Characterization of Smith's Nitrene and 1-Phenyl-3-(α-cyano)benzylidenetriazene with Theoretical, NMR, and Flash Photolytic Methods

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Doubly enriched (^{13}C, ^{15}N) 1-phenyl-3-(α-cyano)benzylidenetriazene, Ph−N*═N−N═C(C*≡N)−Ph, did not show ^{13}C−^{15}N splittings in the NMR spectra in solution that would be expected from the presence of a cyclic nitrene in reversible equilibrium, a theory proposed in 1964 by Smith, Krbechek, and Resemann to explain its chemical behavior. Molecular orbital calculations at the 6-31G* level on the core structures (Ph replaced by H) also indicated substantially greater stability for the open-chain compound. Flash photolysis (337 nm) of 1,4-diphenyl-5-azido-1,2,3-triazole in solution led to the open-chain triazene within about 20 ns but with no observable transient absorbing species.

Introduction

In 1964 Smith, Krbecek, and Resemann[1] reported that 1,4-diaryl-5-azido-1,2,3-triazoles decomposed readily to give crystalline, red-purple, air-stable solids that did not correspond to colorless products from the expected decomposition (Scheme 1, path a). Since no C≡N absorption in the IR spectra of the products was apparent, and reduction easily afforded the parent aminotriazole, the products were initially believed to be examples of a long-sought nitrene (**1**, in Scheme 1). The X-ray crystal structure of a *p*-tolyl analogue, however, revealed an open-chain structure (**2**) corresponding to decomposition by path b.[2] It was suggested that the open-chain structure might exist in solution in equilibrium with a more reactive nitrene that could be responsible for some of the observed reactions.

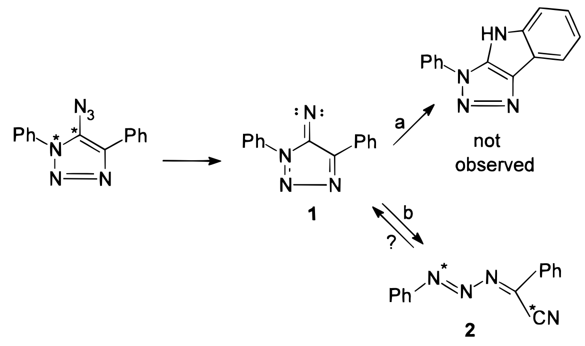
In the present study we provide experimental and theoretical evidence that indicates at most a transient role of a nitrene in this system.

Experimental Section

The doubly labeled compound azide was synthesized as described[1] from the doubly labeled 1,4-diphenyl-5-amino-1,2,3-triazole, which was prepared in turn from phenyl azide (Ph−N*═N═N) and phenylacetonitrile (Ph−CH$_2$C*N). The latter compounds were synthesized by standard routes from commercial samples (>98% enriched) of potassium nitrate-^{15}*N* (benzene → nitrobenzene → aniline → phenyl azide) and sodium cyanide-^{13}*C* (benzyl chloride → phenylacetonitrile). The NMR spectra were run initially on a Varian XL200, with ^{15}N NMR recorded with a 400 MHz Bruker instrument at the University of Michigan. Later, additional spectra of both nuclei were acquired at MTU with a Varian UI400. The spectra in CCl$_4$ were recorded with an acetone-d_6 external reference and lock, and in deuterated solvents the chemical shifts were set electronically to tetramethylsilane at 0 ppm. The ^{15}N NMR spectra were referenced to nitromethane internal standard in CDCl$_3$ set at 379.6 ppm relative to liquid NH$_3$.[3]

Flash photolysis was carried out at the National Research Council of Canada, Ottawa, with a nitrogen laser flash lamp system described elsewhere.[4] A solution of nonlabeled 1,4-diphenyl-5-azido-1,2,3-triazole in benzene (ca. 2mM, absorbance = 0.16 at 337 nm) was photolyzed repeatedly at 337 nm in 7 mm square cells.

