65	7.68	$2^{3}\Pi$
$3\sigma ightarrow \pi_{ m x}, \pi_{ m y}$ 99.4%	$1.8 imes 10^{-2}$	340	0.95	3.65	3.57	$1^{3}\Pi$
			0.95	0.0	0.0	$^{3}\Sigma^{-}$
Configurations	$\operatorname{Strength}$	(uu)	Ref. Weight	$\Delta E_{CASPT2} (eV)$	ΔE_{CASSCF} (eV)	State
	Oscillator					

Source: Pritchina, E.A. and Gritsan, N.P., unpublished results



Abramovitch³⁴ studied in detail photolysis of nine *sec-* and *tert-*alkyl azides. Formation of imines, derived from 1,2-shifts of groups on the ipso carbon atom, was observed.

 $R^{2} \xrightarrow[]{} C \xrightarrow{} N_{3} \xrightarrow{hv} R^{1}R^{2}C \xrightarrow{} NR^{3} + R^{2}R^{3}C \xrightarrow{} NR^{1} + R^{1}R^{3}C \xrightarrow{} NR^{2}$ $R^{3} \xrightarrow{} R^{1} = Ph, 2 - PhC_{6}H_{4}, PhCH_{2}CH_{2}, t-Bu, n-Pr, n-Am$ $R^{2} = Ph, Me, n-Pr, n-Am$ $R^{3} = Ph, Me, H, n-Am$

It was proposed that singlet excited alkyl azides eliminate nitrogen with concomitant rearrangement to form imine products, without the intervention of a nitrene intermediate.³⁴

There are only a few examples of photolysis of alkyl azides that result in any process other than rearrangement to an imine.³³ Photolysis of highly fluorinated azide **1** in cyclohexane gave amide **3** at 18% yield after a hydrolytic workup, implicating a nitrene C–H insertion product **2**.³⁵

$$\begin{array}{c} CF_{3}CHFCF_{2}N_{3} \xrightarrow{hv} CF_{3}CHFCF_{2}NHC_{6}H_{11} \xrightarrow{MeOH} CF_{3}CHFCNHC_{6}H_{11} \\ 1 \end{array} \xrightarrow{0} CF_{3}CHFCNHC_{6}H_{11} \\ 3 \end{array}$$

Intramolecular cyclization via C–H insertion as a minor process was observed upon photolysis of a steroidal azide.³⁶

Dunkin and Thomson³⁷ studied the photochemistry of *tert*butyl azide (4) in an N_2 matrix at 12 K. Using IR spectroscopy, they detected the formation of only one product — imine **5**. DK1234_C005.fm Page 246 Thursday, March 24, 2005 9:41 AM

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The formation of highly strained bridgehead imines was observed on the irradiation of a series of matrix-isolated bridgehead azides.³⁸⁻⁴¹ The photochemistry of matrix-isolated 1-azidonorbornane (**6**) was studied using monochromatic irradiation; IR, UV, and ESR spectroscopy; and trapping with methanol and CO.⁴² The azide photochemistry was very complicated, and the formation of two types of imines (**7** and **8**) and triplet nitrene **9** were observed.



The structure assignment of the nitrene **9** was based on its ESR signal at 8124 G (E = 0, |D/hc| = 1.65 cm⁻¹), a sharp UV peak at 298 nm, and photochemical trapping with CO in Ar at 36 K.

Recently⁴³ photolysis of perfluoromethyl azide **10** was studied in frozen Ar and in pentane at cryogenic temperatures. Photolysis (254 nm) of **10** in pentane at 6 to 10 K produced a persistent ESR spectrum, typical of a triplet nitrene, centered at 8620 G. The spectrum (|D/hc| = 1.736cm⁻¹) is attributed to triplet CF₃-N (³**11**) and is very similar to that of triplet NH (|D/hc| = 1.863 cm⁻¹)⁴⁴ and CH₃-N (|D/hc| = 1.720 cm⁻¹).⁴⁵

Azide 10 ($\lambda_{max} = 257$ nm) was also decomposed in an Argon matrix at 14 K by exposure to 254-nm light, with the



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Figure 5.5 Differential electronic absorption spectra, recorded after irradiation of CF_3N_3 in an Ar matrix at 12 K with 254 nm light after 5-min (curve 1), 25-min (curve 2) and 45-min (curve 3). The calculated absorption bands (TD-B3LYP/6-31^{*}) of triplet CF_3N (positive) and CF_3N_3 (negative) are depicted as solid vertical lines. Insert: differential electronic absorption spectrum detected after 25 min of irradiation.

concurrent formation of sharp, structured absorption bands at 342, 347.5, and 354 nm (Figure 5.5). The UV bands were assigned to the triplet nitrene ³11 on the basis of both the similarity to the spectrum of CH₃N and the results of timedependent density functional theory (TD–B3LYP) calculations.⁴³ The product of formal nitrene rearrangement (CF₂NF, **12**) was also observed and its IR spectrum assigned on the basis of theoretical calculations.^{46a} The formation of ³11 under direct irradiation of **10** indicates that singlet perfluoromethylnitrene ¹11 is indeed an energy minimum on the CF₃N potential-energy surface.



Methylnitrene is the simplest of all alkylnitrenes. Photolysis of methyl azide (CH₃N₃, **13**) does not produce ¹NCH₃ (¹**1**4) as a trappable species, and even attempts to detect it by femtosecond flash photolysis have failed.⁴⁶ Triplet methylnitrene was not formed on direct irradiation^{30,47} of **13**, and only methyleneimine (**15**), the product of formal isomerization of ¹**1**4, was detected in cryogenic matrices.^{48,49}



Triplet methylnitrene can be produced by sensitized photolysis^{30,47} in the condensed phase or in a gas-phase corona discharge.^{50–53} Barash et al.³⁰ and Wasserman⁴⁷ reported a value of the zero-field splitting parameter |D/hc| of 1.595 cm⁻¹ for matrix isolated triplet CH₃N. This earlier experiment is questionable,⁵¹ and a revised value (|D/hc| = 1.720 cm⁻¹) was obtained for CH₃N using gas-phase spectroscopy.⁴⁵ The triplet-triplet absorption spectrum^{54–57} of ³14 and its emission spectrum^{50–53,56–58} are well known. The 0-0 transition in the absorption spectrum of ³14 was found to occur at 316.9 nm in an N₂ matrix⁵⁵ and at 314.3 nm in the gas phase,⁵⁶ similar to the spectrum of the parent NH (336 nm).^{12,13}

The experimental results available in the literature for methylnitrene can be interpreted in two ways. One can posit that singlet methylnitrene is a discrete intermediate but that it does not live long enough, even at cryogenic temperatures, to relax to the lower-energy triplet state. Alternatively, it can also be proposed that singlet excited methyl azide eliminates nitrogen with concomitant rearrangement to form the methyleneimine **15**, without the intervention of a nitrene intermediate.³⁴

The negative ion photoelectron spectrum of CH₃N⁻ contains features that were assigned to the lowest singlet state of 14, and the singlet-triplet splitting was measured to be $\Delta E_{ST} = 1.352 \pm 0.011$ eV (31.2 ± 0.3 kcal/mol).⁵⁹ The features assigned to the singlet nitrene in the photoelectron spectrum of CH₃N⁻ were interpreted as belonging to a resonance, rather than to a true minimum on the singlet CH₃N potential-energy surface.⁵⁹ To further investigate this issue a series of quantum chemical calculations were performed.^{60–69} The results of these calculations are discussed in the next section.

5.3.2 Computational Studies

5.3.2.1 Methyl Azide and Methylnitrene

Most calculations available in the literature are concerned with the simplest alkyl azide and alkylnitrene, CH_3 - N_3 (13) and CH_3 -N (14), respectively. The first *ab initio* theoretical study of the different electronic states of 14 was reported in 1974 by Yakony et al.⁶⁰ The geometries of the lowest ${}^{3}A_2$, ${}^{1}E$, and ${}^{1}A_1$ electronic states of 14 were calculated at the selfconsistent-field level of theory with a double ζ basis set. The ${}^{1}E$ and ${}^{1}A_1$ states were predicted to lie 14,200 and 27,700 cm⁻¹ above the ${}^{3}A_2$ ground state. Yakony et al.⁶⁰ did not try to explain "why 14 has been so difficult to isolate in the laboratory."

In 1980 Demuyanck et al.⁶¹ undertook the first *ab initio* study of the unimolecular rearrangement of triplet and singlet CH₃N to CH₂=NH. Geometries of the stationary points were determined and characterized at the double ζ (DZ) basis set self-consistent field (SCF) level of theory. At these geometries, correlation effects were evaluated using the CI procedure with all single and double excitations, and the DZ basis set was expanded to include polarization functions. The isomerization of triplet nitrene **14** to the triplet state of methyleneimine **15** (in a spin-allowed process) was predicted to be endothermic by 18 kcal/mol, with an activation energy of 48 kcal/mol.⁶¹

$$^{3}CH_{3}-N \rightarrow ^{3}CH_{2}=NH$$

It was concluded that the ground-state triplet **14** is a stable species in the absence of collisions. This conclusion was very important at the time (1980), because the first unequivocal spectroscopic identification of triplet nitrene **14** was achieved only in 1984.⁵⁰

It was found⁶¹ that singlet $CH_2=NH$ lies 46 kcal/mol below the ${}^{3}A_{2}$ ground state of 14 and might be accessible if the spin-orbit coupling is substantial, since rearrangement of the triplet is a spin-forbidden process. The rearrangement of singlet nitrene 14 was also considered, using two-configuration SCF wave functions. Starting from the C_{3V} SCF equilibrium geometry of the ¹E state, no barrier was found for the isomerization of singlet methylnitrene to singlet imine 15.⁶¹

In 1983, Pople et al.⁶² recalculated geometries of ³14 and ³15, using the unrestricted SCF level of theory in conjunction with the $6-31G^*$ basis set. They used the MP4SDQ/ $6-31G^{**}$ method for single-point energy calculations. The results of their calculations for the triplet nitrene rearrangement were very similar to the these in previous paper.⁶¹

The authors⁶² noted that ¹E state of **14** should be subject to Jahn–Teller distortion. At the HF/6-31G^{*} level they found a local minimum at C_S symmetry that was 89.1 kcal/mol higher than the global minimum (**15**). However, after corrections were made the transition structure connecting this minimum to **15** was found to have lower energy and the authors concluded that there is no evidence for ¹**14** as a distinct species.⁶²

A few years later⁵¹ the first experimental evidence for the structure of ³14 was reported. It became clear then that the calculations available at that time^{60–62} did not reproduce the experimental C–N bond length (1.411 A) of ³14. Demuyanck et al.⁶¹ obtained a value for the C–N bond length of 1.471 Å, and Pople et al.⁶² obtained a value of 1.433 Å. An *ab initio* prediction of the C–N bond distance, accurate to within 0.01 Å of experiment, was finally achieved⁶⁴ by using configuration interaction, including all singlet and double excitations (CISD), in conjunction with a basis set of quality quadruple- ζ plus double polarization plus f functions on the C and N atoms (DZ + 2P + f).

Thus, in a period of only a few years (1980 to 1987), methylnitrene in its triplet ground state had gone from the "tenuous" category to what can be considered the best characterized of all known organic nitrenes. Nevertheless, the question of whether singlet methylnitrene ¹14 is an intermediate in the thermal and photochemical decomposition of 13 remained unsolved.

As in the case of NH, at C_{3V} symmetry the closed-shell singlet and the open-shell singlet of ¹14 have exactly the same energy and form the two components of a ¹E state. Demuyanck et al.⁶¹ studied the isomerization of ¹14 in a ¹E state constrained in C_{3V} symmetry. Pople et al.⁶² pointed out that the ¹E state is subject to a Jahn-Teller distortion. The local minimum exhibits $C_{\rm S}$ symmetry, and they examined isomerization in the ¹A' (closed-shell) state. Nguyen⁶³ studied the isomerization of ¹14 in both ¹A' and ¹A" states using Restricted Hartree-Fock (RHF) and Unrestricted Hartree Fock (UHF) procedures with a 3-21G basis set for geometry optimization and MP4SDQ level of theory for single-point calculations. At this low level of the theory, Nguyen found that the ¹A" state lies about 8 kcal/mol above the closed-shell ¹A' state, which is a saddle point on the potential-energy surface. The energy barrier for rearrangement in the ¹A" state was calculated to be 9.5 kcal/mol.⁶³

Richards et al.⁶⁵ examined the same rearrangement on the lowest-lying singlet surface at the CISD level of theory with a two-configuration (TC) reference wave function. A basis set up to triple zeta plus double polarization plus f functions (TZ2P + f) was used. The Jahn–Teller ¹A'-¹A" energy splitting was found to be very small (<0.01 kcal/mol). Richards and $\rm coworkers^{65}$ did, in fact, find a C_s energy maximum. The barrier to rearrangement on the 1A' potential surface was computed to be 12.1 kcal/mol at the DZP TC-SCF level, whereas the TZ2P TC-SCF barrier is reduced to 10.6 kcal/mol. The two-reference CISD method caused the calculated barrier to fall to 1.9 kcal/mol with the DZP basis set and to 1.3 kcal/mol with the DZ2P basis set. The Davidson correction further reduced the barrier, and the TZ2P + f, TC-CISD + Q result was 0.89 kcal/mol. The exothermicity of the rearrangement was calculated to be 85 kcal/mol.

The authors apparently found that the energy of the C_s maximum decreases upon an asymmetric distortion of the geometry, because they concluded, "If there is a ¹A' transition state at this level of theory, it occurs in C_1 symmetry."⁶⁵ The authors proposed⁶⁵ that higher-level correlation effects and excursions into C_1 symmetry would eliminate the barrier entirely, in agreement with the previous, lower-level studies.^{61,62}

The rearrangement of **14** on the ¹**A**" potential-energy surface significantly differs from that on the ¹A' surface.⁶⁵ The formation of the excited ¹A" state of **15** is expected; therefore, the exothermicity of the rearrangement is much more modest (~17 kcal/mol), and a barrier about 30 kcal/mol was computed for this state.⁶⁵

A few years later Nguyen et al.⁶⁶ attempted to calculate the thermal decomposition of **13** using the MP2/6-31G(d,p) method for geometry optimization and QCISD(T)/6-311++G(3df,2p) level for single-point energy calculations. They concluded that the decomposition of **13** occurs through a concerted motion of N₂ elimination with hydrogen shift, giving **15**. A similar conclusion was made on the basis of DFT (B3LYP and B3PW91) calculations.⁶⁷ No singlet nitrene was found by this study.^{66,67}

The process of thermal decomposition of **13** was also reinvestigated in 1999, using the CASSCF(10,8) method and Moller–Plesset theory (CAS/MP2) in conjunction with the 6-31G^{*} basis set.⁶⁸ In contrast to the previous calculations,^{66,67} this reaction was predicted to occur in two steps via a nitrene intermediate.⁶⁸ Therefore, the predicted reaction mechanism is drastically changed by the method used in the calculations. The authors concluded that the CASCCF predictions should be the more reliable, because this method has sufficient flexibility to describe in a balanced way most of the potential energy surface.⁶⁸

A very shallow minimum for singlet methylnitrene in the ¹A' state was found, and its rearrangement to **15** was studied using the CAS(10,8)/MP2 procedure.⁶⁸ It was possible to localize a transition state of C_1 symmetry only 1.4 kcal/mol above the minimum of singlet nitrene.

Independently, Kemnitz and coworkers⁶⁹ undertook CASSCF and CASPT2 calculations on the singlet methylnitrene rearrangement. Their study was motivated by the fact that the closely related rearrangement of singlet methylcarbene to ethylene is computed to have a small but finite energy barrier^{70,71}, and methylcarbene-d₄ has, in fact, been trapped chemically.⁷²⁻⁷⁵ Because the rearrangement of singlet methylcarbene to ethylene does have a barrier, it is not obvious why the rearrangement of singlet methylnitrene to methyleneimine should not.

To investigate the possibility that an energy barrier separates singlet methylnitrene from methyleneimine, CASSCF(12,11) and CASPT2 calculations were performed in which all 12 valence electrons and all 11 valence orbitals were included in the active space.⁶⁹ The CASSCF(12,11) geometry optimizations and the CASPT2 single-point calculations were carried out with Dunning's correction consistant polorized double ζ (cc-pVDZ) and cc-pVTZ correlation-consistent basis sets. The former was used for vibrational analyses, performed at CASSCF(12,11)/cc-pVDZ optimized geometries.

The CASSCF(12,11)/cc-pVTZ optimized geometries for the lowest singlet state of methylnitrene, methyleneimine, and the transition state that connects these two energy minima are shown in Figure 5.6. The CASSCF(12,11) and CASPT2 energies are given in Table 5.2.



Figure 5.6 CASSCF(12,11)/cc-pVTZ geometries (bond lengths in angstroms, bond angles in degrees) of the stationary points along the lowest-energy pathway for the rearrangement of the lowest singlet state of methylnitrene (¹A' MN) to methyleneimine (MI).⁶⁹

TABLE 5.2 Relative CASSCF(12,11) Zero-Point Energies (ZPEs) and
CASSCF(12,11) and CASPT2(12,11) ZPE-Corrected Electronic
Energies (kcal/mol) of ${}^{1}A'$ and ${}^{3}A_{2}$ Methylnitrene 14 and
Methyleneimine 15 and of the Transition Structures Connecting ${}^{1}A'$
14 to 15 (TS1) Computed with cc-pVDZ and cc-pVTZ Basis Sets⁶⁹

ZPE	E (CASSCF/ cc-pVDZ)	E (CASPT2/ cc-pVDZ)	E (CASSCF/ cc-pVTZ)	E (CASPT2/ cc-pVTZ)
1.8	-41.1	-35.9	-39.7	-32.0
$\begin{array}{c} 0.1 \\ 3.2 \end{array}$	$\begin{array}{c} 0.4 \\ -91.7 \end{array}$	2.8 -83.1	$\begin{array}{c} 0.5 \\ -92.0 \end{array}$	3.8 - 82.9
	ZPE 0 1.8 0.1 3.2	E (CASSCF/ ZPE cc-pVDZ) 0 0 1.8 -41.1 0.1 0.4 3.2 -91.7	$\begin{array}{c c} & E (CASSCF') & E (CASPT2') \\ ZPE & cc-pVDZ) & cc-pVDZ) \\ 0 & 0 & 0 \\ 1.8 & -41.1 & -35.9 \\ 0.1 & 0.4 & 2.8 \\ 3.2 & -91.7 & -83.1 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

It was found, as in the previous calculations,^{65,68} that the ¹A' state has one short and two long C–H bonds (Figure 5.6). The ¹A" state distorts from $C_{3^{v}}$ symmetry in the opposite sense. However, the distortions from $C_{3^{v}}$ symmetry of both components of ¹E are quite small; at their C_{s} optimized geometries, the ¹A' and ¹A" states differ in energy by less than 0.01 kcal/mol at the CASSCF(12,11) level of theory with both basis sets. As found by Xie et al.⁶⁴ and Richards et al.,⁶⁵ the C–N bond lengths in the two singlets are nearly the same, and both are slightly shorter than the C–N bond length in the lowest triplet state.

It is in the ${}^{1}A'$ state that migration of the unique hydrogen can most easily occur.⁶⁵ In fact, the lowest-frequency vibrational mode of 564 cm⁻¹ in this state of methylnitrene corresponds to an a' motion that moves this hydrogen toward the nitrogen.

