been reported for the radical cation of 1,6-diazabicyclo[4.4.4]-tetradecane (**3**).[14] Although the N–N bond length in $\mathbf{3}^{\bullet+}$ (2.295 Å) is markedly larger than in $\mathbf{2}^{\bullet+}$, the shortening in the N–N interatomic distance on going from **3** to $\mathbf{3}^{\bullet+}$ (2.806 - 2.295 Å = 0.511 Å)[14] is comparable to that found in the present work for $\mathbf{2}^{\bullet+}$ relative to **2** (2.705 - 2.160 Å = 0.545 Å). On the other hand, the average C–N–C angle in $\mathbf{2}^{\bullet+}$ is (1/3)(2 × 120.8° + 115.8°) = 119.1°, as against the corresponding value of 114.0° in $\mathbf{3}^{\bullet+}$.[14] The N atoms in $\mathbf{2}^{\bullet+}$ should therefore be approximately sp^2 hybridized with the N–N bond having an almost pure p character, whereas a hybridization intermediate between sp^2 and sp^3 is expected for the N atoms in $\mathbf{3}^{\bullet+}$ with a considerable s contribution to the N–N bond. This difference accounts for the far larger ^{14}N-coupling constant for $\mathbf{3}^{\bullet+}$ (3.59 mT)[15] than for $\mathbf{2}^{\bullet+}$ (1.685 mT) and may also be of interest in considering the N–N bond lengths.

The mean C–C bond length, 1.395 Å, and the mean C–C–C bond angle, 125.6°, along the 14-membered perimeter in $\mathbf{2}^{\bullet+}$ are not significantly different from the corresponding values for **2** (1.392 Å and 125.2°). It is evident from Table I that the apparent constancy of the mean bond length is due to compensation of changes which alternate in sign along the perimeter. One is tempted to trace back these changes to the nodal properties of the HOMO by considering the lengthening (shortening) of a bond upon ionization as a consequence of the removed bonding (antibonding) contribution of the lost electron.

An increase in the torsion angles $\phi 1$ and $\phi 4$ for $\mathbf{2}^{\bullet+}$ relative to **2** indicates a flattening of the perimeter brought about by a decrease in the N–N distance. Similar findings are reported in the series of the structurally related hydrocarbons.[16] Thus, the perimeter is flattened when the two bridging C atoms in *syn*-1,6:8,13-propane-1,3-diylidene[14]annulene are linked by a bond to yield the corresponding cyclopropanediylidene-bridged compound. The decrease in the N–N distance also gives rise to substantial changes in the geometry parameters of the N–$(CH_2)_3$–N bridging group: on passing from **2** to $\mathbf{2}^{\bullet+}$, the bond lengths become larger and the bond angles smaller.

Acknowledgment. This work was supported by the Swiss National Science Foundation (F. Gerson) and the Stiftung Volkswagenwerk (E. Vogel). We thank Mr. D. Becker, (Universität Köln) for preparing a batch of **2**.

Supplementary Material Available: Tables listing (i) fractional coordinates, (ii) details of data collection and structure refinements, (iii) structure factors F_o/F_c, and (iv) individual bond lengths and bond angles (15 pages). Ordering information is given on any current masthead page.

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Photochemistry of Phenyl Azide: The Role of Singlet and Triplet Phenylnitrene as Transient Intermediates

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Abstract: The sequence of transient intermediates formed by the photolysis of phenyl azide (**1**) was determined by a combination of techniques including absorption, emission, and EPR spectroscopies as well as quantitative product analyses of irradiated glassy solutions at 77 K, in addition to kinetic and spectrographic flash photolysis at various temperatures. Several ortho, ortho′-disubstituted derivatives of **1** were also studied. The prevailing reaction pathway of **1** at ambient temperature is different from that at 77 K. The change of mechanism is traced to a temperature-dependent branching ratio from the primary photoproduct, singlet phenylnitrene ($^1\mathbf{2}$). It is established that the photoproduct observed by absorption spectroscopy at 77 K is predominantly triplet phenylnitrene ($^3\mathbf{2}$), as was originally postulated by Reiser et al. (*Trans. Faraday Soc.* **1966**, *62*, 3162–3169).