SCHEME 1



Results and Discussion

NMR Evidence. The ^{13}C NMR spectrum of the doubly enriched, parent aminotriazole (Figure 1, top right) showed clearly the splitting of the enriched signal by the adjacent ^{15}N with a coupling constant of 18.3 Hz. This splitting is comparable to textbook examples[3] involving electron-poor compounds, e.g., nitrobenzene, $J_{13C-15N}$ = 14.5 Hz; CH$_3$C≡N, $J_{13C-15N}$ = 17.5 Hz). The ^{15}N NMR spectrum (Figure 1, top left) likewise showed a doublet with a coupling of 18.3 Hz.

The doubly enriched amine was converted to the azide, samples of which were decomposed in acetone-d_6 in the NMR instrument for 5 h at 51 °C. (Since the azide was rather labile and we were using the less sensitive XL270 instrument, no attempt was made to measure the spectrum of the azide itself.) The resulting solution of the doubly labeled, open-chain transformation product showed a clean ^{13}C NMR spectrum with a narrow, intense *singlet* (Figure 1, bottom right) corresponding to the nitrile carbon at 111.2 ppm (23 °C), 111.5 ppm (13 °C), and 111.2 ppm (−16 °C). Other, weaker aromatic signals from the nonenriched carbons were present at 124−150 ppm.

Separately, a more concentrated solution of the nonenriched, open-chain azo compound was examined in CCl$_4$, and the weaker nitrile carbon signal appeared at 110.0 ppm (49 °C), 110.8 ppm (18 °C), and 110.0 ppm (21 °C). Another sample

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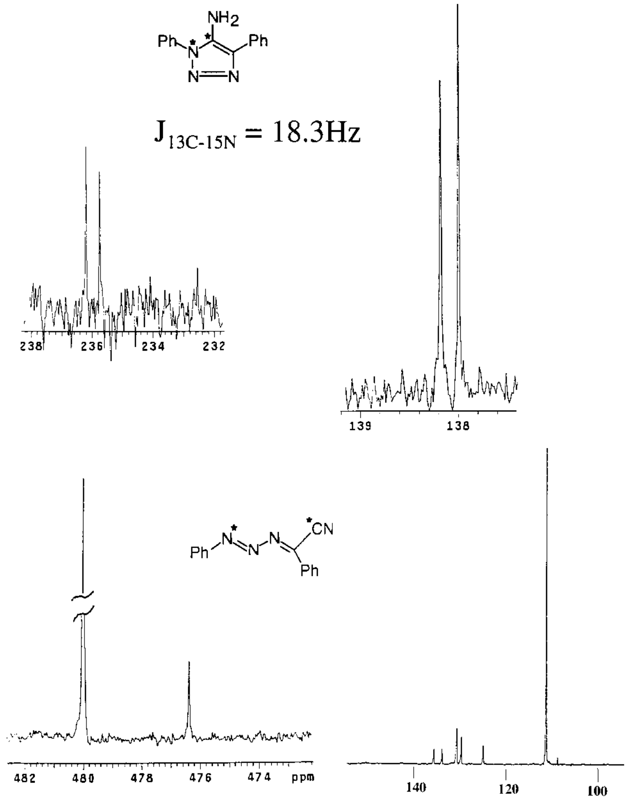


Figure 1. ^{15}N NMR (left) and ^{13}C NMR (right) spectra from 1,4-diphenyl-5-amino-1,2,3-triazole and its azo transformation product **2** isotopically enriched at the starred positions.

of nonenriched azo compound was examined in dimethyl sulfoxide-d_6 at a series of temperatures. Up to 85 °C the ^{13}C NMR spectra resembled those recorded at room temperature, but at 105 and 125 °C irreversible changes were observed.

A sample of doubly enriched azo compound, recovered from solution in acetone-d_6, was dissolved in dimethyl sulfoxide-d_6. The enriched nitrile carbon was again a narrow singlet recorded successively at 110.5 ppm (22 °C), 109.8 ppm (82.5 °C), and 110.0 ppm (61 °C). In some of the spectra a new, narrow singlet at 108 ppm appeared irreproducibly but was later observed in a sample of pure solvent as well.