The zeroth-order wave function for ¹A' has the form ¹A' = $c_1 | ...7a^{12} > - c_2 | ...2a^{112} >$. The 7a' Molecular Orbital (MO) is largely composed of the 2p_y Atomic Orbital (AO) on nitrogen, interacting in an antibonding fashion with the unique hydrogen; 2a" is largely the 2p_x orbital on nitrogen, interacting with the remaining two hydrogens, also in an antibonding fashion. In the reactant, $c_1 \approx c_2$, so that the 7a' and 2a" nonbonding (NB) MOs are each occupied by an average of about one electron.⁶⁹

However, as hydrogen migration from carbon to nitrogen occurs, the electrons that form the unique C–H bond in the reactant are delocalized toward the $2p_v$ orbital nitrogen. Con-

comitantly, c_1 decreases and c_2 increases, so that the pair of electrons that are initially distributed nearly equally between $2p_x$ and $2p_y$ on nitrogen become increasingly localized in $2p_x$. Completion of the formation of methyleneimine can be thought of as requiring rotation around the C–N bond, so that this pair of electrons in $2p_x$ on nitrogen can delocalize into the now largely empty $2p_y$ orbital on carbon, thus forming the C–N π bonds in methyleneimine.

Product formation requires loss of the plane of symmetry that exists in the reactant. Therefore, to establish the existence of an energy barrier to product formation, it is not valid to simply find an energy maximum along a reaction pathway that preserves this symmetry plane. For a C_s energy maximum to be a true transition structure rather than a mountain top on the potential-energy surface for rearrangement of ¹14 to 15, the force constant for rotation around the C–N bond at the C_s energy maximum also must be positive.

The CASSCF(12,11)/cc-pVTZ geometry of the C_s energy maximum (Figure 5.6) is similar to the TC-CISD geometry found by Richards and coworkers⁶⁵ for this species. With both the cc-pVDZ and cc-pVTZ basis sets, the CASSCF(12,11) energy of this species is 0.3 to 0.4 kcal/mol above that of the reactant, and this energy difference increases by 0.1 kcal/mol with inclusion of the correction for differences in zero-point vibrational energies. At the CASPT2 level of theory, the C_s energy barrier increases to 2.8 kcal/mol with the smaller of the two basis sets and to 3.8 kcal/mol with the larger.⁶⁹

Because CASPT2 usually overestimates the effect of including electron correlation because of excitations outside the valence space, the actual height of the barrier to passage over the C_s energy maximum is likely to be lower than 3.8 kcal/mol but closer to it than to the CASSCF(12,11)/cc-pVTZ value of 0.5 kcal/mol. A barrier height in the range of 2.5 ± 1.0 kcal/mol was proposed as being most reasonable.⁶⁹

CASSCF(12,11) vibrational analyses with both the ccpVDZ and cc-pVTZ basis sets found the C_s energy maximum to be a true transition state for rearrangement of ¹14 to 15. Except for the imaginary frequency for the a', symmetry-preserving vibration that corresponds to hydrogen migration, all other frequencies were found to be real. The lowest of these

corresponds to a symmetry-breaking a" vibration, but this mode is computed at the CASSCF(12,11)/cc-pVTZ level to have a frequency of 854 cm⁻¹. CASPT2 calculations along this a" vibrational coordinate also found the force constant along it to be positive. Therefore, at both the CASSCF(12,11) and the CASPT2 levels of theory the C_s energy maximum does appear to be a true transition state on the potential-energy surface for rearrangement of singlet methylnitrene to methyleneimine.⁶⁹

The tremendous exothermicity of the rearrangement of singlet ¹14 to 15, amounting to 83 kcal/mol at CASPT2, results in the C_s energy maximum occurring very early along the reaction coordinate before substantial motion of the hydrogen from carbon to nitrogen has occurred. In this C_s transition structure the unique C–H bond has lengthened by only 0.01 Å, and the C–N distance has decreased from that in the reactant by only 0.016 Å. Nevertheless, the occupation of the 7a' NBMO falls from 1.07 electrons in the reactant to 0.35 electrons in the transition structure.⁶⁹

The CASPT2(12,11)/cc-pVTZ value for the singlet-triplet splitting was found to be $\Delta E_{ST} = 32.0$ kcal/mol,⁶⁹ in excellent agreement with the experimental value of $\Delta E_{ST} = 31.2 \pm 0.2$ kcal/mol. 59 The absence of the ν_6 vibration band from the singlet region of the negative ion photoelectron spectrum of CH_3N^- provides the only experimental evidence that singlet methylnitrene could be a transition structure, because one component of the v_6 vibration leads toward migration of a hydrogen from carbon to nitrogen. The harmonic frequency of this vibration at the singlet energy minimum was calculated to be 564 cm⁻¹. However, there is no peak apparent in this energy region above the singlet origin.⁵⁹ One of the possible reasons for the absence of this band is that the first excited level of the v_6 C-H rocking vibration is above the barrier for the rearrangement that this mode promotes. This would place an upper limit on the barrier to rearrangement of 564 cm⁻¹ = 1.6 kcal/mol.⁶⁹

Based on the results of these CASCF/CASPT2 calculations, singlet methylnitrene is indeed predicted to be an energy minimum rather than a transition state; the barrier to rearrangement is most likely in the range of 2.5 ± 1 kcal/mol.⁶⁹ Thus, at least in principle, ¹14 should be an observ-

able albeit very short-lived intermediate, because tunneling through the small barrier to hydrogen migration should be fast.

The triplet-triplet absorption spectrum of ³14 has a maximum at 316.9 nm in an N₂ matrix⁵⁵ and at 314.3 nm in the gas phase,⁵⁶ similar to the spectrum of the parent NH (336 nm).^{12,13,16} In the latter case the spectra of the nitrene in the lowest triplet and singlet states (X ³ Σ ⁻ and a¹ Δ) have similar bands in the near UV region with maxima at 336 and 324 nm.^{12,13} Therefore, singlet nitrene 14 is expected to absorb in the near-UV region as well.

The electronic absorption spectra of 14 in the lowest singlet and triplet states were calculated^{75a} with the CASSCF(12,11)/CASPT2 procedure with the ANO-L basis set at the bond distances optimized previously.⁶⁹ All 12 valence electrons and all 11 valence orbitals were included in the active space.

The long wavelength transition of the triplet CH₃N was predicted at 307 nm (f = 1.4×10^{-2}), in very good agreement with experiment (314 to 317 nm).⁵² The long wavelength transition of singlet CH₃N in the ¹A' state was calculated at 287 nm (f = 4.9×10^{-3}). As with the case of parent nitrene NH, both transitions were associated with electron promotion from a lone-pair orbital on the nitrogen to a non-bonding p orbital. The calculated value of ΔE_{ST} is 40.7 kcal/mol at the CASSCF level and 34.0 kcal/mol at the CASPT2 level, in good agreement with experiment⁵⁹ and with previous calculations with a different basis set.⁶⁹

5.3.2.2 Calculations for Other Alkylnitrenes

Photolysis of perfluoromethyl azide **10** in an argon matrix at 14 K produced triplet nitrene **11** with sharp, structured absorption bands at 342, 347.5, and 354 nm (Figure 5.5).⁴³ The singlet-triplet splitting of **11** was calculated at the CASSCF(8,8)/6-31G^{*} level of theory to be 43.7 kcal/mol.⁴³ This value is larger than the experimentally determined singlet–triplet splitting in **14** (31.2 kcal/mol).⁵⁹ However, at the CASSCF(12,11)/cc-pVDZ level of theory, the singlet-triplet splitting of **14** is calculated to be 41.1 kcal/mol, too high by

10 kcal/mol.⁵⁹ Thus, the singlet-triplet gap in **11**, calculated by CASSCF, is also likely to be too large by this amount.

Rearrangement of ¹11 to imine 12 ($F_2C=NF$) was predicted by CASSCF(8,8)/6-31G^{*} to be exothermic by 46 kcal/mol,⁴³ probably too high by ~10 kcal/mol, due to the CASSCF error in calculating the energy of ¹11. Even so, the rearrangement of 11 to 12 is computed to be much less exothermic than the rearrangement of ¹14 to 15 (82.9 kcal/mol),⁶⁹ due to the greater strength of the C–F bond relative to the C–H bond. Consequently, the barrier to isomerization is expected to be greater for ¹11 than for ¹14.⁴³ This is presumably the reason intersystem crossing (ISC) of the perfluoromethyl singlet nitrene (¹11) to ³11 can compete with rearrangement to 12 at cryogenic temperatures.

Recently, Tsao et al.⁷⁶ performed CASSCF/CASPT2 calculations of the properties of the cyclopropylnitrene (**16**). This study was motivated by the fact that cyclopropylcarbene can be chemically intercepted and has a lifetime of about 20 ns in solution at ambient temperature.^{77,78} Recall that singlet methylcarbene^{70,71} and singlet methylnitrene^{68,69} have not been detected or chemically intercepted and are predicted to isomerize to, respectively, ethylene and imine over a very small barrier of 1 to 3 kcal/mol. Calculations were performed to estimate the lifetime of ¹**16** and its suitability for laser flash photolysis studies.⁷⁶

Geometry optimizations for singlet and triplet nitrene **16** were performed with the standard 6-31G^{*} basis set, using CASSCF(4,4) calculations with a four-electron and four-orbital active space.⁷⁶ This active space consisted of two 2p AOs on nitrogen and the highest σ and lowest unoccupied σ^* MOs, formed from the two β C–C bonds of the cyclopropyl group.

The CASSCF(4,4)/6-31G^{*} optimized bond lengths in the lowest electronic states (³A", ¹A', and ¹A") of cyclopropylnitrene **16** are shown in Figure 5.7, and their relative energies are given in Table 5.3. The calculated singlet-triplet energy gap (ΔE_{ST}) of **16** is 27.9 kcal/mol at the CASPT2(8,8)/6-31G(2d,p) level with the triplet as the ground state,⁷⁶ ΔE_{ST} in **16** is smaller than that in methylnitrene **14** (31.2 kcal/mol).⁵⁹ Electron donation from the cyclopropyl ring sta-





TABLE 5.3 Relative Energies (kcal/mol) of Triplet and SingletCyclopropylnitrene76a

³ A''	${}^{1}A'$	$^{1}A''$
0.00	34.54	38.51
0.00	30.68	39.4
0.00	28.59	33.66
0.00	29.17	39.00
0.00	29.66	31.80
0.00	27.88	32.26
	³ A" 0.00 0.00 0.00 0.00 0.00 0.00	

^aEnergies were calculated with $CASSCF(4,4)/6-31G^*$ optimized geometries, including corrections for the differences in $CASSCF(4,4)/6-31G^*$ unscaled zeropoint vibrational energies.

bilizes the closed-shell singlet state of the nitrene, relative to the triplet.

As expected, the closed-shell singlet state of 16 (¹A') has a shorter C–N bond length than the biradical-like open-shell singlet state (¹A"). The energy of the closed-shell singlet is calculated to be below that of the open-shell singlet at all levels of theory by 2.1 to 9.2 kcal/mol and 4.4 kcal/mol at highest level (Table 5.3). Note that in the methylnitrene 14 this calculated difference is less than 0.01 kcal/mol. (The opposite situation obtains in the case of vinylnitrene and phenylnitrene, as discussed in Sections 5.4 and 5.6.)

Thermolysis of azidopropane led to hydrogen cyanide (17), ethylene (18), and 1-azetine (19).⁷⁹



Calculations were performed to provide some insight into these reactions.⁷⁶ Geometry optimization of the ¹A' state of **16** and the reaction products and location of possible transition states (**TS1** and **TS2**) were performed at the HF/6-31G* level of theory. Some calculated bond lengths for the intermediates and transition structure of the fragmentation reaction are shown in Figure 5.8. At the HF/6-31G* level of theory, the activation energy of the ring-expansion reaction (**16** \rightarrow **TS1** \rightarrow **19**) was 2.8 kcal/mol, and the activation energy of the fragmentation reaction (**16** \rightarrow **TS2** \rightarrow **17** + **18**) was 0.6 kcal/mol. The activation energy calculated for the ring-expansion reaction is smaller than the previously published value of 9.3 kcal/mol, which was obtained by HF/3-21G calculations without zero-point energy corrections.⁸⁰

From single-point energies (Table 5.4) at correlated levels of theory (B3LYP, MP2, and CASPT2), ¹**16** is predicted to fragment spontaneously if one uses HF/6-31G^{*} derived geometries.⁷⁶ In addition, transition state searches with (restricted) B3LYP and MP2 methods led to barrierless fragmentation.

The CASPT2(8,8)/6-31G(2d,p) calculations on structures along the intrinsic reaction coordinate (IRC) path at the HF/6-31G^{*} level predict that the fragmentation reaction is barrierless, but the ring-expansion reaction has a small activation barrier (\approx 2.4 kcal/mol). Therefore, the calculations indicate that, unlike cyclopropylcarbene, singlet cyclopropylnitrene will have a very short lifetime in solution at ambient temperature, and, like methylcarbene and methylnitrene, ¹16 will be very difficult to detect.⁷⁶



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Figure 5.8 Intermediate and transition structures for the ringexpansion (via **TS1**) and fragmentation (via **TS2**) reactions of cyclopropylnitrene **16** at the HF/6-31G^{*} level of theory.⁷⁶ Relative energies (in kcal/mol) are listed in parentheses at the HF/6-31G^{*} level. Bond lengths are shown in Å.

TABLE 5.4 Relative Energies (kcal/mol) of Intermediates and
Stationary Points for Cyclopropylnitrene Rearrangement and
Fragmentation76^a

					CASPT2(8,8)/
Structure	\mathbf{HF}	B3LYP	MP2	MP4(SDQ)	6-311G(2d,p)
¹ A'-16	0.00	0.00	0.00	0.00	0.00
³ A''-16	-45.16	-17.24	-20.49	-23.50	-27.88^{b}
19	-59.56	-62.53	-70.44	-66.68	<u> </u>
17 + 18	-68.70	-63.05	-74.49	-71.84	c
TS1	2.84	-1.43	-7.78	-1.72	-1.11
TS2	0.64	-6.44	-7.85	-4.95	-8.61

^aEnergies were calculated with a 6-31G^{*} basis set and the HF/6-31G^{*} optimized geometries, including corrections for difference in HF/6-31G^{*} unscaled zero-point vibrational energies, unless noted otherwise. ^bUsing the CASCF(4,4)/6-31G^{*} geometry.

^cNot calculated.

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5.4 PHOTOLYSIS AND THERMOLYSIS OF VINYL AZIDES: PROPERTIES OF VINYLNITRENES

5.4.1 Experimental Results

The simplest member of the class of vinyl azides, $H_2C=CH-N_3$, has been known for about 100 years. However, it was not until the late 1960s that vinyl azides became an important and synthetically useful class of organic compound.⁸¹ The most interesting and important reaction of vinyl azides is the formation of azirines produced upon photolysis and thermolysis of vinyl azides.⁸¹ Smolinsky⁸² and Pryde⁸³ first observed azirine formation, together with a small amount of keteneimine, by gas-phase pyrolysis of α -aryl–substituted vinyl azides.



Hassner and Fowler^{84,85} first discovered that several α -substituted (R \neq H) vinyl azides produce 2-mono- or 2,3-disubstituted-1-azirines in high chemical yield (80 to 90%) upon photolysis.



Isolable 1-azirines were formed upon photolysis of α unsubstituted (R=H) vinyl azides only at low temperature and underwent further decomposition upon heating.^{86,87}



Three plausible mechanisms were postulated to explain these observations: the free nitrene route (pathway a), N_2 extrusion in concert with three-membered ring formation (pathway b), and cyclization to a 4H-1,2,3-triazole followed by rearrangement to azirine (pathway c).⁸¹



Scheme 5.0

The formation of 1-azirines (**AZ**) along with keteneimines (**K**) upon photolysis and thermolysis of vinyl azides was explained by invoking the intermediacy of singlet vinylnitrenes (1 **VN**) (pathway a).^{88,89} Keteneimines can serve as a precursor to nitriles if R' = H.



The intermediacy of a singlet nitrene was supported by the formation of indole during the thermolysis of β -azidosty-rene.⁹⁰



Note that in the early literature $^{81,85,88-90}$ vinylnitrene was thought to be a closed-shell dipolar species. Therefore, attempts were made to intercept this nitrene using 1,3-dipolarophiles.⁸⁵

It was shown that 1-azirines can serve as precursors to vinylnitrenes.^{91,92} A number of 1-azirines rearrange to indoles, most likely via vinylnitrene intermediates, upon heating. Two examples are known in which the nitrene formed during the thermolysis of azirines can be intercepted by tris(dimethy-lamino)phosphine⁹³ or triphenylphosphine.⁹⁴



Triazole formation as a route to azirines (pathway c) was considered to be very unlikely.⁸¹ Hassner,⁸¹ and Fowler et al.⁹⁵ proposed that the concerted formation of azirines upon thermolysis of vinyl azides (pathway b) was more reasonable.





It is difficult to choose among the proposed mechanisms, based on the experimental data available, because both triplet and singlet vinyl nitrenes have still escaped direct observation. The formation of an azirine was observed upon photolysis of α -azidostyrene in an argon matrix at cryogenic temperature (8 K), but even under these conditions nitrene species were not observed.⁹⁶



If a free singlet nitrene is an intermediate, produced upon decomposition of a vinylazide, then the activation energy of vinyl nitrene rearrangement to azirine must be very small. The situation is similar to the case of methylnitrene, produced upon photolysis of methyl azide (see Section 5.3).

Several computational methods have been used to evaluate the mechanism of azirine formation.

5.4.2 Computational Results on the Mechanism of Azirine Formation and Properties of VinyInitrene

5.4.2.1 Semiempirical and Early *Ab Initio* Calculations

All calculations reported in the literature have been concerned with only the simplest vinyl azide and vinylnitrene, $CH_2=CH-N_3$ and CH_2 -CH-N, respectively.⁹⁷⁻¹⁰¹ Until recently, all the theoretical studies on the vinyl azide to azirine transformation used semiempirical calculations⁹⁸ or *ab initio* calculations performed at relatively low levels of theory,^{97,99} at least by current standards. Significantly, early calculations on the vinylnitreneazirine interconversion have focused only on the closed-shell singlet excited state (¹A') of vinylnitrene (**VN**).

According to MNDO calculations,⁹⁸ the concerted mechanism of azirine formation (b) was found to be the most reasonable process (see Scheme 5.0). The free nitrene route (a) (see Scheme 5.0) for the thermal reaction was excluded on the basis of very high activation energy. A similar conclusion was made on the basis of HF, MP2, and CISD calculations with a minimal STO-3G basis set.⁹⁹ But as noted before, the authors of both publications^{98,99} considered the formation and rearrangement of the closed-shell singlet nitrene (¹A'-**VN**).