The chemical reactions initiated by the elimination of molecular nitrogen from aryl azides have found many useful applications in heterocyclic syntheses, in the production of photoimaging devices, and in the biochemical method of photoaffinity labeling.[1] Despite extensive work performed on the parent system, phenyl azide (**1**), essential aspects of the reaction mechanism remain controversial, and the literature concerning phenylnitrene (**2**) as the key reactive intermediate is as abundant as it is confusing.[1-14] Part of the complexity undoubtedly originates in the wide diversity of the reaction conditions employed, which range from gas-phase pyrolysis at temperatures up to 1000 K[2] to pyrolysis and photolysis in solution to photolysis of rigid glassy solutions at 77 K and of inert gas matrices at 10 K. We propose that the competition between two decay processes of singlet phenylnitrene ($^1\mathbf{2}$), the thermally activated isomerization to 1-azacyclohepta-1,2,4,6-tetraene (**3**) and the temperature-insensitive intersystem crossing

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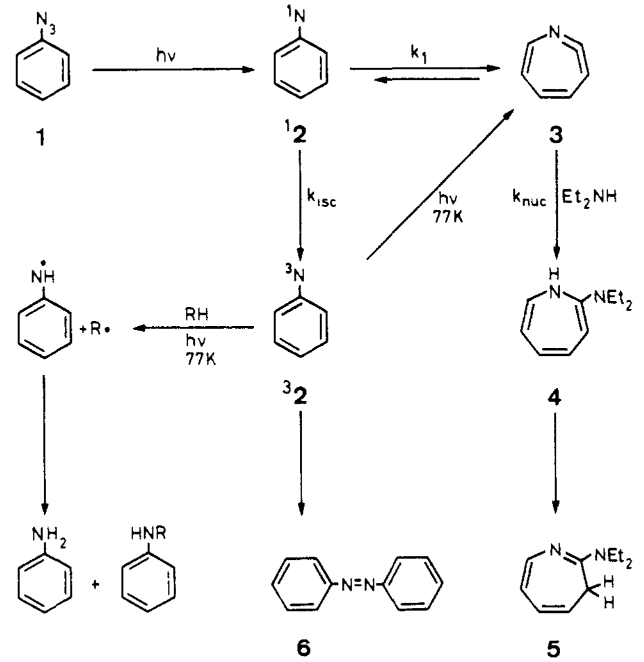
Scheme I



to triplet phenylnitrene (^{3}**2**), is responsible for a near complete change of the prevailing reaction path when the temperature is lowered from ambient to 77 K (Scheme I) .[15]

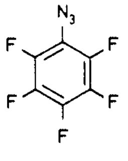
Various spectroscopic methods have been used to detect the primary photoproducts of **1**. The first and unchallenged spectroscopic identification of triplet phenylnitrene (^{3}**2**) was obtained in 1962 by Wasserman and co-workers by irradiation of a glassy solution of **1** at 77 K in the cavity of an EPR spectrometer.[3a] The resulting spectrum of a persistent paramagnetic species was assigned to ^{3}**2** on the basis of the observation of a $\Delta m = 2$ (half-field) transition and characteristic high-field lines reflecting large zero-field parameters. Subsequent work on substituted arylnitrenes has provided strong evidence for this spectral assignment on the basis of ^{14}N hyperfine coupling.[3b]

In 1965 Reiser and co-workers began to study the photochemistry of **1** and other aryl azides in rigid glassy solutions at 77 K.[4] The absorption spectrum of **1** rapidly disappeared upon UV irradiation and was replaced by a new spectrum extending to longer wavelengths. The photogenerated spectrum was persistent at 77 K but disappeared at higher temperatures. Predominantly on the basis of Wasserman≈s related EPR work and a number of ancillary observations, the new absorption was attributed to triplet phenylnitrene (^{3}**2**). Several other groups have since reproduced Reiser's absorption spectrum and have agreed with the previous assignment.[5-7] In 1978 Chapman et al. investigated the photochemistry of **1** in an argon matrix at 10 K using infrared detection.[8] They have provided convincing evidence that the photolysis of **1** ($\lambda > 220$ nm) led to the formation of the cyclic heterocumulene **3** as a major product which was characterized by a strong IR peak at 1895 cm^{-1}. Examination of the same sample by EPR spectroscopy revealed that ^{3}**2** was also present.