The ^{15}N NMR spectrum of the doubly enriched azo compound derived from the amine showed only the signal of the enriched nucleus, and with no splitting (Figure l, bottom left), in agreement with the appearance of the enriched signal in the ^{13}C NMR spectrum. The spectrum showed insignificant shifts and no broadening when recorded at 80 °C. The position of the singlet at 488 ppm is strikingly shifted from the normal range of nitriles (230−250 ppm).[3] A second, smaller singlet appeared in the ^{15}N NMR spectrum at 483 ppm. This signal was probably from an impurity or decomposition product, since it did not appear in preliminary spectra obtained with a different instrument.

Flash Photolysis. The absorbance of a solution of the azide precursor increases after exposure to a laser flash at 337 nm, but the increase appears to be due principally to the fast conversion of the yellow azide to the more strongly absorbing, red azo compound (Figure 2). At times up to 62 ns after the laser flash, the spectra of the new absorbances are all similar, with λ_{max} around 350 nm, corresponding to $\lambda_{max} = 352$ nm for the open-chain azo compound.

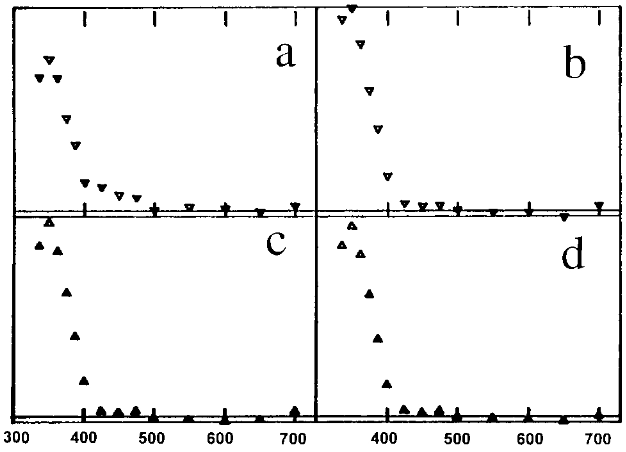


Figure 2. Spectra (350−700 nm) from 1,4-diphenyl-5-azido-1,2,3-triazole (a) 22, (b) 38, (c) 40, and (d) 62 ns following 337 nm N_2 laser flash. Full scale OD 0.0181.

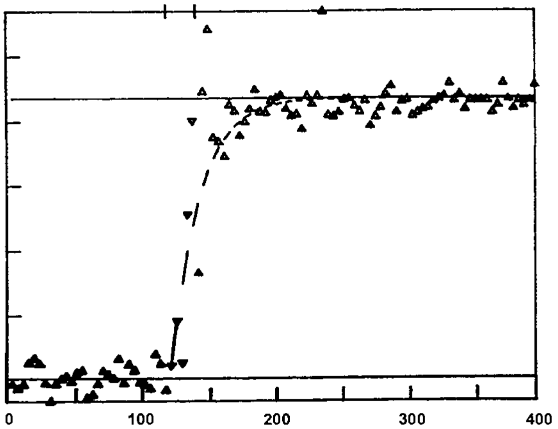


Figure 3. Time-evolution of change in absorbance at 350 nm from solution in Figure 3. End Δ OD = 0.0436. Dotted line fitted to exponential increase with 20.9 ns lifetime.

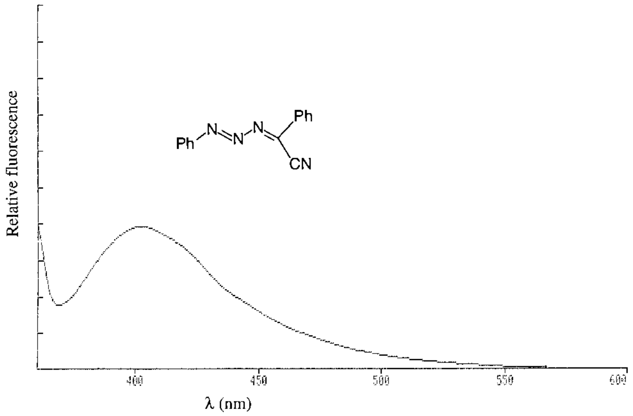


Figure 4. Fluorescence from ca. 1 mM 2 in benzene (λ_{exc} 340 nm).