Lohr et al.,⁹⁷ using a UHF procedure, were the first to discover that the lowest singlet state of **VN** has an open-shell electronic configuration with an energy 50.7 kcal/mol below that of the closed-shell singlet. However, the expectation value of S² for this singlet was 1.17, which indicated that there was substantial triplet character in the UHF wave function, and it was a poor representation of a true singlet. Therefore, these authors did not deal with the open-shell singlet and confined their attention to the rearrangement involving the closed-shell singlet. They found that there is little or no barrier to formation of 2*H*-azirine from the closed-shell singlet **VN**. They also found a pathway for the rearrangement of 2*H*-azirine to the more stable acetonitrile via the intermediate methyliso-cyanide.⁹⁷



5.4.2.2 High-Level Ab Initio Calculations

Recently, Parasuk and Cramer¹⁰⁰ performed very accurate calculations of the electronic structure and energies of the lowest states of **VN**. Single-point calculations at the CASSCF(4,4) geometry were carried out at the MRCI and CASPT2 levels, using cc-pVDZ and cc-pVTZ basis sets. In the

MRCI calculations, single and double excitations of the reference wave functions were performed for all 16 valence electrons. The contribution of quadruple excitations was estimated using the method of Langhoff and Davidson.¹⁰² The calculations predict **VN** to have a ³A" ground state, and the lowest open-shell singlet (¹A") and closed-shell singlet (¹A') states to lie 15 and 40 kcal/mol higher in energy, respectively.

The C–N bond lengths for the three states of **VN** are 1.263 Å (¹A"), 1.309 Å (³A"), and 1.368 Å (¹A'). The C=C bond length (1.346 Å) in the ¹A' state is typical for the carbon-carbon double bond. It is lengthened to 1.391 Å in the ³A" state and to 1.461 Å in the ¹A" state. Therefore, the lowest open-shell singlet ¹A" state can be represented as a biradical.



In the ¹A" state, the electron in the π NBMO is predicted to be almost completely localized in the C1 carbon.

In ¹A", unlike the case in ³A", the σ and π electrons have opposite spin; hence, they are not correlated by the Pauli exclusion principle. Localizing electrons of opposite spin to different regions of space — in this case the σ NBMO on nitrogen and the π NBMO of the C₁ carbon — minimizes their mutual Coulombic repulsion energy. Thus, ΔE_{ST} is much lower in **VN** (15 kcal/mol)¹⁰⁰ than in NH (36 kcal/mol)^{16,17} or CH₃N (31 kcal/mol)⁵⁹ because the C=C substituent allows the π electron in the ¹A" state to become localized in a region of space that is disjoint from the region of space occupied by the σ electron. As will be discussed in Section 5.6, for the same reason the lowest singlet state in phenylnitrene is also the open-shell, ¹A" state.

In CASSCF(4,4)/6-31G^{*} calculations on the rearrangement of the singlet **VN** to azirine, singlet vinylnitrene ($^{1}A''$ -

VN) was found to be the transition state for interchange of the enantiotopic pair of hydrogens in 2*H*-azirine (**AZ**).¹⁰¹ At the CASSCF optimized geometries, the CASSCF, CASPT2N, and MR-CISD (plus Davidson correction)¹⁰² energies (in kcal/mol, with ZPE corrections) of ¹A"-**VN** relative to 2*H*-azirine are, respectively, 25.6, 29.8, and 31.9 with the 6-31G^{*} basis set. With the 6-311G(2d,p) basis set the CASPT2N and MR-CISD+Q values are 27.9 and 31.3 kcal/mol.¹⁰¹ With the larger basis set, it appears that CASPT2 overestimates the energy difference between the open-shell singlet nitrene and 2*H*-azirine by 3.4 kcal/mol.¹⁰¹

Although it is impossible to completely rule out the existence of the singlet **VN**, CASSCF(4,4)/6-31G^{*} prediction, that the nitrene can cyclize to the azirine without any barrier¹⁰¹ suggests that, if a barrier does exist, it is probably very small. This conclusion, based on the results of calculations, is wholly consistent with the fact, noted above, that the triplet and singlet vinyl nitrenes have escaped detection. However, further experimental studies, using very fast laser flash photolysis techniques, along with higher level *ab initio* calculations, are certainly warranted.

5.5 PHOTOLYSIS AND THERMOLYSIS OF ACYL AZIDES: PROPERTIES OF ACYLNITRENES

5.5.1 Early Experimental Results

Acyl azides and acylnitrenes have the following structures:



The substituent R can be an alkyl, aryl, alkoxy, aryloxy, or a hydroxyl group. This section will highlight the development

of the theoretical description of the properties of acylnitrenes. Thus our coverage will be restricted to only those acyl azides and acylnitrenes for which calculations are available. We will not examine the carbamoyl and sulfonyl azides and nitrenes¹⁰³, because no theoretical data on these systems have yet been reported.

The most common thermal reaction of carbonyl azides is isocyanate formation. This reaction, known as the Curtius rearrangement, was reported as early as 1914.¹⁰⁴



Photolysis of carbonyl azides gives rise to two types of reactions. The photo-Curtius rearrangement proceeds to form isocyanate. In addition, bimolecular trapping products, typical of the reactions of singlet carbonylnitrenes, are also observed.¹⁰³

The mechanisms of the Curtius and photo-Curtius rearrangements have long been debated^{103,105–110} Some authors have favored a concerted mechanism,^{105–108} while others preferred a stepwise mechanism involving a carbonylnitrene intermediate.^{109,110} In some cases carbonylnitrenes can be trapped in the photolytic, but not in the thermolytic, decomposition of carbonyl azides, which indicates that carbonylnitrenes are probably not intermediates in those particular thermal Curtius rearrangements.^{103,111} For example, the yield of isocyanate, obtained upon thermolysis of pivaloyl azide (t^r -BuCON₃) in cyclohexane, is 99.4%.^{111,112} No C-H insertion product was found, and it is now generally accepted¹⁰³ that loss of nitrogen and migration of R are concerted processes in the thermal Curtius rearrangement.

The yield of isocyanates, formed upon photolysis of a series of carbonyl azides $(R-CO-N_3, R=t-butyl, aryl)$,

remains constant in the presence and in the absence of a nitrene trap.^{111–114} The yield of isocyanate, produced upon photolysis of pivaloyl azide, is about 40% in both inert and reactive alkene solvents.^{111,112} The yields of the isocyanates were in the range of 40 to 50% upon photolysis of benzoyl azide and its *para*-methoxy, *para*-chloro, and *meta*-fluoro derivatives in both inert solvents and in solvents that intercept acylnitrenes.^{113,114} Therefore, it was concluded that, if carbonylnitrenes (R–CO–N) are formed in these photolysis reactions, they rearrange to isocyanates (R–N=C=O) at a rate that is much lower than their capture by trapping agents.^{103,112–114}



However, upon photolysis and thermolysis of azidoformates (RO–CO–N₃, R=alkyl, aryl), the major reaction path is the formation of products derived from capture of the nitrenes (RO–CO–N).^{103, 115–119} Carbethoxynitrene (**21**) has been studied most extensively. This nitrene has been generated by thermolysis and photolysis of **20**^{116,119} and by α -elimination of an arysulfonate ion from N-(p-nitrobenzenesulfonyloxy) urethane.^{116,118}

The triplet multiplicity of the ground state of the nitrene 21 was first deduced on the basis of products analysis.^{103,116,118,119} Nitrene 21 was generated by photolysis, ther-
molysis, and an α -elimination reaction, and the stereospecificity of its addition to *cis*- and *trans*-4-methylpentene-2 to form aziridines was investigated. It was found that the stereospecificity of the nitrene addition to cis alkenes decreases upon dilution of the alkene trap.

The thermolysis and α -elimination experiments can be quantitatively fit to a scheme in which all of the nitrene **21** is generated in the singlet state (¹**21**), which then decays to the ground triplet state (³**21**), in competition with stereospecific addition of ¹**21** to olefins.^{103,116,118,119} The triplet nitrene (³**21**) also reacts with olefins but nonstereospecifically, presumably through intermediate biradical formation.¹⁰³ The data for the photolytic generation of the nitrene were in accord with a scheme in which one third of the trappable nitrenes are produced in the triplet state, whereas are two thirds are generated in the singlet state.^{103,119}



Insertion of singlet nitrene **21** into the C–H bond of alkanes and into the O–H bond of alcohols, addition of **21** to acetylenes, and reaction of **21** with benzene, followed by azepine formation, are all well documented.¹⁰³

The proposed triplet multiplicity of the ground state of nitrene **21** was proven by ESR spectroscopy.⁴⁷ Wasserman⁴⁷ detected the ESR spectrum of ³**21** at low temperature in a rigid matrix with a |D| value of 1.603 cm⁻¹. Some interaction of one of the spins with the carbonyl group is evident in the nonzero |E| value of 0.0215 cm⁻¹. In subsequent studies, Autrey and Schuster¹²⁰ reproduced the ESR spectrum of ³**21** and, along with Sigman et al.,¹²¹ recorded a very similar ESR spectrum (|D| = 1.65 cm⁻¹, |E| = 0.024 cm⁻¹) upon irradiation of a suspension of (4-acetylphenoxy)carbonyl azide (**22**) in Fluorolube at 77 K. This spectrum was assigned to triplet (4-acetylphenoxy)carbonylnitrene (**23**).



Wilde et al.¹²² photolyzed methyl azidoformate in raregas matrices at 4 K. Methoxyisocyanate, formaldehyde, and isocyanic acid were identified as the photolysis products on the basis of infrared spectroscopy. No ESR observations of triplet carbmethoxynitrene were attempted.¹²²

The photochemistry of benzoyl azide (24) has also been well studied. Early studies^{113,114,123,124} of the photolysis of **24** in the presence of singlet nitrene traps (olefins, sulfides, etc.) demonstrated the formation of products typical of singlet nitrene reactions, along with a high yield (about 40%) of phenyl isocyanate, the product of a photo-Curtius rearrangement. Product distributions in the presence of trapping agents and photosensitizers suggested a triplet ground state for ben-

zoylnitrene (**25**).¹²⁴ However, Inagaki and coworkers^{125,126} have demonstrated that direct and triplet sensitized photolysis of **24** produces the same trapping products and that these products are characteristic of a singlet nitrene. Finally, no nitrenelike triplet ESR spectrum was detected after photolysis of **24** in glassy matrices.^{28,47}

Comprehensive studies of the photochemistry of 2-naphthoyl and substituted benzoyl azides were undertaken to determine the multiplicity of the ground state of aroylnitrenes.^{120,121,127,128} Irradiation (254 nm) of 2-naphthoyl azide (**26**) in cyclohexane at room temperature produces N-cyclohexyl-2-naphthamide (**27**, ~45%), 2-naphthyl isocyanate (**28**, ~50%), and a trace (<1%) of 2-naphthamide (**29**).



Irradiation of **26** in cyclohexane solution containing either cis- or trans-4-methyl-2-pentene forms aziridines with complete (>98%) retention of olefin stereochemistry.¹²⁰ Stereospecific aziridine formation is usually considered as evidence of a concerted, singlet nitrene addition reaction.

Triplet sensitized photolysis of **26** was also studied.¹²⁰ Both direct and triplet-sensitized photolysis generate products characteristic of the reactions of singlet 2-naphthoylnitrene **30**. The triplet nitrene was not detected in either chemical trapping or spectroscopic experiments. ESR signals attributable to triplet nitrene **30** were not observed after irradiation of **26** in fluorolube at 77 K. Therefore, the experimental data are most consistent with a singlet ground state for **30**.¹²⁰

Similar results were obtained for a series of acetyl- and nitro-substituted aroyl azides (31 - 34).^{121,128}

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Irradiation into the π - π^* bands of aroyl azides **31** and **32** with deep-UV light leads to formation of the corresponding aroylnitrenes (**35** and **36**) in competition with photo-Curtius rearrangement to form isocyanates (23 and 40%, respectively).¹²¹ Irradiation into the n- π^* bands of azides **31** and **32** with near-UV light gives products derived from only the singlet aroylnitrenes (**35** and **36**). ESR signals attributable to triplet aroylnitrenes **35** and **36** were not detected after photolysis of **31** and **32** in glassy matrices.¹²¹

The triplet-excited states of azides **31** and **32** were detected chemically and by transient absorption spectroscopy.¹²¹ It was concluded that nitrogen extrusion, after near-UV irradiation of the azides, occurs exclusively from the excited triplet states of the azides. However, products formed under these conditions are consistent with reactions originating from the singlet state of the aroylnitrenes.

As in the case of azides **31** and **32**, irradiation of nitrosubstituted aroyl azides **33** and **34** leads both to photo-Curtius rearrangement (32 and 38% yields) and to the formation of products derived from the capture of singlet aroylnitrenes (**37** and **38**). The chemical and spectroscopic properties of nitrenes **37** and **38** indicate the singlet nature of their ground states.

Although, the authors were unable to determine the multiplicity of aroylnitrenes unambiguously by direct spectroscopic observation, the authors concluded that the sum total of their data left little doubt that aroylnitrenes have singlet ground states.^{120,121,128} On the basis of this finding, they pro-

posed acetyl- and nitro-substituted aroyl azides as potential photolabeling reagents.^{127,128}

However, the opposite conclusion from that drawn for arovlnitrenes was made about ground-state multiplicity of aroyloxynitrene 23.¹²¹ An ESR spectrum attributable to triplet (4-acetylphenoxy) carbonylnitrene $(^{3}23)$ was detected¹²¹ at 8 K after irradiation of a suspension of 22 in fluorolube at 77 K. In addition, it was found that the irradiation of 22 in benzene in the presence of both *cis*- and *trans*-pentenes (0.05 to 3 M) produces a mixture of aziridines, which is typical of the presence of both singlet and triplet nitrene cycloaddition reactions. The triplet-triplet absorption spectrum of azide 22 was detected, and it was found that naphthalene inhibits the photoreaction of **22** by quenching of its triplet state. It was concluded, therefore, that the ground state of nitrene 23 is a triplet and that it is formed exclusively upon sensitized photolysis of azide 22 through the triplet state of 22.¹²¹ No isocyanate was detected in the photolysis products of 22.

Until recently singlet carbonylnitrenes, in a manner reminiscent of alkyl and vinyl nitrenes, had escaped direct spectroscopic detection. Only the ESR spectra of alkyloxy and aroyloxycabonyl nitrenes [RO–CO–N (**³21**, R=Et and **³23**, R=Ar)] have been detected.^{47,121} ESR spectra of carbonyl nitrenes that do not have an oxygen atom attached to the carbonyl group [R–CO–N (R=alkyl, aryl)] have never been observed.^{47,103,121}

The experimental results on acylnitrenes are clearly complicated, and calculations should be very useful for understanding and interpreting them.

5.5.2 Early Theoretical Results

Most of the calculations originally available in the literature were concerned with the simplest acyl azide and acylnitrene: formyl azide (HCO–N₃, **39**) and formylnitrene (HCO–N, **40**).^{129,134} The first *ab initio* theoretical study of the lowest singlet and triplet electronic states of nitrene **40**, acetylnitrene (CH₃CO–N, **41**), and carbohydroxynitrene (HOCO–N, **42**), along with their corresponding amides, was reported in 1973.¹²⁹ The authors calculated the energies and electronic

structures of the triplet and closed-shell singlet states of the nitrenes at the self-consistent-field (SCF) level of theory, using a very small basis set — STO-3G. For nitrenes **40** and **41**, which are models of alkanoylnitrenes, the triplet states were found to be more stable than the corresponding singlet states by 15 and 12 kcal/mol, respectively. The singlet state of **42**, a model of a carbalkoxynitrene, was found to be more stable than the triplet state by 23 kcal/mol. These results contradict the ESR experiments⁴⁷ for carbethoxynitrene **21**.

Harrison and Shalhoub¹³⁰ also performed calculations of the electronic structure and geometry of the low-lying states of a series of carbonylnitrenes (XCO–N [X = H, F, CH₃, and OCH₃]) using the small STO-3G basis set. However, they did include some configuration interaction, using single and double excitations. They found that for all carbonylnitrenes studied, the ground state is the triplet, with the next two states being closely spaced singlets. With nitrene **40**, the results obtained were highly reminiscent of those for alkylnitrenes, because the acylnitrene singlets (¹A' and ¹A'') were predicted to be approximately 35 and 40 kcal/mol above the triplet state (³A'')¹³⁰ using a Dunning basis set.

Shortly thereafter, Rauk and Alewood¹³¹ studied the thermal and photochemical decomposition and Curtius rearrangement of formyl azide **39** by using SCF calculations augmented with CI. They used both STO-3G and extended (9s5p/4s contracted to 4s2p/2s) basis sets and calculated the structures of the six isomers of the formula HNCO. Isocyanic acid HN=C=O, **43** the parent isocyanate and the product of the Curtius rearrangement of **39** was predicted to be the most stable isomer, 91 kcal/mol lower energy than nitrene **40** in the singlet ¹A' state. Figure 5.9 displays the geometry of the ¹A' state of **40** and of oxazirene **44**, which were calculated to be very close in energy (within 1 kcal/mol).¹³¹ The authors¹³¹ also attempted calculations of the potential-energy surface for the decomposition of the azide **39** in the ground and low-lying excited states.

Poppinger et al.¹³² explored the singlet potential-energy surface of the CHNO system with the aid of the restricted HF method and with STO-3G, 4-31G, and $6-31G^*$ basis sets. These authors found the structures of **40** and **44** to be minima on the singlet potential-energy surface by using an STO-3G basis





Figure 5.9 Structures of singlet nitrene and oxazirene calculated by Rauk and Alewood.¹³¹ Bond lengths are in angstoms, angles in degrees.

set. The attempted optimization of **40** or **44** at the 4-31G level led to the HNCO global minimum **43**. The transition state for rearrangement to **43** was calculated to lie 23 kcal/mol above **44** at the STO-3G level, but 4-31G calculations at the STO-3G transition state placed it 9 kcal/mol below **44**. As a result, the authors¹³² predicted that singlet formylnitrene **40** should collapse in a barrierless process to isocyanic acid **43** and that cyclic oxazirene **44** corresponds to a very shallow minimum or may not be a minimum at all.

In their next paper, Poppinger and Radom¹³³ studied the effect of substituents (R=H, Li, BH₂, CH₃, NH₂, OH, F, Cl, CN, C_6H_5 , p-NO₂-C₆H₄, and p-NH₂-C₆H₄) on the structure and stability of the RNCO isomers at the previously applied level of theory.¹³² On the basis of these calculations, they concluded that singlet acetylnitrene and chlorocarbonylnitrene both collapse to isocyanates without an activation barrier. However, they found hydroxycarbonylnitrene, the parent carbalkoxynitrene, and fluorocarbonylnitrene to be energy minima, although they were predicted to lie in relatively shallow potential wells. There was no theoretical evidence for the existence of a substituted oxazirene that would be sufficiently stable to observe directly.¹³³

In 1980, Mavridis and Harrison¹³⁴ recalculated the electronic structures of the triplet and low-lying singlet states of formylnitrene **21** using self consisent field (SCF) and generalized valence bond (GVB) procedures with double ζ plus polarization functions (DZ + P) basis set. The triplet ³A" state was found to be the ground state, whereas the first two excited states (¹A' and ¹A") were calculated to be 36.8 and 39 kcal/mol

above the triplet state. The geometries of the singlet states were not optimized, and the open-shell singlet ¹A" was assumed to have a geometry identical to its companion ³A" state. In constructing the wave function for a closed-shell singlet, ¹A', all bond angles were taken to be 120°.

5.5.3 Recent Computational and Experimental Studies

Recently,¹³⁵ calculations of the properties of the singlet and triplet states of benzoyl and 2-naphthoylnitrenes (**25** and **30**) were perfomed at the B3LYP/6-31G^{*} level of theory. It was found that the structure of the CON fragment in the lowest singlet state of **25** and **30** (¹A') resembles that of a cyclic oxazirene, although the calculated N–O distance (~1.76 Å) is much longer than in a normal N–O single bond (about 1.5 Å in strained rings).^{136,137} It is interesting to note that Cornell et al.¹³⁸ proposed a cyclic structure for carbalkoxylnitrenes about 40 years ago.