In view of Chapman's work one is uncertain whether Reiser's absorption spectrum is due exclusively to ^{3}**2** or to a mixture of ^{3}**2** and **3** and possibly other species. Furthermore, preparative work indicates that at room temperature the predominant primary product formed by direct irradiation of **1** is a long-lived, trappable singlet species, presumably **3**; entirely different products have been obtained by triplet sensitization of **1**.[9-11]

Considering the uncertainty in the absorption spectrum of ^{3}**2**, it is not surprising that two recent laser flash photolysis studies of **1** in solution have produced conflicting assignments of the observed transients.[11,12] Both groups have stated that the initial transient absorption is quite similar to Reiser's spectrum. Feilchenfeld and Waddell thus identified this transient with ^{3}**2**.[12] In contrast, Schrock and Schuster have questioned the assignment of Reiser's spectrum and maintain that ^{3}**2** is not observed by flash photolysis.[11] Their work confirms and extends the results and conclusions of an earlier study by De Graff et al. using conventional flash photolysis.[13] Finally, flash photolysis of **1** in the gas phase was reported to yield ^{3}**2** when sufficient inert quenching gas was added to prevent excessive heating.[14] It is seen that the results of different experiments so far did not combine to give a consistent, overall mechanism for the reactions following nitrogen elimination from phenyl azide, and there is disagreement over the sequence, yield, and lifetime of the reactive intermediates involved.

We have sought to determine the absorption spectrum of authentic triplet phenylnitrene (^{3}**2**) as an essential prerequisite to interpret flash photolysis data. A series of substituted phenyl azides (**7**–**10**) were included for comparison; the first two of these



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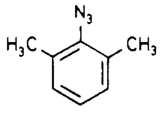

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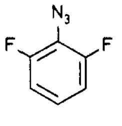

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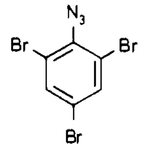

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were recently studied by Dunkin and co-workers using matrix isolation with IR detection.[16] We will show that brief photolysis of **1** at 77 K indeed predominantly if not exclusively yields ^{3}**2**, in agreement with Reiser's original assignment; nevertheless, we agree with Schrock and Schuster that this intermediate is not observed by flash photolysis of **1** at room temperature in solution. It turns out that none of the above-mentioned results are inconsistent with the relatively simple, conventional reaction mechanism shown in Scheme I,[1,8,11,15] provided that the temperature-dependent branching ratio from ^{1}**2** is taken into account.

Experimental Section

General. All quantitative product studies were performed on a Hewlett-Packard gas chromatograph using a 6 ft × $^1/_8$ in. 10% SE-30 column on 80/100 Chromosorb W-HP. Naphthalene was used as an internal standard; the reproducibility was ±2%. The light sources used for the preparative photolyses were either a 1000-W Hg–Xe arc lamp with appropriate filters or Rayonet RPR 3500 bulbs as indicated in the text. The EPR spectrometer was a Varian Model E112.

EPA glass (five parts diethyl ether, five parts isopentane, two parts ethanol) was used for optical spectroscopy at 77 K. The degassed solutions in 1 × 1 × 4 cm^3 cylindrical quartz cells were seated in a hollow copper sample holder which was kept in a quartz Dewar with optically flat windows. The sample holder was equipped with a thermocouple and internally cooled by a cold stream of nitrogen gas at slightly reduced pressure. Low-pressure (predominant emission at 254 nm) or high-pressure (Osram XBO 250 W with appropriate filters) mercury arcs were used for photolysis of the azides. The absorption spectra before and after photolysis were recorded on a Beckman UV 5240 (0.2 nm resolution) and fluorescence excitation and emission spectra on a Spex Fluorolog 2 (Model 111 C) spectrometer equipped with a multialkali R 928 photomultiplier tube operated as a quantum counter. Fluorescence spectra

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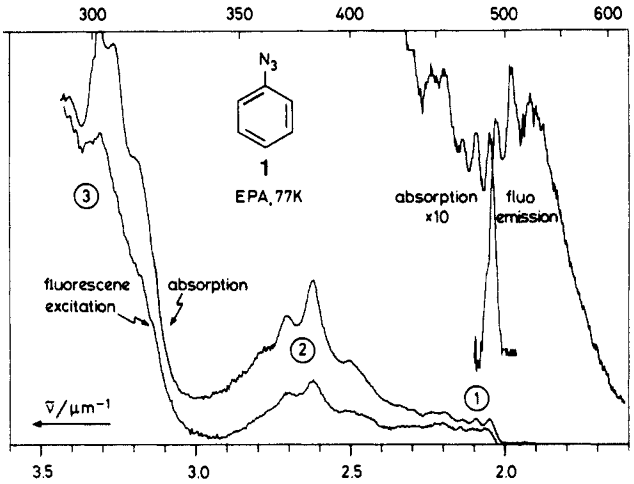