The absorbance of the solution of the azide at 350 nm following the laser flash increases rapidly to a constant value (Figure 3), with a half-life of about 21 ns. We observed an interfering fluorescence from the sample at very short times, which became more intense with successive flashes. Solutions of the azide when examined in a fluorimeter showed nonreproducible emission that was traced to the thermal and photochemical production of the open-chain azo product, which was found to be highly fluorescent (Figure 4).

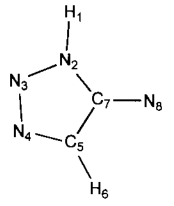
Molecular Orbital Calculations. The experimental work was followed by a series of ab initio calculations with several objectives in mind. It was necessary to characterize the labile nitrene, (**1** in Scheme 1), since no spectrum was obtained for it. Characterizing both **1** and the azo compound, **2**, was also desired in order to assess their relative stabilities. The origin of the rapid conversion from **1** to **2** is also of some interest, which necessitated the determination of the energy and location of the intermediate transition state(s) and saddle points on the potential energy surface. Finally, a variety of conformers were studied in order to ascertain if there were any other accessible local minima that may play a role. As the size of the diphenyl compounds make an accurate study prohibitive, all calculations were performed on the core structure with the phenyl groups replaced with hydrogens atoms (**1H**−**6H**).

All calculations reported here were at the HF/6-31g(d)//HF/6-31g(d) and also the MP2/6-31g(d)//MP2/6-31g(d) levels, where this notation has the usual meaning, "method for the energy"//"method for the geometry optimization". In the following discussion, we simply refer to these two methods as the HF/6-31g(d) and MP2/6-31g(d) methods, respectively. Some of the initial exploratory calculations were completed at the HF/STO-3G//HF/STO-3G level. Vibrational analyses were at the HF/6-31g(d) level to determine the IR spectra and the thermodynamical properties and to verify the authenticity of the extremum points as either minima or transition states. The transition states were located using the STQN method[5] and manual and relaxed scans of the potential energy surface. The close proximity of the one important transition state to a local minimum made its determination particularly problematic. All calculations were performed using the Gaussian 94 program.[6]

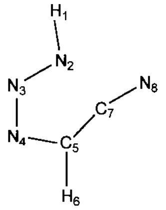
The relative energies of the structures studied are detailed in Table 1, while the explicit **Z**-matrix coordinates for the important structures are given in Table 2. Figure 5 illustrates some of the optimized structures along with their relative energies (HF method).

HF/6-31g(d) Level. For the hydrogen analogues used in this study, it is clear from the tabulated data that the nitrene is considerably less thermodynamically stable than the open-chain isomers (if it is stable at all). At this level of theory, structure **2** is more stable by 34.3 kcal/mol. Both structures **1** and **2** show valid minima since the vibrational analysis of each reveals no imaginary frequency. The lowest lying vibrational mode does exhibit a C−N bond breaking mode that will lead to the bond scission responsible for producing the open-chain azo compound. A transition state connecting structures **1** and **2** was located. It resembles a slightly distorted cyclic nitrene (structure **1**), where the C−N bond has been elongated from 1.44 Å in **1** to 1.66 Å in the transition state. However this transition state lies only 2.5 kcal/mol above that of the nitrene. This activation energy of near thermal proportions explains the rapid conversion of the nitrene to the open-chain azo compounds. For this C−N bond scission, this transition state than leads to an open planar structure with the C−N bond distance equal to 2.55 Å, as illustrated in structure **7** in Table 1. This opened structure is a saddle point with respect to rotation about the N_3-N_4 torsional angle. A rotation of 180° about this angle gives structure **2**, which is 10.5 kcal/mol lower in energy.