Starting from the geometry of either a closed-shell singlet nitrene or an oxazirene structure with normal N–O bond lengths, geometry optimizations led to the minimum with the 1.76 Å N–O bond length. The optimized structures of triplet and singlet benzoylnitrenes are presented in Figure 5.10. The energy difference between the triplet states of **25** and **30** and the corresponding singlet species, with cyclic structures but unusually long N–O bonds, was calculated to be small. However, the triplet state was still computed to be lower in energy by about 5 kcal/mol.¹³⁵



Figure 5.10 Bond lengths (in angstroms) and bond angles (in degrees) in the singlet A' and triplet A'' states of benzoylnitrene optimized at the B3LYP/6-31G^{*} level.¹³⁵

The reason for the dramatic stabilization of ¹A', relative to the ³A" state of aroylnitrenes, appears to be a bonding interaction between a lone pair on the carbonyl oxygen atoms and an empty 2p orbital on nitrogen. The resulting weak sigma bond results in the structure of the singlet being intermediate between those of a normal nitrene and an oxazirene. Since B3LYP/6-31G^{*} calculations might overestimate the value of ΔE_{ST} the authors¹³⁵ conjectured that aroylnitrenes probably do have singlet ground states, in agreement with the experimental results of Autrey and Schuster¹²⁰ and Sigman et al.¹²¹

Shapley and Bacskay¹³⁹ performed high-level calculations on the structure and energy of triplet formylnitrene and a "cyclic" singlet. The geometries of these intermediates, calculated using the MP2/6-31G^{*} and CASSCF(11,11)/cc-pVDZ methods, are very similar to those optimized by Gritsan and Pritchina¹³⁵ using the B3LYP/6-31G^{*} procedure. The ΔE_{ST} values, calculated by Shapley and Bacskay,¹³⁹ are 3.6 kcal/mol and 0.7 kcal/mol, respectively, at the CASPT2(11,11) and QCISD(T) levels of theory with the cc-pVTZ basis set. Using data obtained with the G2 method,¹³⁹ ΔE_{ST} was calculated to be -2.5 kcal/mol; that is, the singlet was predicted to be the ground state.

To analyze the influence of the basis set and the level of the theory on the calculated value of ΔE_{ST} the energies of the lowest singlet and triplet states of **40** were also computed at the coupled cluster level with single and double substitutions (CCSD) and with non-iteratively included triple substitutions (CCSD(T)) levels of theory.¹⁴⁰. Dunning's correlation-consistent basis sets were used, ranging in size from double-zeta to quadruple-zeta. It was found that B3LYP/6-31G* provides very good geometries for the singlet and triplet states of formylnitrene. However, whereas the B3LYP calculations predict $\Delta E_{ST} > 8$ kcal/mol, benchmark CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ calculations give $\Delta E_{ST} = -0.13$ kcal/mol. Furthermore, basis set extrapolation¹⁴¹⁻¹⁴³) leads to $\Delta E_{ST} = -0.72$ kcal/mol and an even clearer prediction of a singlet ground state.

The prediction of a singlet ground state should also be valid for the aroylnitrenes. A ΔE_{ST} value of about 5 kcal/mol was calculated for aroylnitrenes **25** and **30** by a B3LYP/6-31G^{*} procedure,¹³⁵ but higher-level calculations show that B3LYP/6-31G^{*} overestimates ΔE_{ST} for formylnitrene by about 9 kcal/mol. Assuming errors of similar size in the B3LYP calculations on **25** and **30**, the B3LYP values of ΔE_{ST} for these two nitrenes suggest that they too have singlet ground states.

Although the triplet ESR spectra of a carbonylnitrene with a structure of R–CO–N (R=Alkyl, Aryl) has never been detected,^{47,103,121} the ESR spectra of triplet carbethoxynitrene ³21 and aroyloxynitrene ³23 (RO–CO–N, R=Et and Ar) have been obtained.^{47,121} To understand the difference between these two types of nitrenes (R–CO–N and RO–CO–N), some preliminary calculations were performed on carbohydroxynitrene (HOCO–N, 42), using it as a model for carbalkoxy and carbaryloxynitrenes.^{143a} The geometries of the singlet and triplet states of 42 were optimized at the B3LYP/6-31G^{*} level, and the energies of the optimized structures were recalculated at the CCSD(T) level with cc-pVDZ and cc-pVTZ basis sets.

Figure 5.11 compares the optimized structures of the lowest singlet states (¹A') of formylnitrene and two rotamers of nitrene **42**. It was found at the B3LYP/6-31G^{*} level that the ΔE_{ST} value is 16.1 kcal/mol for rotamer **42a** and 11.0 kcal/mol for rotamer **42b**. Recall that at this level of theory $\Delta E_{ST} = 8.1$ kcal/mol for **40**. The value of ΔE_{ST} for **42a** at the CCSD(T)/ccpVTZ level drops but only to 7.8 kcal/mol, providing computational stronger evidence for a triplet ground state in **42**.



Figure 5.11 Bond lengths (in angstroms) and bond angles (in degrees) in the singlet ${}^{1}A'$ states of formylnitrene and carbohydroxynitrene optimized at the B3LYP/6-31G^{*} level.

The difference in ΔE_{ST} between 42 and formylnitrene 40 is attributed to the smaller bonding interaction between the nitrogen and the oxygen atoms in 42, which manifests itself in the longer N–O bond length in 42 than in formylnitrene (Figure 5.11). The replacement of the hydrogen in formylnitrene by the hydroxyl group in 42 apparently inhibits σ bonding between the nitrogen and the carbonyl oxygen by increasing the strain in the three membered oxazirene ring.

In order to determine experimentally the multiplicity and the structure of the lowest state of benzoylnitrene (25), a study of the photochemistry of benzoyl azide (24) was performed in an Ar matrix at 12 K.¹⁴⁰ The formation of two species was observed upon exposure of 24 to 254 nm light. One of these species has an IR spectrum, which is consistent with that expected for phenyl isocyanate (45). The IR and UV spectrum of the second intermediate are in very good agreement with the calculated spectra of singlet nitrene in the ¹A' state (25). This intermediate undergoes isomerization to isocyanate (45) upon further exposure of the sample to 313-nm light.¹⁴⁰



Structure 5.26

A definitive answer can now be given^{135,140} to the question posed by Autrey and Schuster¹²⁰: "Are aroylnitrenes ground-state singlets?" Calculations and experiments now agree that aroylnitrenes are indeed ground-state singlets, but calculations show that these singlets have electronic structures and geometries that are intermediate between those of nitrenes and oxazirenes.

5.6 PHOTOLYSIS OF ARYL AZIDES: PROPERTIES OF ARYLNITRENES

Before discussing recent experimental and theoretical studies on the reactivity and spectroscopy of arylnitrenes, we will describe some of the earliest experimental and theoretical work on these molecules. Our purpose is to give a brief overview in order to provide a context for discussion of more recent results. For detailed descriptions of the chemistry of arylnitrenes, we refer the reader to the many excellent reviews in this area¹⁴⁴⁻¹⁵¹

5.6.1 Early Experimental and Theoretical Studies

5.6.1.1 Experiments

Phenylazide (46) was first synthesized by Greiss¹⁵² in 1864. Wolf¹⁵³ first studied the thermal decomposition of phenylazide. In the presence of aniline, thermolysis of 46 leads to extrusion of molecular nitrogen, generation of a reactive intermediate C_6H_5N , and eventual formation of azepine 47, a reaction elucidated by Huisgen and Vossius¹⁵⁴ and Huisgen.¹⁵⁵



Similarly, Doering and Odum¹⁵⁶ demonstrated that photolysis of **46** leads to the evolution of molecular nitrogen, the formation of a diethylamine-trappable intermediate, and ultimately azepine **48**.





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For almost 100 years; chemists have argued over the identity of the C_6H_5N species. Candidate structures for C_6H_5N have been singlet (¹49) and triplet (³49) phenylnitrene, benzazirine (**50**), and cyclic ketenimine (**51**), a menagerie of species described by Schrock and Schuster¹⁵⁷ as "wonderfully complex."



The question of the intermediates formed by the photolysis of **46** is not just of academic interest, because aryl azides have important applications as photoresists in lithography,⁸ in the formation of electrically conducting polymers,¹⁵⁸ in organic synthesis,^{144,159} as photoaffinity labels,^{4–6} and in the covalent modification of polymer surfaces.⁷

Chemical analysis of reaction mixtures has provided evidence for all these intermediates, **49** to **51**, under different conditions.

Triplet phenyl nitrene and other triplet arylnitrenes dimerize to form azo compounds.^{147,160}



The products of nucleophilic trapping (**47**, **48**), after decomposition of **46**, were initially rationalized as arising from benzazirine **50**.^{154,155} This explanation was generally accepted in subsequent studies^{161–163} and supported by calculations,¹⁶⁴ but in 1978, Chapman and LeRoux¹⁶⁵ detected 1aza-1,2,4,6-cycloheptatetraene (**51**) using matrix isolation techniques. The existence of the cyclic ketenimine **51**, was confirmed by later spectroscopic studies in matrices¹⁶⁶ and in solution.^{167–169} It was also established that ketenimine **51** is the species trapped by nucleophiles in solution to form azepines **47** and **48**.¹⁶⁹

Chapman and LeRoux 's experiments produced no evidence for the intermediacy of $50.^{165}$ The strongest experimental evidence to date for the intermediacy of 50 is the observation that photolysis of 46 in ethanethiol affords o-thioethoxyaniline (52) in 39% yield, presumably from the nucleophilic trapping of $50.^{170}$



Unfortunately, the major product obtained upon decomposition of phenylazide (and many, if not most, of its derivatives) in solution is polymeric tar.¹⁵⁸ Thus, progress in classical nitrene chemistry was much slower than with carbenes, which form robust, easily characterized adducts with most organic molecules and even with alkanes.¹⁷¹

Before moving on to the contribution of spectroscopic methods, we will note two early experiments. First, high dilution of phenylazide suppresses polymer formation and encourages the formation of the azo compound, ^{168,172,173} implying that a singlet intermediate, such as benzazirine or ketenimine, can serve as a reservoir for generation of triplet arylnitrenes, which subsequently dimerize.

Second, Leyva et al.¹⁷⁴ found that the solution phase photochemistry of phenylazide (46) was temperature dependent. Photolysis of 46 in the presence of diethylamine at ambient temperature yields azepine 48, first prepared by Doering and Odum.¹⁵⁶ Lowering the temperature suppresses the yield of 48 and encourages the formation of the azo compound. Thus, high temperatures favor reactions of singlet state intermediates, whereas low temperatures favor reactions associated with triplet phenylnitrene.

Smolinsky and coworkers¹⁷⁵ obtained the EPR spectrum of triplet phenylnitrene (${}^{3}49$), immobilized in a frozen glass. The temperature dependence of one EPR signal demonstrated that ${}^{3}49$ is lower in energy than ${}^{1}49$.

Reiser's and Frazer¹⁷⁶ published an important series of papers beginning in 1965. They were the first to observe the low-temperature UV-Vis spectrum of triplet phenylnitrene ³**49**.¹⁷⁷ A later study¹⁷⁴ of low-temperature glassy matrices revealed an additional long-wavelength band in the spectrum of ³**49**, reported earlier,¹⁷⁷ showing that it was contaminated by the presence of ketenimine **51**. It was found that ³**49** is extremely light sensitive and, upon photo excitation at 77 K, ³**49** rapidly isomerizes to the isomeric **51**.¹⁷⁴

Initial flash photolysis experiments involving 46 gave conflicting results, with different authors favoring the presence of either triplet phenylnitrene ${}^{3}49$, 180,181 benzazirine

50,¹⁶² or cyclic ketenimine 51^{157} as the carrier of the transient spectra.

The currently accepted spectroscopic assignments were obtained by a combination of techniques. Leyva et al.¹⁷⁴ applied matrix absorption and emission spectroscopy, along with flash photolysis techniques. Chapman and LeRoux¹⁶⁵ obtained the matrix IR spectrum of cyclic ketenimine **51**, and Hayes and Sheridan¹⁸² obtained the matrix IR and UV-Vis spectrum of triplet phenylnitrene and cyclic ketenimine **51**. Shields et al.¹⁶⁸ and Li et al.¹⁶⁹ applied time-resolved IR and UV-Vis spectroscopy to demonstrate that cyclic ketenimine **51** is formed in solution and that this species absorbs strongly at 340 nm.







Scheme 5.2

By 1992, Schuster and Platz¹⁴⁹ could write Scheme 5.1, which economically explained much of the condensed-phase photochemistry of **46**. UV photolysis of **46** produces singlet phenylnitrene and molecular nitrogen. In the liquid phase, ¹**49** isomerizes over a small barrier to form cyclic ketenimine **51**. Later computational work from Karney and Borden¹⁰¹ showed this to be a two-step process involving benzazirine **50** (Scheme 5.2), the species trapped by ethanethiol. At ambient temperature in the liquid-phase ¹**49** prefers rearrangement to intersystem crossing (ISC) to the lower-energy triplet state.

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The rate of cyclization slows upon cooling but ISC is not expected to be an activated process so its rate is not expected to vary with temperature. The isokinetic temperature is about 180 K, measured with two precursors: **46** and sulfoximine **53**,^{174,183} Below 180 K, ISC to triplet **49** predominates.



The key intermediate in Scheme 5.1 is singlet phenylnitrene ($^{1}49$) — the only intermediate that by 1992 had not been detected directly or chemically intercepted in the parent system. However, in 1997, Gritsan et al.¹⁸⁴ and the Born et al.¹⁸⁵

simultaneously reported that laser flash photolysis of **46** or of phenyl isocyanate **54** produces a previously undetected transient with $\lambda_{max} = 350$ nm and a lifetime of ≈ 1 ns at ambient temperature.



The transient decays at the same rate that cyclic ketenimine **51** is formed, suggesting that the newly detected transient is singlet phenylnitrene (¹**49**).¹⁸⁴ This assignment was secured with the aid of computational chemistry¹⁸⁶ and by studying the temperature dependence of the kinetics.^{184,186} The barrier to rearrangement of ¹**49** has been determined to be 5.6 ± 0.3 kcal/mol, with an Arrhenius pre-exponential factor of 10^{13.1± 0.3} s⁻¹.¹⁸⁶ A value for the rate constant for intersystem crossing was also extracted: $k_{\rm ISC} = 3.2 \pm 0.3 \times 10^6$ s⁻¹, which is nearly four orders of magnitude smaller than $k_{\rm ISC}$ for phenylcarbene.

5.6.1.2 Semiempirical Calculations

The C₆H₅N potential-energy surface originally received less attention from theoreticians than from experimentalists. Until recently, species on the reaction pathway for ring expansion of ¹49 and some of its simple derivatives had been studied using only semiempirical methods.^{150,164,169,173,187} MNDO calculations by the Schuster group¹⁶⁹ predicted the intermediacy of azirine **50** and placed azepine **51** below **50** in energy. Their calculations found barriers of 12.4 and 3.6 kcal/mol for the first and second steps of the ring expansion, respectively.¹⁶⁹ The much lower barrier computed for the ring opening of **50** to **51** is consistent with the experimental finding that **51**, not **50**, is the species that is trapped in solution.¹⁶⁹

Li et al.¹⁶⁹ also performed calculations on azacycloheptatrienylidene (**55**), the planar carbene isomer of ketenimine **51**. On the basis of their MNDO results, they proposed that the experimentally observed thermal reversion of **51** to triplet phenylnitrene (³49) occurs not via singlet **49** but rather via a triplet state of **55**.¹⁶⁹

Gritsan and Pritchina^{150,173} performed AM1 and MNDO calculations of the electronic structure of phenylnitrene **49** and its para-substituted derivatives **56** to **58**.







electron-donor (NH₂) and electron-withdrawing (NO₂) substituents reduced ΔE_{ST} to 6.6 and 7.4 kcal/mol, respectively.¹⁷³ The next singlet state of nitrene **49** was calculated to be a closed-shell singlet, 12.7 kcal/mol above the open-shell singlet. The energy difference between open-shell and closed-shell singlets were predicted to be 9.5 kcal/mol for **57** and 14.3 kcal/mol for **58**.¹⁷³ Subsequent *ab initio* calculations revealed that these results were only qualitatively correct and significantly underestimated the value of ΔE_{ST}

5.6.2 Phenylnitrene: Electronic Structure and Spectroscopy

In phenylnitrene **49**, a lone pair occupies a hybrid orbital, rich in 2s character; and, unlike the case in phenylcarbene (**59**), the two nonbonding electrons both occupy pure 2p orbitals. One of these is a 2p- π orbital, and the other a 2p orbital on nitrogen that lies in the plane of the benzene ring. The near-degeneracy of the two 2p orbitals gives rise to three low-lying spin states: a triplet (³A₂), an open-shell singlet (¹A₂), and a closed-shell singlet (¹A₁). The orbital occupancies and CASSCF(8,8)/6-31G^{*} geometries of these are shown in Figure 5.12.¹⁰¹



In the ${}^{3}A_{2}$ and ${}^{1}A_{2}$ states, the $2p-\pi$ orbital and the inplane 2p orbital on N are both singly occupied. The ${}^{1}A_{1}$ state of **49** is a mixture of two dominant configurations — one in which the in-plane 2p orbital on N is doubly occupied and the

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Figure 5.12 Orbital occupancies for nonbonding electrons and CASSCF(8,8)/6-31G* optimized geometries of the lowest triplet and singlet states of phenylnitrene.^{49,101} Bond lengths are in angstroms.