Figure 1. Absorption, fluorescence excitation, and fluorescence emission spectra of $^3\mathbf{2}$ produced by 334-nm photolysis of **1** in EPA solution at 77 K. The fluorescence spectra are corrected (cf. Experimental Section) and plotted in arbitrary units of quanta per wavenumber. The ordinate full scale amounts to ca. $\epsilon = 3 \times 10^3$ M^{-1} cm^{-1} for the absorption spectrum (cf. Discussion).

were corrected with the aid of a built-in Rhodamine 6 G quantum counter. Fluorescence emission spectra were corrected with a calibration curve for the spectral sensitivity of the setup which was determined with a standard tungsten light source. The calibration was occasionally checked with standard fluorescent samples emitting in the appropriate wavelength range. The slit widths on the scanning monochromator were chosen to give a resolution of 2 nm or better, depending on the fluorescence intensity. All optical spectra were converted to digital form and processed by computer. Fluorescence spectra were plotted in units of quanta per wavenumber.

Kinetic and Spectrographic Flash Photolysis. Most experiments were performed using the setup at the University of Basel which has been described previously.[17] The detection system allowed for the simultaneous capture of the kinetics at a given wavelength (using a Tektronix 7912 AD transient digitizer) and of the transient spectrum at a given time delay after excitation (time window ≥ 5 ns). The transient spectrum was captured by a B+M diode array viewing a gateable microchannel plate image intensifier. The optical resolution was 2 nm. One of the following excitation sources was chosen for optimal performance as indicated in the text: a Lambda-Physik EMG 101 excimer laser operated at 308 nm (XeCl) or at 248 nm (KrF) with a pulse energy of ca. 200 mJ and a pulse width of ca. 20 ns, a JK 2000 Nd glass laser frequency tripled (353 nm, 60 mJ) or quadrupled (265 nm, 40 mJ) with a pulse width of ca. 15 ns, and a self-built conventional electric discharge of up to 1000 J through two coaxial quartz tubes of 15-cm length, pulse width at maximum energy ca. 20 µs with some tailing due to afterglow. The Nd laser pulses were directed at an angle of ca. 10° to the monitoring light beam, the other excitation pulses at 90°. Flow cells were used for preliminary experiments, but eventually entirely fresh samples were used for each single shot due to the high photochemical decomposition of the azides. Care was also taken to minimize exposure of the samples to the monitoring light by using light shutters and appropriate filters.

Materials. All of the azides used in this work have been prepared previously and were obtained by the published procedures. Spectrograde solvents were used throughout without further purification except for diethyl ether which was refluxed over Na-K alloy and vacuum distilled immediately prior to use.

Results

Absorption Spectra of Triplet Phenylnitrenes in Rigid Glassy Solutions. Brief photolysis (15 s, 254 nm) of 10^{-4} M phenyl azide (**1**) dissolved in EPA at 77 K produced a new absorption extending to the visible range. The spectrum shown in Figure 1 was generated by deducing as a base line the original spectrum registered prior to irradiation; since **1** absorbs only weakly in the wavelength range shown, bleaching due to photolysis of an unknown amount of **1** is insignificant. At very low conversions, the spectral changes were uniform with increasing irradiation time. However, upon continued irradiation secondary photolysis of the photoproduct(s) became apparent by an overproportional increase of the new absorbance at wavelengths below 370 nm.