TABLE 1: Z-Matrix Coordinates of Structures 1H and 2H at the Optimized Geometries for the HF/6-31g(d) and MP2/6-31g(d) Methods with the MP2 Values Given in Parentheses. For Structure 1H, the MP2 Method Gave a Ring Opening at the N_2-C_7 Bond To Structure 7H

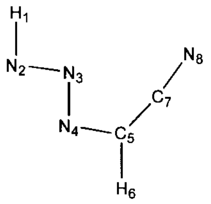


Structure 1H



Structure 7H

H						
N	**1**	**1.0009 (1.0339)**				
N	**2**	**1.2402 (1.2572)**	**1**	**120.1 (105.1)**		
N	**3**	**1.3443 (1.4558)**	**2**	**109.8 (113.5)**	**1**	**180.0 (180.0)**
C	**4**	**1.2992 (1.2942)**	**3**	**107.6 (120.4)**	**2**	**0.0 (0.0)**
H	**5**	**1.0700 (1.0893)**	**4**	**121.8 (114.0)**	**3**	**180.0 (180.0)**
C	**5**	**1.4266 (1.4440)**	**4**	**111.9 (131.8)**	**3**	**0.0 (0.0)**
N	**7**	**1.2564 (1.1847)**	**5**	**136.3 (168.4)**	**4**	**180.0 (180.0)**



Structure 2H

H						
N	**1**	**1.0111 (1.0353)**				
N	**2**	**1.2097 (1.2603)**	**1**	**106.4 (103.9)**		
N	**3**	**1.3974 (1.4378)**	**2**	**110.3 (108.0)**	**1**	**180.0 (180.0)**
C	**4**	**1.2538 (1.2943)**	**3**	**112.6 (109.0)**	**2**	**180.0 (180.0)**
H	**5**	**1.0746 (1.0877)**	**4**	**118.2 (116.9)**	**3**	**180.0 (180.0)**
C	**5**	**1.4549 (1.4442)**	**4**	**126.2 (126.0)**	**3**	**0.0 (0.0)**
N	**5**	**2.5870 (2.6254)**	**4**	**128.4 (128.3)**	**3**	**0.0 (0.0)**

TABLE 2: Energies and Entropies of Structures 1H through 7H

structure	method[a]	E (hartrees)	ΔE (kcal/mol)[b]	S (cal/(K mol))
1H	HF	−294.524 67	34.4	68.4
2H	HF	−294.579 36	[0]	75.8
	MP2	−295.465 54	[0]	
3H	HF	−294.577 08	1.4	75.8
	MP2	−295.465 65	−0.1	
4H[c]	HF	−294.549 07	19.0	72.2
5H[c]	HF	−294.569 77	6.0	72.0
6H	HF	−294.582 29	−1.8	68.6
	MP2	−295.472 83	−4.5	
7H[c]	HF	−294.562 77	10.5	71.2
	MP2	−295.451 96	8.5	

[a] HF means the HF/6-31g(d)//HF/6-31g(d) method. MP2 means the MP2/6-31g(d)//MP2/6-31g(d) method. [b] The energy of the structure relative to that of structure **2H**. [c] This structure exhibited one imaginary vibrational frequency.

This ring opening of the nitrene by the C−N bond scission should produce an azo structure with a cis relationship between the CN and the Ph−N═N moieties. This is indeed the preferred conformation, as determined by X-ray analysis[2] and confirmed by the MO calculations. The trans conformers, structures **4** and **5**, are indeed saddle points, as determined by the vibrational analysis which produced an imaginary vibrational frequency at the HF level. The two cis conformers, structures **2** and **3** in Figure 5, are almost energetically equivalent. In the phenyl analogues, structure **2** will almost certainly be lower in energy since it will be sterically less hindered, but minor amounts of **3** may account for the new peak in the ^{15}N NMR spectrum.

The IR and Raman intensities determined at the HF/6-31g(d) level reveal that the IR transition for the C≡N stretching mode is very weak, in pleasing accord with the absence of a band near 2200 cm^{-1} in the IR spectra of **2**. The absence of this