 $2p-\pi$ orbital is empty, which is slightly lower in energy than the configuration in which these orbital occupancies are reversed. $^{\bar{1}88,189}$ In both the $^{3}A_{2}$ and $^{1}A_{1}$ states, the C–N bond is relatively long and the phenyl ring shows little bond-length alternation. In the ${}^1\!A_2$ state, however, strong delocalization of the electron in the nitrogen p- π orbital into the ring leads to a very short C–N bond (1.276 Å), and the bond lengths within the aromatic ring resemble those of a cyclohexadienyl radical.^{188,189}

As discussed in Section 5.2, in NH ${}^{1}A_{1}$ and ${}^{1}A_{2}$ are degenerate and form the two components of a 1'E state. However, in phenylnitrene the ${}^{1}A_{2}$ state lies well below the ${}^{1}A_{1}$ state. In the ${}^{1}A_{2}$ state delocalization of the electron in the singly occupied π orbital into the benzene ring confines this electron and the opposite-spin electron in the in-plane 2p AO on nitrogen to different regions of space, thus minimizing their mutual Coulomb repulsion energy.^{190–192} This strong delocalization of the

unpaired π electron in ${}^{1}A_{2}$ accounts for the difference between the bond lengths in this state and those in ${}^{3}A_{2}$.^{188,189} The calculated^{101,188,189,193,194} and experimentally

The calculated^{101,188,189,193,194} and experimentally determined^{193,194} relative energies of the spin states of **49** are shown in Table 5.5. All levels of theory shown predict the lowest singlet state, (¹A₂) to lie about 18 kcal/mol higher in energy than the triplet ground state (³A₂), in excellent agreement with the results of photoelectron¹⁹³ and electron photodetachment¹⁹⁴ spectroscopy. Predictions for the relative energy of the ¹A₁ state vary substantially, with the DFT result of 29.5 kcal/mol¹⁹⁵ (relative to the ³A₂ state) apparently giving the best agreement with the experimental estimate.¹⁹³

Both phenylnitrene **49** and the isoelectronic phenylcarbene **59** have triplet ground states; however, the lowest singlet

TABLE 5.5 Relative Energies (kcal/mol) of the Lowest SpinStates of Phenylnitrene (49)

Method	Electronic state			Ref.
	³ A ₂	${}^{1}A_{2}$	$^{1}A_{1}$	
CISD+Q/DZ+d	0	18.3	32.4	188
σ-S, π-SDCI/6-31G*//	0	18.3	38.7	189
CASSCF(8,8)/3-21G				
SDCI/6-31G*//	0	18.3	30.6	195
CASSCF(8,8)/3-21G				
CASSCF(8,8)/6-31G*	0	17.5	42.2	101
CASPT2(8,8)/6-311G(2d,p)//	0	18.5	36.9	101
CASSCF(8,8)/6-31G*				
BLYP/cc-pVTZ//	0	-	29.5	196
BLYP/cc-pVDZ				
CCSD(T)/cc-pVDZ//	0	-	35.2	196
CASSCF(8,8)/cc-pVDZ				
Experiment	0	18 ± 2	30 ± 5	193
	0	18.3 ± 0.7	-	194

is the open-shell (¹A₂) state in **49** but the lower singlet is the closed-shell (¹A') state in **59**. This difference between the carbene and the nitrene can be ascribed to the fact that in singlet **59** the two nonbonding electrons can occupy a hybrid AO, whereas in **49** the two nonbonding electrons occupy two pure 2p orbitals. Therefore, the near degeneracy of the nonbonding MOs in **49** is strongly lifted in **59**, and in the lowest singlet state of **59**, both nonbonding electrons preferentially occupy the lower-energy, hybridized σ -orbital rather than the 2p- π orbital.¹⁹⁷⁻²⁰⁰

As a result, the energy difference between the lowest singlet and the triplet state is much smaller in **59** ($E_{\rm ST} \approx 2$ kcal/mol²⁰¹) than in **49** ($E_{\rm ST} \approx 18$ kcal/mol^{193,194}). The smaller value of $E_{\rm ST}$ in **59** than in **49** contributes to the much faster rate of intersystem crossing in phenylcarbene^{202,203} relative to phenylnitrene.¹⁸⁶

Another contributor is the difference between the nature of the lowest singlet states in **49** and **59**. The transition of an electron from a σ -orbital in the ¹A' state of **59** to a π orbital in the ³A" state creates orbital angular momentum, and spin-orbit coupling facilitates the change in spin angular momentum that occurs in intersystem crossing in the carbene. In contrast, the ¹A₂ and ³A₂ states of **49** have the same orbital occupancy, so there is no change in orbital angular momentum to facilitate intersystem crossing.

5.6.2.1 UV-Vis Spectroscopy of Triplet Phenylnitrene ³49

The calculations^{101,188,189,193–196} predict that the ground state of phenylnitrene has a triplet multiplicity (${}^{3}A_{2}$) in accordance with the earlier EPR experiment of Smolinsky et al.¹⁷⁵ Figure 5.13 represents the electronic absorption spectrum of ${}^{3}49$ in an Ether-pentane-alcohol (EPA) matrix at 77 K.¹⁷⁴ There is a strong sharp band at 308 nm, a broad structured band at 370 nm, and a broad unstructured feature, which tails out to 500 nm.^{174,177}

The π system of **³49** is closely related to that of the benzyl and anilino radicals. Thus, it is no surprise that the triplet absorption spectrum of **³49** is very similar to the experimental





Figure 5.13 The absorption spectrum of triplet phenylnitrene in EPA glass at 77 K.¹⁷⁴ The computed positions and oscillator strengths (f, right-hand axes) of the absorption bands are depicted as solid vertical lines.¹⁸⁶ For very small oscillator strength, the value multiplied by 10 is presented (f \times 10).

spectra of the benzyl ($C_6H_5CH_2$) and anilino (C_6H_5NH) radicals. Benzyl radical has a medium intensity feature at 316 nm and a very weak band at 452 nm.²⁰⁴ The anilino radical has a medium intensity band at 308 nm and a weak transition at 400 nm.^{205–207}

Using the INDO/S method, Shillady and Trindle¹⁶⁴ performed the first calculation of the electronic absorption spectrum of **³49**. The long wavelength maximum was calculated to be at 380 nm and was assigned to an $n \rightarrow \pi^*$ transition. The long wavelength transition, observed at about 450 nm, was not reproduced by this calculation. The next transition was computed to be at 330 nm, and it was assigned to the excitation of a nitrogen lone-pair electron into the singly occupied nitrogen 2p orbital that lies in the molecular plane (2p_y). Note that the latter transition is of the same nature as those in triplet nitrenes NH and in CH₃N (Sections 5.2 and 5.3).

Later, Kim et al.¹⁸⁸ performed configuration interaction calculations of ground and excited states of ³49 with all single

and double excitations, but they failed to reproduce the electronic absorption spectrum of triplet phenylnitrene quantitatively.

However, recently¹⁸⁶ the spectrum of ³49 was calculated using the CASPT2 level of theory. The computed spectrum was in very good agreement with experiment (Figure 5.13). The improved correspondence is a result of the combination of an improved description of the reference wave function and an adequate treatment of the dynamical electron correlation by the CASPT2 procedure.

CASPT2 calculations predict that the vertical excitation energy to the first excited state $(1^{3}B_{1})$ will be at 432 nm (f = 3.4×10^{-4}). This excited state consists principally of two electronic configurations: $\pi (1a_{2}) \rightarrow \pi (3b_{1})$ and $\pi (3b_{1}) \rightarrow \pi_{1}^{*} (2a_{2})$, where $\pi (3b_{1})$ is the singly occupied π -orbital. The second excited state is $2^{3}A_{2}$, and it has a vertical excitation energy of 393 nm (f = 9.4×10^{-3}), which is associated with the $\pi (2b_{1})$ $\rightarrow \pi (3b_{1})$ and $\pi (3b_{1}) \rightarrow \pi_{2}^{*} (4b_{1})$ transitions.

Triplet phenylnitrene has a very strong absorption band at 308 nm. The CASPT2 calculations predict that transitions to the $2^{3}B_{1}$ (at 301 nm, f = 0.013) and $3^{3}B_{1}$ (at 299 nm, f = 0.044) states contribute to this absorption. The electronic configurations for the $3^{3}B_{1}$ state are the same as for the $1^{3}B_{1}$ state. The main configuration involved in the $1^{3}A_{2} \rightarrow 2^{3}B_{1}$ transition consists of excitation of an electron from the lone pair orbital (n_z) on nitrogen to the singly occupied nitrogen 2p orbital that lies in the molecular plane (p_y). This transition, $1^{3}A_{2} \rightarrow 2^{3}B_{1}$ (around 300 nm), is very similar to those observed from the triplet ground states of the parent NH (336 nm),^{12,13} methylnitrene (315 nm),^{55,56} 1-norbornylnitrene (298 nm),⁴² and perfluoromethylnitrene (354 nm).⁴³

5.6.2.2 UV-Vis Spectroscopy of Singlet Phenylnitrene ¹49

The electronic absorption spectrum of ¹**49** was first detected in 1997.¹⁸⁴ Laser flash photolysis (266 nm, 35 ps) of **46** in pentane at 233 K produces a transient absorption spectrum, which shows two sharp bands with maxima at 335 and 352 nm (Figure 5.14). In later work¹⁸⁶ the spectrum of ¹**49** was



Figure 5.14 Transient spectrum of singlet phenylnitrene produced upon LFP of phenyl azide. Spectrum 1 was recorded 2 ns after laser pulse (266 nm, 35 ps) at 233 K. Long-wavelength band (spectrum 2) was recorded with an optical multichanal analyzer at 150 K (with a 100-ns window immediately after the laser pulse, 249 nm, 12 ns). The computed positions and oscillator strengths (f, righthand axes) of the absorption bands are depicted as solid vertical lines.¹⁸⁶ For very small oscillator strengths a value multiplied by 10 is presented (f × 10).

reinvestigated and an additional very weak, long wavelength absorption band at 540 nm was observed. The transient spectrum in Figure 5.14 was assigned to singlet phenylnitrene in its lowest open-shell electronic configuration: ${}^{1}A_{2}$.

This assignment was supported by the similarity of the spectrum (Figure 5.14) to that of the long-lived perfluorinated singlet arylnitrenes.²⁰⁸ The decay of this transient absorption is accompanied by the formation of cyclic ketenimine **51**. Furthermore, the electronic absorption spectrum of ¹**49** in the ¹A₂ state, calculated at the CASPT2 level, is in good agreement with the transient spectrum that is observed for ¹**49** (Figure 5.14).

Calculations on ¹**49** are more challenging than those on ³**49**, because the ¹A₂ state of **49** is an open-shell singlet state. The first two electronically excited singlet states of ¹**PN** are both of A₁ symmetry and are predicted computationally to be found at 1610 and 765 nm. Neither of these transitions has been detected, because not only do excitations from ¹A₂ into both of

these states have zero oscillator strength because of symmetry considerations, but these excited states are predicted to lie outside the wavelength range accessible to the spectrometer.¹⁸⁶

The CASPT2 calculations predict a transition at 581 nm to a $1^{1}B_{1}$ excited state, with a very small oscillator strength (1.6×10^{-4}) . This transition could be assigned to a very weak band with a maximum around 540 nm (Figure 5.14). This state consists of the same electronic configurations as the long wavelength transition in ³49.

The next excited state in the singlet manifold is the $2^{1}A_{2}$ state. This transition has a small oscillator strength (2.1 × 10^{-3}) and an excitation energy of 429 nm. In the experimental spectrum (Figure 5.14), this band seems to be a shoulder on the tail of a strong band at 350 nm.

The only intense absorption band in the absorption spectrum of ¹49 is localized around 350 nm, which is a pronounced shift from the 308 nm band in ³49. This band has a long tail out to 450 nm and displays some fine structure that may be associated with the vibrations of the phenyl ring in ¹49 (Figure 5.14). The strongest absorption band in $^{1}49$, predicted by the CASPT2 method, is the transition to the 2¹B₁ exited state, which has a 368 nm excitation energy. The main configuration involved in this transition is similar to that of the $2^{3}B_{1}$ state and consists of an electron from the lone-pair orbital on nitrogen (n_z) , which is promoted to the singly occupied nitrogen 2p orbital that lies in the molecular plane (p_v) . Therefore, the nature of this band is the same as that of the most intense band in the spectrum of ³49. Note also the same origin as the UV bands of the triplet and singlet nitrene NH (Section 5.2) and triplet and singlet alkylnitrenes (Section 5.3).

Although, the electronic absorption spectra of ${}^{1}49$ and ${}^{3}49$ are very similar (Figure 5.13 and Figure 5.14). However, all of the calculated and experimental bands of ${}^{1}49$ exhibit a red shift compared with those of ${}^{3}49$.

5.6.3 Dynamics of Singlet Phenylnitrene

5.6.3.1 Recent Experiments

The decay of singlet phenylnitrene in pentane was monitored at 350 nm over a temperature range of 150 to 270 K, which

allowed direct measurement of the rate constant for intersystem crossing $(k_{\rm ISC})$ and of accurate barriers to cyclization.^{186} The disappearance of 149 at 298 K was faster than the time resolution of the spectrometer, and the lifetime (τ) of 149 was estimated to be ${\sim}1$ ns under these conditions.^{184,186} This estimated lifetime of 149 is consistent with that of about 0.6 ns, measured in CH_2Cl_2 at ambient temperature by Born and coworkers.^{185}

The formation of the products (cyclic ketenimine **51** and triplet nitrene ³**49**) was monitored at 380 nm.¹⁸⁴ The decay of ¹**49** and growth of the products are first order and can be analyzed to yield an observed rate constant, k_{OBS} . An Arrhenius treatment of the k_{OBS} data (open circles) is presented in Figure 5.15.

The magnitude of k_{OBS} decreases with decreasing temperature until about 170 K, whereupon it reaches a limiting



Figure 5.15 Arrhenius treatment of the k_{OBS} data (open circles) and k_R data (filled circles) for singlet phenylnitrene deduced upon assuming that k_{ISC} is independent of temperature.¹⁸⁶ Insert: temperature dependence of k_{OBS} data.

value of about 3.2×10^6 s⁻¹. Below this temperature, k_{OBS} remains constant.¹⁸⁶ The breakpoint in the Arrhenius plot is about 180 to 200 K and is in exactly the same temperature range where the solution-phase chemistry changes from trapping of ketenimine **51** with diethylamine to dimerization of ³49.¹⁷⁴ Thus, the low-temperature data in Figure 5.15 is associated with the rate constant for intersystem crossing of ¹49 to ³49 ($k_{ISC} = 3.2 \pm 0.3 \times 10^6$ s⁻¹) and the high-temperature data with k_R , the rate constant for rearrangement of ¹49 (Scheme 5.1).

Because at any temperature k_{OBS} = k_R + k_{ISC} , by assuming that k_{ISC} does not change with temperature, it was possible to deduce values of k_R as a function of temperature and to obtain its Arrhenius parameters. Indeed, an Arrhenius plot of k_R = $k_{OBS} - k_{ISC}$ was linear (Figure 5.15, solid circles), giving an activation energy for rearrangement of E_a = 5.6 \pm 0.3 kcal/mol and pre-exponential factor A = $10^{13.1 \pm 0.3 \cdot \mathrm{s}^{-1}.^{186}$

5.6.3.2 Recent Ab Initio Calculations

Recent calculations on the ring expansion of the lowest singlet state of phenylnitrene (${}^{1}A_{2}$ -49) to azacycloheptatetraene (51) predict a two-step mechanism, which involves the bicyclic azirine intermediate 50.¹⁰¹ The CASPT2 energetics are depicted in Figure 5.16, and the CASSCF optimized structures of the stationary points are shown in Figure 5.17.

The first step, cyclization of ¹49 to the azirine **50**, is predicted to be the rate-determining step. The CASPT2 calculated barrier of 9.2 kcal/mol is somewhat higher than the experimental barrier of 5.6 ± 0.3 kcal/mol.¹⁸⁶ The discrepancy between the calculated and the experimental barrier heights is due to the general tendency of the CASPT2 method to overstabilize open-shell species (in this case, ¹A₂-49) relative to closed-shell species (in this case, all the other stationary points on the reaction path).²⁰⁹

This tendency is also seen in comparing the CASPT2 and multireference configuration interaction (MR-CISD + Q) values for the energy difference between open-shell singlet ($^{1}A''$) vinylnitrene and 2H-azirine.^{100,101} The nitrene and azirine

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Figure 5.16 Energetics of the ring expansion of singlet phenylnitrene (${}^{1}A_{2}$ - ${}^{1}49$), calculated at the CASPT2(8,8)/6-311G(2d,p)//CASSCF(8,8)/6-31G^{*} level.¹⁰¹



Figure 5.17 CASSCF(8,8)/6-31G^{*} optimized geometries of stationary points in the ring expansion of singlet phenylnitrene $({}^{1}A_{2}-{}^{1}49)$.¹⁰¹ Bond lengths are in angstroms, and bond angles are in degrees.

serve as models for ${}^{1}A_{2}$ -49 and 50, respectively. This comparison with MR-CISD + Q shows that CASPT2 underestimates the energy of the open-shell nitrene reactant relative to the closed-shell 2*H*-azirine product by 3.4 kcal/mol.¹⁰¹ If the relative energy of ${}^{1}A_{2}$ -49 is also too low by a comparable amount, then a better computational estimate of the barrier for the

first step in the ring expansion of **49** would be about 5.8 kcal/mol, in excellent agreement with experiment.¹⁸⁶

The CASPT2/6-311G(2d,p) barrier for the process $50 \rightarrow 51$ is only about 3 kcal/mol, and this reaction is calculated to be exothermic by about 6 kcal/mol. These computational results are consistent with the failure of time-resolved IR experiments by Shields et al.¹⁶⁸ and Li et al.¹⁶⁹ to detect **50**. A 3-kcal/mol barrier implies rapid conversion of **50** to **51** at room temperature, and a 6-kcal/mol difference in energy between **50** and **51** means that at 25°C the equilibrium would overwhelmingly favor **51**. In addition, azirine **50** probably absorbs less strongly than cyclic ketenimine **51** in the infrared, rendering detection of the azirine even more difficult. Nevertheless, although **50** has not been observed spectroscopically, it apparently can be intercepted by ethanethiol to form an orthosubstituted aniline.¹⁷⁰

If the MRCI-derived upward correction of 3.4 kcal/mol to the energy of ${}^{1}A_{2}$ -49 is made, the energy difference between ${}^{1}A_{2}$ -49 and 51 is estimated to be only 5 kcal/mol. Therefore, at equilibrium, a small amount of singlet 49 should be present at ambient temperatures. Intersystem crossing of singlet 49 to triplet 49 should then lead to the irreversible conversion of 51 to the triplet ground state of 49. It has, in fact, been observed that 51 ultimately reverts to triplet 49 over time in inert solvents.^{168,172,173}

5.6.4 Spectroscopy of Substituted Phenylnitrenes

Direct observations of singlet arylnitrenes before 1997 were exceedingly rare. Before the detection of the spectrum of ${}^{1}49^{184,186}$ and its 2,4,6-tribromosubstituted analogue,¹⁸⁵ only the spectrum of singlet 1-pyrenyl nitrene (${}^{1}60$), reported by Sumitani et al.²¹⁰ in 1976, was known. In 1985, Kobayashi et al.²¹¹ studied p-(dimethylamino)phenyl azide by picosecond laser flash photolysis (LFP). They detected the transient spectrum of triplet nitrene (${}^{3}61$) and that of a precursor, which had a lifetime of 120 ps. The authors did not specify the nature of this precursor to the triplet, but in our opinion this inter-

mediate must have been singlet p-(dimethylamino)phenylnitrene ($^{1}61$).



Miura and Kobayashi²¹² studied the photochemistry of 4,4'-biphenyl bisazide. They concluded that photolysis of this diazide leads to extrusion of a single molecule of nitrogen with the formation of a singlet-state species, "X," with a lifetime of 19 ns. Miura and Kobayashi did not specify the nature of X. However, this species absorbs at 380 nm, and its spectrum and lifetime are similar to those we found for singlet parabiphenylnitrene.²¹³ Therefore, we conclude that X is singlet 4'-azido-4-biphenylnitrene.



After the spectrum and dynamics of parent phenylnitrene were measured, our group began a comprehensive study of the influence of substituents on the spectroscopy and reactivity of simple substituted phenylnitrenes.^{213–218}The spectra

of many *para-* and *ortho*-substituted singlet phenylnitrenes as well as ortho, ortho-disubstituted singlet phenylnitrenes were recorded (Table 5.6). The spectra of most singlet arylnitrenes reveal strong absorbtion bands in the near UV region with maxima in the range of 320 to 440 nm (Table 5.6). We detected the spectra of all singlet aryl nitrenes studied, with the notable exceptions of *para*-nitro- and *para*-cyanophenylnitrenes.