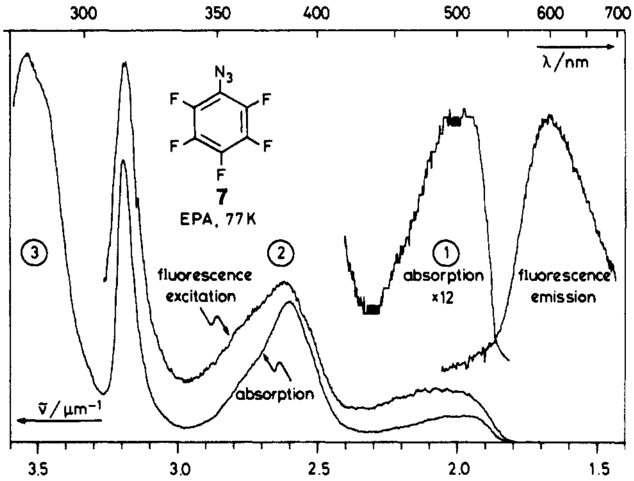

Figure 2. Absorption, fluorescence excitation, and fluorescence emission spectra of the nitrene produced by 254-nm photolysis of **7** in EPA solution at 77 K. Ordinate scales: cf. caption to Figure 1.

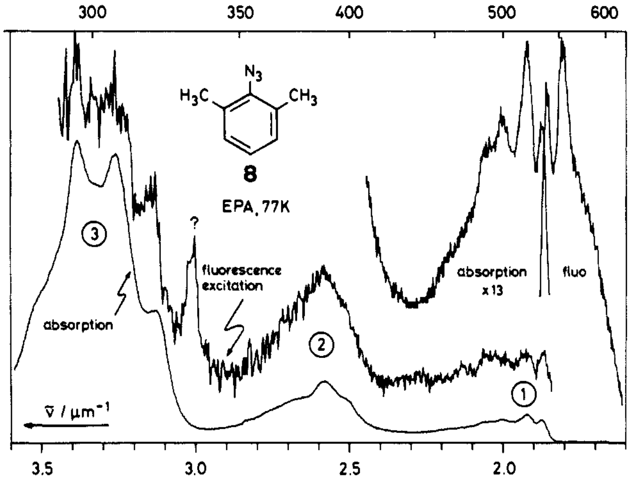

Figure 3. Absorption, fluorescence excitation, and fluorescence emission spectra of the nitrene produced by 254-nm photolysis of **8** in EPA solution at 77 K. Ordinate scales: cf. caption to Figure 1.

Attempts to decompose **1** by triplet sensitization at 77 K have failed. Photolysis of a mixture of 10^{-4} M 2,3-dimethylnaphthoquinone and 10^{-2} M **1** in EPA at 365 nm gave the same photoproduct spectrum as above. Under these conditions most of the light was absorbed by the sensitizer. However, a control experiment showed that the conversion of **1** was more rapid in the absence of the naphthoquinone, which, therefore, acted as an internal light screen rather than as a sensitizer.

The absorption spectra produced by direct (254 nm) irradiation of the phenyl azide derivatives **7**–**10** at 77 K are shown in Figures 2–5.

Fluorescence Emission and Excitation Spectra of Triplet Phenylnitrenes in Rigid Glassy Solutions. Fluorescence excitation spectroscopy can be used as an analytical tool to distinguish individual components in the absorption spectra of composite mixtures. It is therefore the method of choice to decide whether the photolysis of **1** at 77 K yields exclusively $^3\mathbf{2}$ as postulated[4-7] or a mixture of products, e.g., $^3\mathbf{2}$ and **3**. Unfortunately, the fluorescence emission of such samples is extremely weak. Brichkin and co-workers originally reported that photolyzed samples of **1** at 77 K were nonfluorescent ($\phi_f < 10^{-3}$)[18] but later found a weak, short-lived emission in the range 490–650 nm which was attributed to T_1–T_0 fluorescence of $^3\mathbf{2}$.[6] It was claimed that the fluorescence

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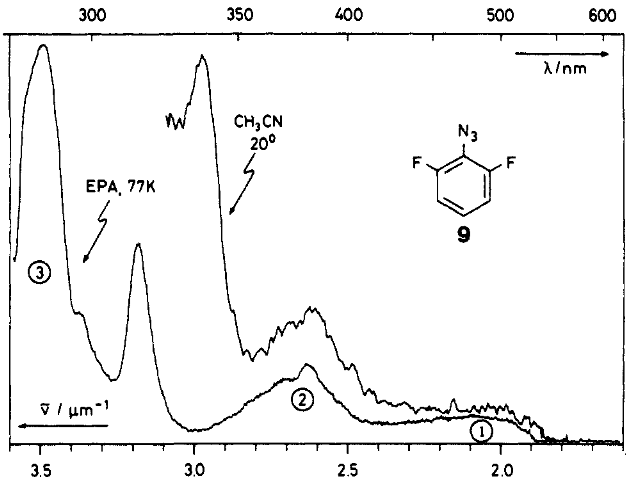