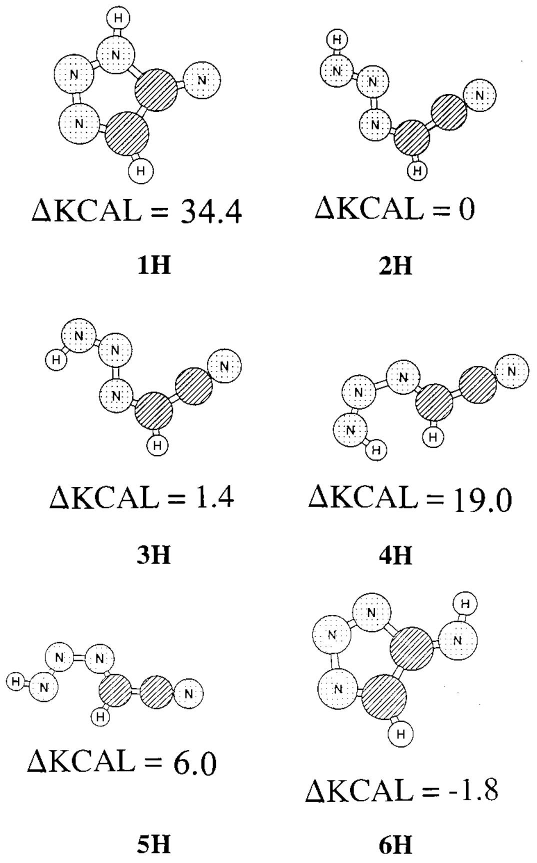


Figure 5. Relative energies from core isomers **1H** and **2H** optimized at the 6-31G* level.

band was a central piece of evidence for assigning a nitrene structure to the decomposition product.[1]

MP2/6-31g(d) Level. The results give a somewhat altered pathway from **1** to **2**. There is no perceptible transition state for the bond scission. Beginning with the HF/6-31g(d) optimized structure, the MP2/6-31g(d) optimization leads directly to the saddle point (structure **7**), preceding the torsional conversion to **2**. At the MP2 level, this saddle point lies 8.5 kcal/mol above **2**. These results cast some doubt on the viability of a stable nitrene structure, at least for the hydrogen analogue. Quite possibly, in the phenyl analogues with the three-ring structure, resonance stabilization may make the nitrene a viable structure.

The lowest energy isomer of all of the molecules in Figure 5 is the cyclic azafulvalene, structure **6H**. This is not surprising since in the substituted cases, the thermal isomerization of 1,4-diaryl-5-amino-1,2,3-triazoles to the substituted isomers **6** has been well documented.[7]

The flash photolysis results argue that any cyclic nitrene, if present, must have a rate constant for the scission in excess of 5×10^{7} s^{-1}. The azo compounds we are dealing with are sufficiently unique that their thermodynamic properties are difficult to estimate by group additivity.[8] However the equilibrium constant can be estimated from the HF/6-31g(d) vibrational analysis and the MP2/6-31g(d) energies given in Table 2. The MP2/6-31g(d) energy with all of the thermal corrections at 298 K determined from the vibrational analysis and the entropy determined from the same vibrational analysis give $\Delta G = -36.5$ kcal/mol and $K_{\mathrm{eq}} = 10^{27}$ for the nitrene to azo conversion, as depicted in Scheme 1. Assuming the rate constant from flash photolysis represents a lower limit for ring opening of the nitrene, we can then estimate a *lower* limit at 298 K for the rate of cyclization of **2** to **1** of 7×10^{-20} s^{-1}. Even assuming that the ring-opening rate is as large as 10^{17} s^{-1} leads to a calculated half-life for cyclization of over a century. We infer that mechanisms involving a nitrene intermediate are not very likely explanations of the unusual reactions of **2,** which presumably occur instead by various forms of direct attack on the open-chain azo structure.

Conclusions

The experimental observations do not provide any positive evidence for a dynamic equilibrium between the open-chain azo compound and a cyclic nitrene, and the theoretical calculations indicate that such an equilibrium is highly disfavored. A large number of reactions analogous to the ring-opening decomposition of 1,4-diphenyl-5-azido-1,2,3-triazole have been observed in pyrazoles,[9] thiazoles,[10] and other heterocycles.[11] In all of these cases a distinction cannot presently be made between a reaction proceeding by way of a nitrene and one involving two-bond scission in the parent azide (or its excited state) to give ring-opened products directly.

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Supporting Information Available: The **Z**-matrix coordinates for structures **3H**−**6H** (4 pages). Ordering information is given on any current masthead page.

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