Figure 5.18 displays representative spectra of singlet *ortho*-fluoro, *ortho*-phenyl, and *ortho*,*ortho*-dicyanophenylnitrenes as well as that of parent singlet **49**. Figure 5.18 shows that the maximum of the o-fluorosubstituted ¹49 is shifted slightly to the blue region, and the maxima of cyano-substi-

TABLE 5.6Maxima (in nm) of the Most Intense AbsorptionBands in Electronic Absorption Spectra of Substituted Singlet andTriplet Phenylnitrenes (Near UV and Visible)

	Singlet		Triplet	
Substituent	Nitrene	Ref.	Nitrene	Ref.
4-F	365	214	а	
4-Cl	360		а	
4-Br	361	_	а	
2,4,6-triBr	395	185	326, 340	174
4-I	328	214	а	
4-Me	365		315	219
$4-CF_3$	~320		а	
4 -COCH $_3$	334	_	No	219
4-Ph	345	213	320	219
4-(4'-azido-phenyl)	380	212	а	
2-Me	350	215	а	
2,6-diMe	350		297, 310	174
2,4,6-triMe	348, 366		319	_
2-F	342	218	294, 315	
2,6-diF	331, 342		313	174
2,3,4,5,6-pentaF	330	184	315	_
2-CN	382	217	328	217
2,6-diCN	385, 405	_	341	_
2-Ph	409	213	344	213
2-Ph,4,6-diCl	437	b	355	b

^aSpectrum was not detected.

^bTsao, M.L., Gtitsan, N.P., and Platz, M.S., unpublished data.





Figure 5.18 Electronic absorption spectra of selected singlet arylnitrenes: phenylnitrene (curve 1), 2-fluorophenylnitrene (curve 2) and 2-phenyl-4,6-dichlorophenylnitrene (curve 4) in pentane and 2,6-dicyanophenylnitrene (curve 3) in CH_2Cl_2 .

tuted and especially of *ortho*-phenyl–substituted phenylnitrenes undergo a more pronounced shift to the red.

In the case of ¹49 the origin of the absorption band at 350 nm largely involves the excitation of an electron from the lone pair orbital on nitrogen (n) to the singly occupied nitrogen 2p orbital that lies in the molecular plane (p_y) . In the case of ³49 two transitions $(T_0 \rightarrow T_3, T_0 \rightarrow T_4)$ contribute to the absorption band around 300 nm, one of which is the same in nature as in the case of ¹49 $(n \rightarrow p_y)$. It is reasonable to assume that the same situation will be found with the substituted phenylnitrenes. Therefore, we can predict that the influence of the substituted singlet and triplet phenylnitrenes will be similar. Indeed, Figure 5.19 shows that the maxima of triplet *ortho*-biphenylnitrenes and *ortho,ortho*-dicyanophenylnitrenes (Figure 5.18).





Figure 5.19 Electronic absorption spectra of selected triplet arylnitrenes: phenylnitrene (curve 1, EPA), 2-fluorophenylnitrene (curve 2, MCH), 2,6-dicyanophenylnitrene (curve 3, MCH), and 2-phenyl-4,6-dichlorophenylnitrene (curve 4, MCH) at 77 K.

In the case of triplet ortho-fluorophenylnitrene, it is most probable that two excited states (T_3 and T_4) are separated (~2200 cm⁻¹, Figure 5.19) in energy. A similar separation of T_3 and T_4 states was observed experimentally¹⁷⁴ and verified computationally²²⁰ for triplet perfluorophenylnitrene.

Figure 5.20 displays the correlation between the maxima in the spectra of substituted triplet and singlet phenylnitrenes. A clear linear dependence of the maximum of the electronic spectra of various singlet nitrenes with the maxima in the spectra of the corresponding triplet nitrenes (slope = 1.36 ± 0.12 and correlation coefficient 0.98) is observed. Furthermore, analysis of the data of Table 5.6 verifies that *ortho*substituents influence the absorption spectra of singlet and triplet phenylnitrenes more significantly than do *para*-substituents.









5.6.5 Substituent Effects on the Intersystem Crossing

Values of k_{OBS} in substituted singlet phenylnitrenes were measured by the decay of singlet nitrene absorptions at the wavelength of their maxima as a function of temperature.^{213–218} As in the case of unsubstituted phenylnitrene (Figure 5.15), the magnitude of k_{OBS} decreases as the temperature decreases, until a limiting value is reached (Figure 5.21 and Figure 5.22). The temperature-independent rate constant observed at low temperature was associated with k_{ISC} . In the case of 4-bromo, 4-iodophenylnitrene (Figure 5.21), and 2,6-dimethylphenylnitrene (Figure 5.22), the values of k_{OBS} are independent of temperature over a very large temperature range (~120 to 200 K). This confirms that the rate constants for ISC in arylnitrenes are temperature independent in solution over typical temperature ranges.

5.6.5.1 *Para*-Substituted Derivatives of Phenylnitrene

Values of k_{ISC} for singlet *para*-substituted phenylnitrenes are given in Table 5.7. Table 5.7 also contains the k_{ISC} value for




Figure 5.21 Temperature dependence of k_{OBS} values of *para*-fluoro (curve 1), *para*-chloro (curve 2), *para*-bromo (curve 3), and *para*-iodo (curve 4) singlet phenylnitrene in pentane.²¹⁴



Figure 5.22 Arrhenius treatment of k_{OBS} values of singlet *para*methyl (curve 1) and *ortho*-methyl (curve 2) phenyl nitrene in pentane and singlet *ortho*, *ortho*-dimethylphenylnitrene (curve 3) in hexane.²¹⁵

singlet para-dimethylaminophenylnitrene^{211} and a lower limit to $k_{\rm ISC}$ for para-nitrophenylnitrene, based on the data of Liang and Schuster. 172

The rate constant of ISC for *para*-bromo singlet phenylnitrene is about seven times larger than that of parent ¹**49** and the *para*-fluoro and *para*-chloro analogs. This is easily attrib-





TABLE 5.7 Kinetic Parameters of *Para*-Substituted Singlet Aryl Nitrenes $(X-C_6H_4-N)$ in Pentane

	τ_{295K} ,	$\mathbf{k}_{\mathrm{ISC}}$	$\mathbf{E}_{\mathbf{a}}$	Log A	
Para-X	ns	$(\times 10^{6} \text{ s}^{-1})$	(kcal/mol)	(s^{-1})	Ref.
Η	~1	3.2 ± 0.3	5.6 ± 0.3	13.1 ± 0.3	186
CH_3	~1	5.0 ± 0.4	5.8 ± 0.4	13.5 ± 0.2	214
CF_3	1.5	4.6 ± 0.8	5.6 ± 0.5	12.9 ± 0.5	_
$C(O)CH_3$	5.0	8 ± 3	5.3 ± 0.3	12.5 ± 0.3	_
F	~0.3	3.5 ± 1.4	5.3 ± 0.3	13.2 ± 0.3	_
Cl	~1	3.9 ± 1.5	6.1 ± 0.3	13.3 ± 0.3	_
Br	~3	17 ± 4	4.0 ± 0.2	11.4 ± 0.2	
Ι	а	72 ± 10	а	а	
OCH_3	<1	>500	а	а	_
CN	8 ± 4	6 ± 2	7.2 ± 0.8	13.5 ± 0.6	217
Ph	15 ± 2	12 ± 1	6.8 ± 0.3	12.7 ± 0.3	213
N(CH ₃) ₂ ^b	0.12	8300 ± 200	а	а	211
NO_2^c	<20	>50	а	а	172

^aNot measured.

^bIn toluene.

°In benzene.

utable to a small heavy atom effect. The heavy atom effect of iodine is larger than that of bromine, as expected, and increases the rate of ISC by more than a factor of 20, relative to parent ${}^{1}49$.

A very large increase in $k_{\rm ISC}$ is observed with *para*-methoxy and -dimethylamino substituents (Table 5.7). This result is consistent with the solution phase photochemistry of *para*methoxy and para-dimethylaminophenyl azides,¹⁶⁹ which largely yield azobenzenes on photolysis.

The CH₃-, CF₃-, acetyl-, fluoro-, and chloro-substituents are not sufficiently strong π donors or acceptors to significantly influence the size of k_{ISC} (Table 5.7). However, the strong π -donating *para*-methoxy and *para*-dimethylamino groups do have a huge influence on k_{ISC}.

The electron-withdrawing substituents $(CF_3, COCH_3, CN, and NO_2)$ have a smaller, but measurable, influence on

 $k_{\rm ISC}\,(\textbf{x10}^{6}~{\rm s}^{\textbf{-1}})$ Substituent Solvent Ref. 2-Methyl Pentane $10\,\pm 1$ 2152,6-Dimethyl Pentane 15 ± 3 CF₂ClCFCl₂ 30 ± 8 2,4,6-Trimethyl Pentane 29 ± 3 $CF_2ClCFCl_2$ 20 ± 1 2-Fluoro 218Pentane 3.3 ± 0.5 3,5-Difluoro Pentane 3.1 ± 1.5 2,6-Difluoro Hexane 2.4 ± 0.3 CCl_4 2.7 ± 0.3 2,3,4,5,6,-Pentafluoro Pentane 3.3 ± 1.5 CH₂Cl₂ 10.5 ± 0.5 2082-Cyano Pentane 2.8 ± 0.3 2,6-Dicyano CH₂Cl₂ 4.5 ± 0.5 217Pentane 6.2 ± 0.8 THF 5.9 ± 1.5 2-Pyrimidyl CH_2Cl_2 800 ± 200 216

TABLE 5.8	Intersystem	Crossing	Rate	Constants	of Or	rtho-	and
Meta Subst	ituted Phenyl	nitrenes					

 k_{ISC} . It is interesting to note that both donating and withdrawing substituents accelerate ISC.

5.6.5.2 Ortho- and Meta Substituted Derivatives of Phenylnitrene

Intersystem crossing rate constants of ortho- and meta substituted singlet phenyl nitrenes are presented in Table 5.8. Mono- and di-ortho fluorine substituents have no influence on ISC rate constants. No effect with meta, meta diffuoro substitution is observed either. Pentafluoro substitution has no efffect on k_{ISC} in pentane, although a modest acceleration is observed in the slightly more polar solvent, methylene chloride.

An increase of triplet nitrene absorption, relative to azepine absorption, was observed upon LFP of perfluorophenyl azide in methanol.²²¹ This effect was not observed in acetonitrile, which has a similar dielectric constant, nor in

tetrahydrofuran, which contains an oxygen atom but cannot donate hydrogen bonds. It was proposed that the ISC rate constant for singlet perfluorophenylnitrene is dramatically increased in methanol, which explains much of the solutionphase organic chemistry of this nitrene in this solvent.²²¹

An *ortho* cyano group has little influence on k_{ISC} , but two *ortho* cyano groups slightly accelerate intersystem crossing. Electron-withdrawing groups in the *para* positions of singlet arylnitrenes have a modest effect on increasing the rate constant of ISC.

An *ortho* methyl group accelerates intersystem crossing relative to singlet *para*-tolylnitrene. Two *ortho* methyl groups are more effective than one at accelerating intersystem crossing. Singlet 2,4,6-trimethylphenylnitrene undergoes intersystem crossing about as readily as 2,6-dimethylphenylnitrene. These results suggest that *ortho* methyl groups may accelerate intersystem crossing through a steric effect that forces the nitrogen out of the plane of the aromatic ring, thus facilitating vibronic mixing of the low-lying singlet excited states into the lowest singlet state.

5.6.5.3 Calculations of the Spin-Orbit Coupling

Recently Johnson et al.²²² calculated the electronic structures and energies of the triplet and three singlet states for phenylnitrene and 31 singly substituted derivatives. The spin-orbit coupling constants (SOC) were calculated as well to better understand the factors affecting rates of ISC.

All structures were optimized at the CASSCF(8,8) level with the cc-pVDZ basis set. For multireference calculations involving bromine and iodine, the Cowan–Griffin *ab initio* model potential with a relativistic effective core potential was used.²²² CASPT2 calculations were performed on all optimized CASSCF(8,8)/cc-pVDZ geometries, using the CASSCF wave functions as the reference wave functions. SOCs were computed by using the Pauli–Breit Hamiltonian.

The geometries and energies of the triplet and three singlet states of arylnitrenes were also calculated using DFT at the BPW91 level.²²² In the case of calculations of the lowest singlet states the unrestricted DFT was used, and the energies were computed using the sum method of Ziegler. et al.²²³ and Cramer et al.²²⁴

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Table 5.9 lists the electronic energies of the three singlet states S_1 , S_2 , and S_3 relative to the triplet as computed at the CASPT2 and BPW91 levels of the theory for 31 substituted phenylnitrenes studied. Analysis of Table 5.9 shows that for all substituents except those having a σ value more negative than -0.14, a near constant T_0 - S_1 energy separation is predicted. Even in the case of substituents with the most negative σ values, the decrease of the energy separation does not exceed 2 to 3 kcal/mol.

It was noted previously that the strong π -donating paramethoxy and para-dimethylamino groups (Table 5.7) have a huge influence on k_{ISC} . For biradicals where two electrons are spatially proximate, as in nitrenes, SOC is the primary mechanism for ISC. For small amounts of SOC, relative rate constants k_{ISC} between two systems can be estimated from the Landau–Zener model²²⁵ as

$$\frac{k_{ISC}'}{k_{ISC}} = \left(\frac{\left\langle S_1 \middle| H_{SO} \middle| T_0 \right\rangle'}{\left\langle S_1 \middle| H_{SO} \middle| T_0 \right\rangle}\right)^2 \left(\frac{\Delta E}{\Delta E'}\right)^2, \tag{5.1}$$

where H_{SO} is the spin-orbit coupling Hamiltonian and ΔE is the energy difference between T_0 and S_1 . In phenylnitrenes, however, the SOC matrix elements between T_0 and S_1 states are required by symmetry to be zero (Table 5.10). SOC can be accomplished only dynamically, whereby S_2 and S_3 character is mixed into S_1 by geometric distortion. Johnson et al.²²² used a (2,2) CI model^{225–227} to obtain a qualitative picture of SOC in the arylnitrenes. It was concluded that the vibrationally averaged SOC matrix elements are required for a more quantitative description of the ISC in arylnitrenes.²²²

5.6.6 Substituent Effects on the Rates and Regiochemistry of the Ring Expansion of Phenylnitrene

Cyclic ketenimine **51** is the major, trappable, reactive intermediate in solution when phenyl azide (at moderate concentrations) is decomposed photolytically at 298 K. The rate of decay of singlet phenylnitrene is equal to the rate of formation

TABLE 5.9 the Triplet	Hammett σ Va State for R-Sub	lues and CAS stituted Phen	SPT2 and F nylnitrenes	3PW91 Sing	let Energies	(kcal/mol) R	elative to
		S.	1	S	2	S	
R	Ø	CASPT2	BPW91	CASPT2	BPW91	CASPT2	BPW91
p-NHCH ₃	-0.46	16.7	12.2	30.4	23.3	63.7	53.9
D-d	-0.38	18.3	13.4	34.5	27.6	61.2	49.9
$P-N(CH_3)_2$	-0.32	16.3	12.2	30.5	24.4	63.2	52.4
$\mathrm{p} ext{-}\mathrm{NH}_2$	-0.30	17.1	12.5	31.2	23.9	63.5	53.4
$p-CH_3$	-0.14	18.8	13.8	36.9	32.2	58.6	44.5
p-OCH ₃	-0.12	18.3	13.3	34.5	27.7	65.2	49.4
$m-N(CH_3)_2$	-0.10	19.3	14.1	36.7	32.7	57.4	43.0
m-NHCH ₃	-0.10	19.6	14.3	36.8	33.1	57.0	42.8
m-NH"	-0.09	19.2	14.1	37.1	33.3	57.2	43.2
$m-CH_3$	-0.06	19.5	14.3	37.3	33.6	57.6	43.1
, H	0.00	19.3	14.3	37.4	33.9	57.8	43.0
$m-OCH_3$	0.10	20.0	14.7	37.4	33.9	57.1	43.1
MO-m	0.13	19.6	14.5	37.6	34.3	57.0	43.1
p-F	0.15	19.1	14.1	36.3	30.8	59.5	47.1
p-Cl	0.24	18.4	13.7	37.3	32.6	58.2	45.1
p-Br	0.26	18.4	13.8	37.5	33.0	57.9	44.5
p-I	0.28	18.2	13.7	37.7	33.1	57.4	43.7
m-F	0.34	19.4	14.4	37.9	34.3	57.5	43.9
m-I	0.34	19.3	14.2	37.6	32.2	57.2	41.8
m -COCH $_3$	0.36	19.8	14.7	37.7	35.1	57.1	39.2
m-Cl	0.37	19.4	14.3	37.8	а	57.5	43.3
m-Br	0.37	19.3	14.3	37.7	33.0	57.3	42.8

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$p-CU_2H$	0.44	18.0	15.4	38.7	38.1	55.9	
p-CO ₂ CH ₃	0.44	18.0	13.4	38.6	36.7	56.0	
$m-CF_3$	0.46	19.8	14.7	37.8	а	57.4	
$p-COCH_3$	0.47	17.5	13.0	38.7	37.1	56.1	
p-CHO	0.47	17.2	12.9	38.9	37.9	56.0	
p-CF ₃	0.53	19.1	14.2	38.3	40.7	62.8	
m-CN	0.62	19.7	14.7	37.9	35.1	57.3	
p-CN	0.70	17.5	13.2	39.5	37.0	56.7	
$m-NO_2$	0.71	19.7	14.7	38.0	а	57.4	
$p-NO_2$	0.81	18.1	13.5	38.8	38.8	55.5	

^aSCF convergence for this state was not achieved.



TABLE 5.10 Spin-Orbit Coupling Constants for the First ThreeSinglet States of Four Para-Substituted Phenylnitrenes in cm^{-1.222}

State	$R = NO_2$	R = F	R = H	R = NHMe
\mathbf{S}_1	0.0	0.0	0.0	0.0
\mathbf{S}_2	11.9	16.6	15.5	18.8
\mathbf{S}_3	44.3	43.5	43.5	41.8

of the cyclic ketenimine.¹⁸⁴ Nevertheless, the calculations of Karney and Borden¹⁰¹ reveal that this is a two-step process (Scheme 5.2). The first step, cyclization to benzazirine **50**, is rate determining, followed by fast electrocyclic ring opening to cyclic ketenimine **51**. The predicted potential-energy surface is shown in Figure 5.16.

In the absence of nucleophiles, the cyclic ketenimine polymerizes. At high dilution it slowly reverts to benzazirine **50** and from there to the singlet nitrene ¹**49**. Eventually the singlet nitrene relaxes to the lower-energy triplet nitrene, which dimerizes^{167,169}

A study by Younger and Bell^{228} nicely demonstrated the interconversion of a disubstituted benzazirine and singlet nitrene.



Structure 5.39

There is little direct experimental evidence for the intermediacy of **50** and its derivatives. Benzazirine **50**, has not been detected by matrix IR.¹⁶⁵ However, fluorinated²²⁹ and naphthalenic²³⁰ derivatives of **50** have been generated as persistent species in cryogenic matrices and characterized. Parent benzazirine **50** has been intercepted with ethanethiol,¹⁷⁰ and certain derivatives of **50** have been trapped with amines.²³¹⁻²³⁴

For most substituted phenyl azides of interest^{214–218} the rate constants of singlet nitrene decay and product formation (triplet nitrene and ketenimine) were found to be the same. With these arylnitrenes, cyclization to substituted benzazirines is the rate-determining step of the process of nitrene isomerization to ketenimine as in case of the parent phenylnitrene (Scheme 5.2). The only exception, o-fluorophenylnitrene, will be discussed in detail in Section 5.6.6.3.2.