Figure 4. Lower curve: absorption spectrum of the nitrene produced by 254-nm photolysis of **9** in EPA solution at 77 K (ordinate full scale ca. $\epsilon = 3 \times 10^3$ M^{-1} cm^{-1}). Upper curve: transient absorption spectrum observed 50 ns after 308-nm laser flash photolysis of **9** in aerated acetonitrile solution at ambient temperature (arbitrary scale).

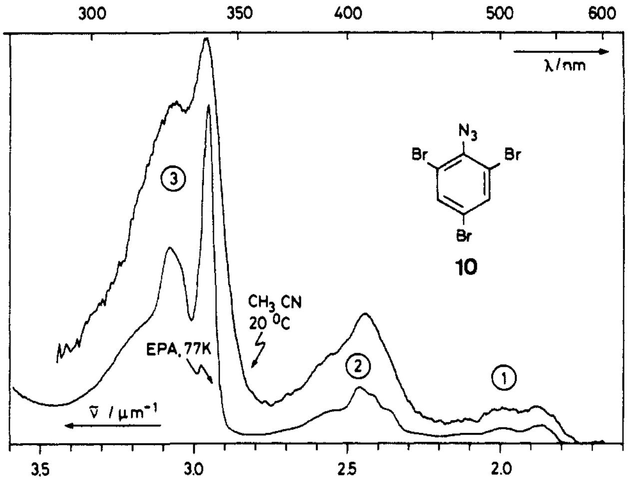

Figure 5. Lower curve: absorption spectrum of the nitrene produced by 254-nm photolysis of **10** in EPA solution at 77 K (ordinate full scale ca. $\epsilon = 3 \times 10^3$ M^{-1} cm^{-1}). Upper curve: transient absorption spectrum observed 50 ns after 308-nm laser flash photolysis of **10** in aerated acetonitrile solution at ambient temperature (arbitrary scale).

excitation spectrum was "coincident with the nitrene absorption" without further specification.

After several fruitless attempts we have detected a weak fluorescence emission from samples of **1**, **7**, and **8** photolyzed at 77 K; the emission appeared and subsequently disappeared (upon overirradiation) concomitantly with the photoproduct absorption. The 0–0 bands of absorption and emission were nearly coincident, and the excitation spectra were in satisfactory agreement with the photoproduct absorption spectra as shown in Figures 1–3. This is strong evidence that *the new absorption spectra produced by the photolysis of phenyl azides at 77 K are due to a single new product.*

Spectrographic Flash Photolysis of Phenyl Azides in Solution at Ambient Temperature. Initial absorbance changes produced by laser flash photolysis of the azides **1** and **7**–**10** were formed within the duration of the laser pulses (ca. 20 ns). Subsequent changes occurred on a time scale of tens to hundreds of microseconds. Variation of the solvent (acetonitrile, benzene, hexane) and the sample concentration (concomitant with the excitation wavelength: 10^{-3} M at 308 nm, 10^{-4} M at 248 nm) and the presence or absence of atmospheric oxygen had very little effect on the spectra or the dynamics of the transients. The spectra shown in Figures 4–7 were taken within a time window of 20 ns and a delay of 50 ns after the peak of the laser flash (308 or 248 nm, acetonitrile).

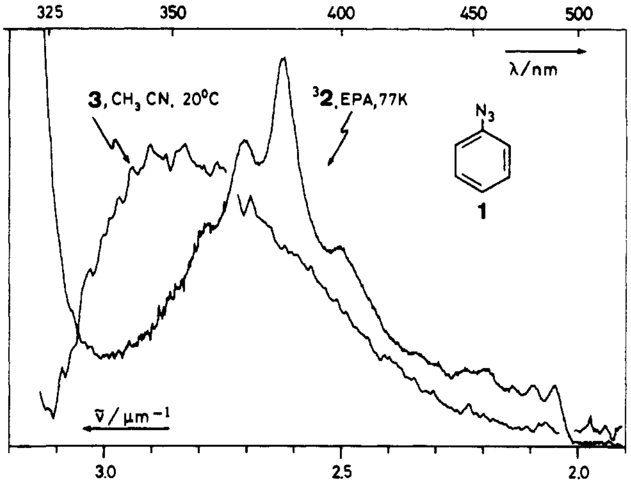

Figure 6. Comparison of the transient absorption spectrum of **3** observed 50 ns after 308-nm laser flash photolysis of **1** in aerated acetonitrile at ambient temperature and the spectrum of ^{3}**2** at 77 K (cf. Figure 1, arbitrary scales).