The kinetics of rearrangement of substituted penyl nitrenes have been studied by laser flash photolysis. The temperature-independent observed rate constants are associated with k_{ISC} . Plots of ln ($k_{OBS}-k_{ISC}$) were linear (Figure 5.23 to Figure 5.25), and these plots were used to deduce the Arrhenius parameters for cyclization of the substituted singlet arylnitrenes (Table 5.7, Table 5.11 to Table 5.13).

5.6.6.1 Influence of *Para*-Substituents: The Electronic Effect

5.6.6.1.2 Recent Experiments

Activation parameters of cyclization of *para*-substituted singlet phenylnitrenes are presented in Table 5.7. It is readily



Figure 5.23 Arrhenius treatment of $k_R (= k_{OBS} - k_{ISC})$ data for singlet *para*-methyl **69d** (curve 1) and *ortho*-methyl **69a** (curve 2) phenylnitrene in pentane and for singlet *ortho*,*ortho*-dimethylpenylnitrene **69b** (curve 3) in hexane.²¹⁵





Figure 5.24 Arrhenius treatment of $k_R (= k_{OBS} - k_{ISC})$ data for singlet *para*-cyano **62a** (curve 1), *ortho*-cyano **62b** (curve 2) phenylnitrene in pentane, for singlet *ortho*, *ortho*-dicyanophenylnitrene **62c** in CH₂Cl₂ (curve 3), and for singlet *para*-biphenylnitrene (curve 4) in pentane.^{213,217}



Figure 5.25 Arrhenius treatment of k_R (= $k_{OBS} - k_{ISC}$) data for singlet *para*-fluoro **70b** (curve 1), *meta,meta*-difluoro **70c** (curve 2), *ortho*-fluoromethylnitrene **70a** (curve 3) in pentane, and ortho,ortho-difluorophenylnitrene **70d** (curve 4) in CCl₄. Curve 5: Arrhenius treatment of the rate constant for the ring-opening reaction (k_E) for benzazirine**71a**.²¹⁸

TABLE 5.11Summary of Kinetic Results for Singlet Methyl-
Substituted Phenylnitrenes215

	t (295)	log A	\mathbf{E}_{a}	
Substituent	(ns)	(s^{-1})	(kcal/mol)	Solvent
2-methyl , 69a	~1ª	12.8 ± 0.3	5.3 ± 0.4	C_5H_{12}
2,6-dimethyl, 69b	12 ± 1	13.0 ± 0.3	7.0 ± 0.3	C_6H_{14}
2,6-dimethyl, 69b	13 ± 1	12.9 ± 0.3	7.5 ± 0.5	$CF_2ClCFCl_2$
2,4,6-trimethyl, 69c	8 ± 1	13.4 ± 0.4	7.3 ± 0.4	$CF_2ClCFCl_2$
4-methyl, 69d	~1ª	13.2 ± 0.2	5.8 ± 0.4	C_5H_{12}

^aLifetime estimated by extrapolation of the data to 295 K.

TABLE 5.12 Summary of Kinetic Results for Singlet Cyano-Substituted Phenylnitrenes217

Substituent	τ (295) (ns)	$log A (s^{-1})$	Ea (kcal/mol)	$\begin{array}{c} \text{Solvent} \\ \text{C}_5\text{H}_{12} \end{array}$
<i>para-</i> cyano, 62a	8 ± 4	13.5 ± 0.6	7.2 ± 0.8	
ortho-cyano , 62b	~2ª	12.8 ± 0.3	5.5 ± 0.3	$\mathrm{C}_{5}\mathrm{H}_{12}$
2,6-dicyano, 62c	~2.5ª	13.3 ± 0.2	6.4 ± 0.3	$\begin{array}{c} \mathrm{CH}_{2}\mathrm{Cl}_{2}\\ \mathrm{C}_{5}\mathrm{H}_{12}\\ \mathrm{THF} \end{array}$
2,6-dicyano, 62c	~2.3ª	13.5 ± 0.2	6.5 ± 0.4	
2,6-dicyano, 62c	~2.3ª	13.1 ± 1.0	6.0 ± 1.1	

^aLifetime estimated by extrapolation of the data to 295 K.

seen from the table that substituents such as *para* CH₃, CF₃, halogen, and acetyl have little influence on k_R . This is not very surprising, given that theory predicts emphatically that singlet phenylnitrene has an open-shell electronic structure.^{188,189} Therefore, cyclization of singlet **49** requires only that the nitrogen bend out of the molecular plane, so that the singly occupied σ NBMO on it can interact with the singly occupied π NBMO.¹⁰¹ Azirine formation is simply the cyclization of a quinoidal 1,3-biradical, which originally has two orthogonal, antiparallel spins. Consequently, large substituent effects are not anticipated.

It was impossible to study the effect of strong π -donor substituents on the rate of cyclization, because with *para*methoxy and dimethylamino substituents the phenylnitrene underwent intersystem crossing to the triplet faster than cyclization at all temperatures.²¹⁴

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TABLE 5.13

	T ₂₉₈	log A	ы		
Substituent	(ns)	(s^{-1})	(kcal/mol)	Solvent	Ref.
Η	~1	13.1 ± 0.3	5.6 ± 0.3	$ m C_5H_{12}$	186
2-Fluoro, 70a	8 ± 1	13.0 ± 0.3	6.7 ± 0.3	$ m C_5H_{12}$	218
	10 ± 2			CH_2CI_2	218
	10 ± 2			$CF_2CICFCI_2$	218
4-Fluoro, 70b	~ 0.3	13.2 ± 0.3	5.3 ± 0.3	$ m C_5H_{12}$	218
3,5-Difluoro, 70c	<u>ج</u> ئ	12.8 ± 0.3	5.5 ± 0.3	C_5H_{12}	218
2,6-Difluoro, 70d	240 ± 20	11.5 ± 0.5	7.3 ± 0.7	$ m C_6H_{14}$	218
	260 ± 20	12.0 ± 1.2	8.0 ± 1.5	CCI_4	218
2,3,4,5,6-Pentafluoro, 70e	56 ± 4	12.8 ± 0.6	7.8 ± 0.6	C_5H_{12}	218
	32 ± 3	13.8 ± 0.3	8.8 ± 0.4	CH,CI,	208
Perfluoro-4-biphenyl, 70f	260 ± 10	13.2 ± 0.2	9.4 ± 0.4	$\mathrm{CH_{2}Cl_{2}}$	208
	220 ± 10	12.5 ± 0.4	8.9 ± 0.3	CH ₃ CN	235
$4\text{-CONHC}_{3}\text{H}_{8}$ - 2,3,5,6-				5	
tetrafluoro, 70g	210 ± 20	13.2 ± 0.3	7.5 ± 0.3	CH ₃ CN	235

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Two *para*-substituents, phenyl and cyano, depress k_R and retard the rate of cyclization significantly (Table 5.7). Phenyl and cyano are both radical stabilizing substituents. When attached to the carbon atom *para* to the nitrene nitrogen, these substituents concentrate spin density at this carbon and reduce the spin density at the carbons *ortho* to the nitrene nitrogen. The reduced spin density at carbons *ortho* to the nitrogen lowers the rate at which the 1,3-biradical cyclizes. The lifetimes of these singlet nitrenes at ambient temperature are 8 and 15 ns, respectively, and the activation barriers to cyclization are 7.2^{217} and 6.8 kcal/mol,²¹³ respectively, compared with 5.6 kcal/mol for the unsubstituted parent. The longer lifetime of nitrene **62a** explains the high yield of hydrazine (~70%) observed upon photolysis of *para*-cyanophenyl azide in dimethylamine.²³⁶



5.6.6.1.2 Recent Computational Studies

Prior to these experiments, CASPT2/6-31G^{*} calculations on the ring expansion reactions of *para*-cyanophenylnitrene (**62a**) were performed.²¹⁷ Table 5.14 shows that the barrier computed for cyclization of *para*-cyanophenylnitrene (**62a**) is more than 1 kcal/mol higher than that for parent phenylnitrene **49**. This prediction is in quantitative agreement with subsequent experiments (Table 5.7).

ASPT2/6-31G [*] Energies (kcal/mol), ^a Relative to the	ctures and Products in the Cyclization Reactions of	Para-, Ortho-, Meta- and 2,6-dicyano Derivatives ²¹⁷
TABLE 5.14 (8/8)CASSCF and CASPT2/(Reactants, for the Transition Structures	Singlet Phenylnitrene and of the Para-, (

Substituent H Para-cyano, 62a <i>Ortho</i> -cyano, 62b 2,6-Dicyano, 62c <i>Meta</i> -cyano, 62d	Cyclization Mode ^b Away from Award Away from	Azirine 50 63a=63a' 63b 63b' 63c = 63c' 63d	C2 TS 0.4 0.4 0.4 0.4 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6	ASSCF Product 4.7 5.0 4.5 2.6 3.1 4.4	TS 10 10 10 10 10 10 10 10 10 10	ASPT2 Product 1.6 3.3 2.2 0.3 1.5 1.2	
2	Toward	63d'	8.1	2.9	7.6	-0.7	

^aIncluding zero-point energy (ZPE) corrections, which range from -0.3 to 0.1 kcal/mol for transition structures and from 0.9 to 1.4 kcal/mol for products. ^bMode of cyclization, toward or away from the substituted carbon.

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Recently, Johnson et al.²²² performed calculations of the ring-expansion reaction for three *para*-substituted singlet phenylnitrenes with substituents ranging from highly electron donating (NHCH₃) to highly electron withdrawing (NO₂).



The structures for the stationary points were optimized at the BPW91, BLYP, and CASSCF levels of theory. Table 5.15 gives data from only the most accurate calculations, those performed at the CASPT2/CASSCF level of theory.

The calculations showed that in the case of F and NO_2 substituents, similar to the case for the parent system, cyclization is weakly exothermic, and formation of azirine (**66**) is the rate-determining step. In the case of the highly electron-with-drawing NO_2 substituent, the barrier for cyclization was cal-

TABLE 5.15CASPT2 Enthalpies (H_{298} , kcal/mol) of StationaryPoints Relative to the Singlet Arylnitrenes (65) for DifferentPara-Substituents R^{222}

R	TS1	66	TS2	67
NHCH ₃ , 65a	12.3	8.5	13.3	1.7
H, 65b=49	8.5	2.7	5.8	-1.9
F, 65c	8.9	3.0	7.3	-1.6
NO ₂ , 65d	9.5	3.7	4.8	-0.7

Note: All structures were optimized at the CASSCF(8,8)/cc-pVDZ level.

culated to be 1 kcal/mol higher than that for parent phenylnitrene **49**.²²² Unfortunately, it was impossible to measure the rate constant for cyclization of **65d** because of its very fast rate of ISC.²¹⁴ No trace of the 3*H*-azepine was reported among the products of p-nitrophenyl azide (**68**) photolysis in neat dimethylamine²³⁶ or diethylamine.¹⁶⁹ At the same time, photolysis of **68** in diethylamine gives a hydrazine in 9% yield.¹⁷² This indicates that the lifetime of **65d** is not very short. This finding is consistent with the absence of azepine only if the cyclization reaction is suppressed (Table 5.15).

For the NHMe-substituted case, ring expansion was predicted to be weakly endothermic, and electrocyclic opening of **66a** was predicted to be the rate-determining step.²²² The barrier to the cyclization of **65a** was found to be about 4 kcal/mol higher than that of the parent system **49**.²²² The predicted reduction of the reactivity, along with much faster ISC ($k_{ISC} = 8.3 \pm 0.2 \times 10^9 \text{ s}^{-1}$) than in parent, accounts for the absence of 3H-azepines as products of *para*-dimethyaminophenyl azide photolysis in the presence of nucleophiles.¹⁷²

5.6.6.2 The Influence of *Ortho*-Substituents: Steric and Electronic Effects

5.6.6.2.1 Ortho-Methyl Substituents

Ring expansion of alkyl-substituted phenylnitrenes has also been studied. Sundberg et al.¹⁶³ found that generation of several *ortho*-alkyl arylnitrenes (e.g., *ortho*-methylphenylnitrene, **69a**) in diethylamine affords nucleophilic trapping products that are consistent with initial cyclization to only the unsubstituted *ortho* carbon. Dunkin et al.²³⁷ reported that matrixisolated 2,6-dimethylphenylnitrene (**69b**) undergoes inefficient ring expansion, and Murata et al.²³⁸ have observed the trapping of singlet mesitylnitrene (**69c**), as well as of its ringexpansion product, by tetracyanoethylene (TCNE).





The results for methyl derivatives 69a-c suggest that steric effects play a role in determining the barrier to ring expansion, as suggested by Dunkin et al.²³⁷

A recent kinetic study²¹⁵ demonstrated that a single *ortho* (**69a**) or *para* (**69d**) methyl substituent has no influence on the rate of cyclization of the singlet tolylnitrene to the azirine (Table 5.11). Spin localization effects are not observed, as they are with cyano and phenyl substitution.

In contrast to the case of **69a**, cyclization of **69b** or **69c** necessarily proceeds toward an *ortho* carbon bearing a substituent. The resulting steric effect raises the barrier to cyclization by 1.5 to 2.0 kcal/mol, in quantitative agreement with the results of calculations by Karney and Borden,²³⁹, who predicted that the barrier to rearrangement of **69a** away from the methyl group is lower by 2 kcal/mol than cyclization toward the methyl group. The steric effect extends the lifetime of **69b** at ambient temperature to 13 ns in freon-113 and of **69c** to 8 ns, in the same solvent.

5.6.6.2.2 Ortho-Cyano Substituents

A cyano group is a smaller substituent than methyl and should help localize an unpaired electron at the carbon to which this substituent is attached. Thus, cyclization toward and away from the substituted *ortho*-carbon should be more evenly balanced for a cyano- than for a methyl substituent.

Consistent with this hypothesis, Lamara et al ²⁴⁰ found that singlet *ortho*-cyanophenylnitrene **62b** undergoes ring expansion to afford not only **63b**, the product formed by cyclization away from the cyano substituent, but also **63b'**, the product formed by cyclization toward the cyano group (Scheme 5.3). Similar results have been found in the ring expansion of singlet *ortho*-acetylphenylnitrene.²⁴¹



Scheme 5.3

Laser flash photolysis studies were performed on *para*cyano (**62a**), *ortho*-cyano (**62b**), and *ortho*, *ortho*-dicyanophenyl (**62c**) azide.²¹⁷ The results are given in Table 5.12. In pentane the barrier to cyclization of *ortho*-cyanophenylnitrene is the same, within experimental error, as that of parent phenylnitrene. The barrier to cyclization of 2,6-dicyanophenylnitrene (**62c**) is about 1 kcal/mol larger than that of parent phenylni-

trene $(^{1}49)$. Variation of solvent has only a small effect on the kinetics of this nitrene.

Product studies demonstrated that *ortho*-cyanophenylnitrene (**62b**) prefers slightly to cyclize toward the carbon bearing the cyano-group (63:37) in pentane solvent.²¹⁷ Thus, the spin localization effect and the steric effect of cyano, relative to hydrogen, essentially cancel, and there is no net influence of the substitutent on the reaction barrier. The barrier to cyclization of 2,6-dicyanophenylnitrene **62c** increases, but the increase is smaller than that found for 2,6-dimethylphenylnitrene (**69b**).

5.6.6.2.3 Theoretical Analysis of the Influence of Cyano Substitution

The qualitative predictions and experimental findings in the case of cyano-substituents have been analyzed computationally by performing CASSCF(8/8) and CASPT2/6-31G^{*} *ab initio* calculations.²¹⁷ Table 5.14 summarizes the results for the cyclization reactions of *ortho-*, *meta-*, *para-*, and 2,6-dicyanophenylnitrene (**62a–d**). The zero-point corrected energies of the two possible products, **63** and **63'**, are given, relative to the reactants. Also shown are the relative energies of the transition structures, TS (**62** \rightarrow **63**) and TS (**62** \rightarrow **63'**), leading to each of the products. For comparison, the CASSCF and CASPT2 relative energies for the cyclization reactions of unsubstituted phenylnitrene¹⁰¹ are given as well.

CASSCF and CASPT2 calculations both overestimate the stability of the open-shell electronic structure of singlet nitrenes **62a–d** by about 3 kcal/mol,²¹⁷ as in the case of parent ¹**49**.¹⁰¹ The ring opening is computed to require passage over a 2 to 3 kcal/mol lower energy barrier than reversion of the intermediates to the reactants. Therefore, cyclization is the rate-determining step in the ring-expansion reactions of cyano-substituted phenylnitrenes **62a–d** to derivatives of **64** and **64'** (Scheme 5.3).

Of particular interest in Table 5.14 are the results for cyclication of *ortho*-cyanophenylnitrene (62b). Cyclication toward the cyano-substituent is predicted to have a slightly lower barrier height than cyclication away from the cyano

group, which is calculated to have the same barrier height as cyclization of **49** at the CASPT2 level of theory.

This prediction is very different from the computational²³⁹ and experimental results for cyclization of *ortho*-methylphenylnitrene (**69a**)^{163,215} and *ortho*-fluorophenylnitrene,^{218,242} where cyclization away from the *ortho*-substituent is strongly preferred over cyclization toward the substituent.

In the cyclization of *m*-cyanophenylnitrene (**62d**), where the cyano group is located on a carbon at which the π NBMO in the reactant has a node, it seems unlikely that radical stabilization will influence the direction in which **62d** cyclizes. In fact, the barrier heights connecting **62d** to either of the two possible azirines are quite comparable, and the small kinetic preference predicted for cyclization toward the cyano group may well be a consequence of the slightly lower energy computed for the linearly conjugated product, relative to the cross-conjugated product.

The barrier to cyclization of *para*-cyanophenylnitrene (**62a**) is more than 1 kcal/mol higher than that for either of the other cyanophenylnitrenes. In addition, the cyclization of **62a** is more endothermic than any of the other cyclizations shown. Both facts are attributable to ~3 kcal/mol lower energy of **62a** compared with either **62b** or **62d**.

5.6.6.3 Ring Expension of Fluoro-Substituted Singlet Phenylnitrenes

Abramovitch et al.^{243,244} and Banks' group^{245–249} discovered that, unlike most arylnitrenes, polyfluorinated arylnitrenes have bountiful bimolecular chemistry. Polyfluorinated arylnitrenes are useful reagents in synthetic organic chemistry,²⁵⁰ in photoaffinity labeling,^{251–258} and for the covalent modification of polymer surfaces.⁷ The effects of the number and positions of fluorine substituents on the ring expansion of phenylnitrene have been extensively investigated by members of the Platz group.^{250, 259–263} Using the pyridine ylide probe method,²⁶⁴ they found that, whereas both pentafluorophenylnitrene (**70e**) and 2,6-difluorophenylnitrene (**70d**) give nitrene ylides, 4-fluorophenylnitrene (**70b**) yields only the ketenimine ylide, and 2,4-difluorophenylnitrene affords a mixture of nitrene ylide and ketenimine ylide.^{260–261} They con-

cluded that fluorine substitution at both *ortho* positions is required to inhibit ring expansion effectively.

To understand the fluorine effect quantitatively, we studied the kinetics of fluoro-substituted phenylnitrenes (Scheme 5.4, **70a–e**) and interpreted the data with the aid of molecular orbital calculations.^{218,239}



Scheme 5.4

Laser flash photolysis of a series of fluorinated aryl azides produced the transient spectra of the corresponding singlet nitrenes.²¹⁸ With the exception of singlet 2-fluorophenylnitrene (**70a**), the rate of decay of the singlet nitrene was equal to the rate of formation of the reaction products, for example, didehydroazepines (**72**) and triplet nitrenes (**73**). The temperature dependence of k_{OBS} , typical for nitrenes, was

again observed. The data were interpreted in the usual manner to give k_{ISC} and the Arrhenius parameters for azirine formation. The latter are summarized in Table 5.13.

5.6.6.3.1 Influence of Fluorine Substituents on the Cyclization Reaction

Singlet 2,6-diffuorophenylnitrene (**70d**) and singlet perfluorophenylnitrene (**70e**) react with hydrocarbon solvents by insertion into C–H bonds.^{259–261,265} Therefore, in the case of nitrenes **70d** and **70e** in hydrocarbon solvent, k_{OBS} is

$$k_{OBS} = k_{ISC} + k_R + k_{SH}[SH]$$

where the latter term reflects the contribution of the reaction of the singlet nitrene with solvent. In these cases, the slope of a plot of $\log(k_{OBS} - k_{ISC})$ versus 1/T is not simply related to the barrier to cyclization. Thus, values of E_a in hydrocarbon solvents are smaller than those measured in the less reactive solvents CH_2Cl_2 , CCl_4 , and $CF_2ClCFCl_2$ (Table 5.13). On the basis of on product studies,^{259, 266} we are confident that the activation energy barriers determined in the latter solvents can be associated with the cyclization of the singlet nitrene.

Placement of fluorine substituents at both *ortho* positions (**70d**) raises the barrier to cyclization by about 3 kcal/mol relative to the unsubstituted system (Table 5.13). The life-times of singlet phenylnitrene (**149**) and 4-fluorophenylnitrene (**70b**) are about 1 ns or less at 298 K. The lifetime of 3,5-difluorophenylnitrene (**70c**) is about 3 ns at 298 K, but that of 2,6-difluorophenylnitrene (**70d**) is 260 ns, in CCl₄. Because a *para*-fluoro group fails to exert an electronic influence on the cyclization process, it is tempting to attribute the effect of two *ortho*-fluorine substituents on the singlet nitrene lifetime to a simple steric effect.

This interpretation is consistent with the calculations of Karney and Borden,²³⁹ who found that cyclization away from an *ortho*-methyl or an *ortho*-fluorine group is favored by 2 to 3 kcal/mol relative to cyclization toward the substituent (Table 5.16).

Leyva and Sagredo²⁴² demonstrated that cyclization of the singlet nitrene **70a** proceeds away from the fluorine sub-

TABLE 5.16Calculated Relative Energies (kcal/mol)^a for SpeciesInvolved in the First Step of the Ring Expension ofFluorosubstituted Phenylnitrenes²³⁹

Substituent		Mode	CAS/6 ^b	PT2/6 ^c	PT2/cc ^d
Н	49	_	0	0	0
	TS		8.9	8.6	9.3
	50	_	4.7	1.6	3.5
	70a		0	0	0
2-F	TS1	Away	9.5	9.5	9.9
	71a	_	6.1	3.6	4.8
	TS2	Toward	13.6	12.3	13.0
	71a'	_	0.7	-2.4	-0.3
	70b		0	0	0
4-F	TS		7.9	8.5	9.1
	71b		3.3	1.6	3.3
	70c		0	0	0
3,5-diF	TS		8.5	7.9	8.6
	71c		3.2	-0.7	1.1
	70d		0	0	0
2,6-diF	TS		13.9	13.0	13.4
	71d		2.1	-0.5	1.0

^aEnergies pertain to CASSCF(8,8)/6-31G^{*} optimized geometries. ^bCASSCF(8,8)/6-31G^{*} energy ^cCASPT2N/6-31G^{*} energy ^dCASPT2N/cc-pVDZ energy

stituent. The steric argument predicts that a single *ortho*-fluorine substituent will have little influence on the rate of conversion of **70a** to **71a**, because cyclization occurs at the unsubstituted *ortho* carbon.



However, the barrier to this process is larger (outside experimental error) than that of the parent system (Table 5.13). In

fact, the lifetime of singlet 2-fluorophenylnitrene (**70a**) at 298 K is 8 to 10 times longer than that of the parent (¹**49**) and 20 to 30 times longer than that of 4-fluorophenylnitrene (**70b**). Therefore a single *ortho*-fluorine atom exerts a small but significant bystander effect on remote cyclization that is not simply steric in origin. This result is in good quantitative agreement with the computational data of Karney and Borden,²³⁹ who predicted that the barrier to cyclization of **70a** away from the fluorine substituent is about 1 kcal/mol higher than that for parent system ¹**49** (Table 5.16).

To understand this substituent effect, the atomic charges for the different centers were computed²¹⁸ using the CASSCF(8,8)/6-31G^{*} wave functions and the natural population analysis (NPA) method of Reed et al.²⁶⁶ It was found that fluorine substitution makes the adjacent carbon very positively charged (+0.48 e). In the transformation of 2-fluorophenylnitrene (**70a**) to TS1 (away from F) or TS2 (toward F), there is an increase in positive character at the (ipso) carbon bearing the nitrogen. The increased activation barrier to cyclization for 2fluorophenylnitrene (**70a**) relative to ¹49 or 4-fluorophenylnitrene (**70b**) is due to the build up of positive charges on theneighboring *ortho* and *ipso* carbons in TS1 for cyclization of **70a**.

For insertion toward F in TS2, there is an even greater amount of Coulombic repulsion between the *ortho* and *ipso* carbons than in TS1, and this effect is responsible, in part, for a higher activation barrier for insertion toward F than away from F. Therefore, the origin of the influence of *ortho,ortho*-difluoro substitution on prolonging the lifetime of singlet arylnitrene and increasing the activation energy for cyclization is due to a combination of the steric effect and the extraordinary electronegativity of the fluorine atom. In this case, the electronic and steric effects reinforce each other. This is the opposite of the case for *ortho,ortho*-dicyanophenylnitrene, where the electronic and steric effects oppose and nearly cancel each other.

5.6.6.3.2 Ortho-Fluorophenyl Azide

Unique kinetic results were obtained upon LFP of orthofluorophenyl azide **70a**.²¹⁸ In this case, the decay of **70a** was

much faster than the formation of products (ketenimine 72a and triplet nitrene 73a) at temperatures above 230 K. For all the other substituted singlet phenylnitrenes described in this review, the rates of nitrene decay were equal to the rates of product formation.

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Between 147 and 180 K, **70a** behaves normally. The rate constant for the growth of the triplet is equal to the rate constant for the disappearance of **70a**, and both rate constants are temperature-independent and close to the value of k_{ISC} for parent ¹49 (Figure 5.26). In this temperature range (147 to 180 K), singlet nitrene **70a** cleanly relaxes to the lower-energy triplet nitrene **73a**.



Figure 5.26 The temperature dependencies of the rate constant of decay of singlet 2-fluorophenylnitrene **70a** (curve 1) and the apparent rate constant of formation of triplet 2-fluorophenylnitrene **73a** and ketenimine **72a** (curve 2). Solid lines (1) and (2): results of nonlinear global fit of the data to an analytical solution according Scheme 5.5.²¹⁸ Insert: transient absorption spectra produced by LFP (249 nm) at 295 K of 2- fluorophenyl azide in pentane, detected 500 ns after the laser pulse (curve 1) and 4-fluorophenyl azide detected 50 ns after the laser pulse (curve 2) and persistent spectrum of triplet 2-fluorophenylnitrene (**73a**) in methylcyclohexane at 77 K (curve 3).

Above 180 K, **70a** decays by both intersystem crossing (k_{ISC}) and cyclization (k_R) , with the latter process gaining relative to the former as the temperature increases. The data in Figure 5.26 for temperatures above 180 K were explained by positing that singlet nitrene **70a** and azirine **71a** (Scheme 5.5) interconvert under the experimental conditions.²¹⁸ This hypothesis was supported by analysis of the transient spectrum (Figure 5.26, insert) obtained upon LFP of 2-fluorophenyl azide. The small ratio of k_{ISC}/k_{OBS} can be reconciled with both the appearance of triplet nitrene **73a** in the transient spectrum at ambient temperature and the large chemical yield of triplet-derived azo product **74a**, if benzazirine **71a** serves as a reservoir for singlet 2-fluorophenylnitrene **70a**. The singlet nitrene eventually relaxes to the triplet, which is observed spectroscopically and dimerizes to form **74a**.



Scheme 5.5

Kinetic data for singlet *ortho*-fluoronitrene **70a** were analyzed²¹⁸ following Scheme 5.5. The equilibrium constant K_R ($K_R = k_R/k_R$) was estimated to be ~0.5 and ΔG to be ~350 cal/mol. Thus, **70a** and **71a** are very close in energy. The rate

constant, k_{E} , for the ring opening reaction was measured and the Arrhenius parameters for it were found to be A = $10^{13.5 \pm 0.4}$ M^{-1} s⁻¹ and E_{a} = 9.0 \pm 0.5 kcal/mol.

To test computationally the proposed explanation of the unique kinetics observed for **70a**, a series of *ab initio* and DFT calculations on the second step of the ring expansion (electrocyclic ring opening of azirines **71a–e** to form the corresponding cyclic ketenimines **72a–e**) were performed.²¹⁸ The CASPT2/cc-pVDZ//CASSCF(8,8)/6-31G^{*} and B3LYP/6-31G^{*} energies are given in Table 5.17. The CASPT2 results are also depicted graphically in Figure 5.27 in a way that permits energetic comparisons of isomeric species.

As shown in Figure 5.27, in all cases except the "away" ring expansion of 2-fluorophenylnitrene (**70a**), the transition state for the second step of the ring expansion (**71** \rightarrow **72**) is computed to be lower in energy than that for the first step (**70** \rightarrow **71**) at the CASPT2 level of theory. This is consistent with the experimental finding that, for nitrenes **70b–d**, the nitrene decays at the same rate at which the corresponding ketenimine is formed, whereas for nitrene **70a**, nitrene decay is faster than ketenimine growth. Of the five electrocyclic ring-opening reactions investigated, the opening of **71a** to form **72a** is predicted to be the least exothermic ($\Delta E = -1.6$ kcal/mol). The exothermicity of this step for the other systems ranges from $\Delta E = -2.7$ kcal/mol to $\Delta E = -6.0$ kcal/mol.

The CASPT2 results are supported qualitatively by B3LYP/6-31G^{*} calculations (Table 5.17). The DFT calculations predict that benzazirine **71a** has the second-highest barrier (after **71e**) to rearrangement to a ketenimine (**72a**). It also has the lowest barrier to reversion to the corresponding singlet nitrene (**70a**). Thus, **71a** reverts to the corresponding singlet nitrene (**70a**) more readily than does the parent system **50**. The DFT calculations also predict that, of the four fluoro-substituted arylnitrenes considered, the ring opening of **71a** \rightarrow **72a** is the least exothermic. Thus, both CASPT2 and B3LYP calculations correctly predict that **71a** is the benzazirine most likely to revert to the corresponding singlet nitrene **70a**.

Ketenimines 72, and th	e Transition States	(TS) Conn	ecting Ther	$n^{218.a}$		
	Azirine		Transiti	on State	Keten	imine
Method	E	ZPE	rel E	ZPE	rel E	ZPE
	50		L	S	21	1
CASPT2/cc-pVDZ ^b B3LYP/6-31G [*] c	-285.41815 -286.27659	60.9 57.7	2.5 4.7	59.8 56.7	-4.5 -5.1	60.8 57.6
	71a		Ţ	Sa	7:	2a
CASPT2/cc-pVDZ ^b B3LYP/6-31G [*] c	-384.47462 -385.50238	55.7 52.8	7.0 8.1	54.6 51.7	-1.6 -3.0	55.8 52.8
B3LYP/6-311+G(2d,p) ° CCSD(T)/6-31+G [*] °	-385.62115 -384.48202		$7.0 \\ 11.2$		-5.5	
	71a'		T	Sa	27	ื่ล่
CASPT2/cc-pVDZ ^b B3LYP/6-31G ^{* c}	-384.48308 -385.51174	55.9 52.7	$2.4 \\ 4.1$	54.8 51.8	-6.0 -6.8	55.7 52.8
	71b		Ţ	Sb	32	ab B
CASPT2/cc-pVDZ ^b B3LYP/6-31G* c	-384.48077 -385.50865	55.6 52.6	4.5 5.7	54.5 51.5	-4.3 -5.5	55.5 52.6
	71c		Т	Sc	12	CC
CASPT2/cc-pVDZ ^b B3LYP/6-31G [*] ^c	-483.52115 -484.74392	50.5 47.7	5.2 6.4	$\begin{array}{c} 49.3 \\ 46.6 \end{array}$	-2.7 -3.9	$50.3 \\ 47.6$



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	71d		Ĩ	Sd	2	2d
CASPT2/cc-pVDZ ^b B3LYP/6-31G [*] c	-483.51566 -484.73747	50.7 47.8	5.7 6.8	49.6 46.8	-3.7 -5.1	50.6 47.9
	71e		Ţ	Se	7	2e
B3LYP/6-31G * $^{\circ}$	-382.41002	32.6	8.5	31.5	-6.0	32.6

^aAzirine energies are absolute energies, in hartree. Energies for transition states and ketenimines are relative energies, compared to azirine, and are corrected for differences in zero-point vibrational energy. ^bObtained using CASSCF(8,8)/6-31G^{*} optimized geometry and zero-point vibrational energy. ^cObtained using B3LYP/6-31G^{*} optimized geometry and zero-point vibrational energy.





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Figure 5.27 Relative energies (in kcal/mol) of species involved in the ring expansions of singlet fluoro-substituted phenylnitrenes calculated at the CASPT2/cc-pVDZ//CASSCF(8,8)/6-31G^{*} level. (a) Difluorinated phenylnitrenes. (b) Monofluorinated phenylnitrenes.^{218,239}

Significantly, this is the only system in which the rates of formation and disappearance of the benzazirine are predicted to be comparable, and this is the only case where there is compelling experimental evidence for formation of an intermediate between the singlet nitrene and its ketenimine isomer in solution.²¹⁸

The experimental data reveal that singlet nitrene **70a** and benzazirine **71a** are very close in energy ($\Delta G \approx 350$ cal/mol). This value is much smaller than that predicted by

CASPT2 calculations (4.8 kcal/mol, Figure 5.27). However, as discussed above, the CASPT2 method typically underestimates the energies of open-shell species, such as **70a**, relative to closed-shell molecules, such as **71a**. Applying, as in the case of ¹**49**, an upward correction of ~3 kcal/mol to the energy of the singlet nitrene brings the computed energy difference between **70a** and **71a** into much better agreement with experiment.

Why is the barrier for ring opening of **71a** to **72a** so much higher than the corresponding barriers for **50** and **71b–d**? As shown in Figure 5.27 the energy of the transition state for this step roughly parallels the energy of the ketenimine product (**72**). The marked instability of ketenimine **72a**, relative to **72a'** and **72b**, is consistent with recent computational results, which predict that fluorine substitution destabilizes ketenimines.²⁶⁷ This destabilization can be attributed to Coulombic repulsion between the two carbons of the ketenimine moiety. Because both of these carbons are attached to more electronegative atoms (one to N, one to F), both bear a partial positive charge, and severe electrostatic repulsion results.



The effect of Coulombic repulsion described for ketenimine **72a** can also be used to rationalize the higher energy of nitrene **70a** relative to **70b**, as well as the higher energy of azirine **71a** compared with **71a'** and **71b**. It is possible that the changes in relative orientation of the C=N and C-F bond dipoles that occur for **70a** \rightarrow **71a** and **71a** \rightarrow **72a** are at least partly responsible for this process being predicted to be substantially more endothermic (in the case of **70a** \rightarrow **71a**) or

less exothermic (in the case of $71a \rightarrow 72a)$ than the other systems studied.

Curiously, the addition of a second *ortho*-fluorine substituent (i.e., in benzazirine 71d) raises the barrier to reversion to singlet nitrene **70d**, relative to the mono *ortho*-fluoro system (Figure 5.27). This is partly due to steric hindrance by fluorine in the transition state for cyclization but also to the stabilization of **71d** by the fluorine attached directly to the azirine ring (vide supra).²³⁹ The addition of the second fluorine substituent (benzazirine 71d) slightly decreases the barrier to conversion of azirine **71d** to ketenimine **72d** (Figure 5.27). This is related to the more favorable thermodynamics of conversion in the case of **71d** compared with **71a**, due to the slight stabilization of ketenimine **72d** by the fluorine adjacent to nitrogen. The barrier for $71d \rightarrow 72d$ is still predicted to be ~2.5 kcal/mol higher than the barrier for $50 \rightarrow 51$ at the same level of theory,¹⁰¹ which helps explain why Morawietz and Sander²²⁹ successfully detected benzazirine **71d** in their matrix isolation experiments.

5.7 CONCLUSIONS

Theoretical methods have been used extensively to understand properties of the simplest nitrene, NH, also known as imidogen. The experimental bond lengths and the spectroscopy of the singlet and triplet states of imidogen and the energy separation of these states are in excellent agreement with the predictions of theory. Imidogen is easy to study by experimental and theoretical methods because it is small and because it is not rapidly consumed by intramolecular rearrangement. Alkyl, vinyl, and acyl nitrenes are difficult to study experimetally because they have facile unimolecular decay pathways available. The key question with these singlet nitrenes is whether or not they are true intermediates, which are minima on the potentialenergy surface and have finite lifetimes under any experimental conditions. More theoretical and experimental work is needed before this question can be definitively answered for singlet alkyl, vinyl, and acyl nitrenes.

In earlier reviews,^{150,151} two of the authors wrote that the most important tasks remaining in the field of aryl azide

photochemistry were the direct observation of singlet aryl nitrenes, direct study of the kinetics of singlet nitrene reactions, and high-level quantum chemical calculations of the nitrene potential-energy surface. This review illustrates that great progress has been made in these areas over the past few years. Singlet phenylnitrene has been detected directly and its spectrum analyzed with the aid of modern computational methods. The rate constant of intersystem crossing to the lower energy triplet state has been measured, and is much smaller than the corresponding values observed with aryl carbenes. This is a consequence of the open-shell electronic structure of phenylnitrene. The activation parameters for cyclization of singlet phenylnitrene to benzazirine have been obtained and are in good agreement with modern quantum chemical calculations.

The effect of substituents on the spectra and kinetics of singlet aryl nitrenes has been examined systematically. Groups that act as strong π donors dramatically accelerate the rate of ISC. Electron-withdrawing groups also slightly accelerate ISC. Para-substituents such as cyano and phenyl reduce spin-density ortho to the nitrene-bearing carbon and reduce the rate of cyclization to the corresponding benzazirine. Ortho substituents generally direct cyclization away from the substituted center because of unfavorable steric interactions. Ortho fluorine substituents retard cyclization toward and even away from the substituted carbon because of the development of unfavorable Coulombic interactions between the aryl carbons bearing the nitrogen and the fluorine substituents. The kinetics of cyclization of singlet ortho-fluorophenylnitrene reveal that cyclization to the corresponding benzazirine is reversible. All of these experimental observations are in agreement with the results of electronic structure calculations.

In the early 1990s, singlet aryl nitrenes had still avoided detection, and the influence of structure on reactivity was only dimly appreciated. Laser flash photolysis studies, in combination with calculations, have provided insight and have led to a comprehensive theory of substituent effects. We are proud to have been part of the progress that has been made in aryl nitrene chemistry during the past decade.



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