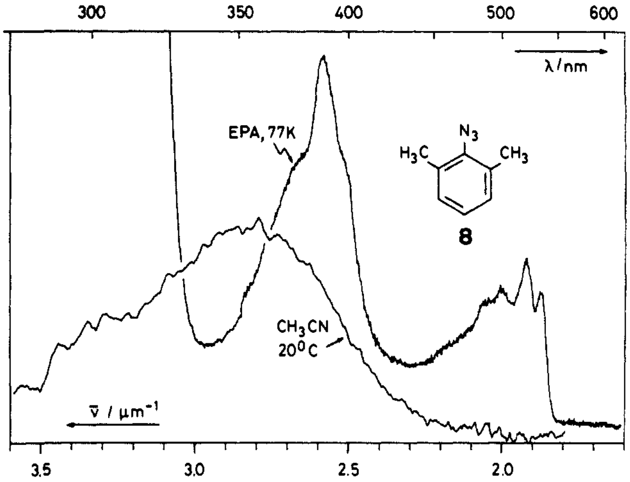

Figure 7. Comparison of the transient absorption spectrum observed 50 ns after 308-nm laser flash photolysis of **8** in aerated acetonitrile at ambient temperature and the photoproduct spectrum at 77 K (cf. Figure 3, arbitrary scales).

The reader should first compare the spectrum photogenerated from the tribromo precursor at 77 K with the corresponding transient spectrum observed at ambient temperature (Figure 5). It is obvious that the same species was generated by the two methods and, furthermore, that wavelength shifts due to the change in solvent and temperature are insignificant. If we now turn to parent **1** (Figure 6) and its dimethyl derivative **8** (Figure 7), it is seen that different photoproducts were produced at the two temperatures. There is indeed, as noted previously,[11,12] a rough similarity between the two spectra from **1** in the range 330–450 nm. However, the similarity is deceptive, and a closer examination shows that the distinct maxima at 490, 382, and 303 nm of the low-temperature spectrum are entirely absent in the transient spectrum. The difference is quite conspicuous in the spectra of **8** (Figure 7). If we attribute the low-temperature spectra to the triplet nitrenes exclusively (cf. Discussion), then this finding implies that *phenyl azide* **1** *and its dimethyl derivatives* **8** *give no triplet nitrene detectable by flash photolysis at room temperature* under conditions where the triplet nitrene from **10** is easily observed. The fluorinated derivatives **7** and **9** gave relatively weak transient absorptions compared with **10**. The shape of these spectra essentially followed that of the corresponding low-temperature spectra in the visible range, but differences in the near-UV region indicated that one or more additional products were formed by flash photolysis (Figure 4).

Several attempts were made to generate and observe the triplet phenylnitrenes derived from **1** and **8** in solution by sensitized flash

Table I. Yield and Rate of Formation of **4** as Measured by Laser Flash Photolysis[a]

T/K	$A_\infty - A_0$	k_{nuc}[DEA]/10^6 s^{-1} [b]
293	0.048	1.8
262	0.034	1.9
244	0.024	1.5
205	0.012	1.3
193	0.007	1.3
164	0.003	

[a] 0.5 M DEA and 0.001 M **1** in MTHF, the transient growth is monitored at 340 nm. [b] All pseudo-first-order rate constants are ±20%.

photolysis using excitation at 353 nm and either benzophenone or 2,3-dimethylnaphthoquinone as triplet sensitizers. Although both of the sensitizer triplets were quenched by the azides at near diffusion-controlled rates, the transient spectra observed after completion of the energy transfer gave no clear-cut evidence for the presence of triplet nitrenes. Actually, this is not surprising for two reasons: (i) Schuster has shown that the quantum yield of photodecomposition by triplet sensitization of **1** is low ($\phi_r < 0.1$),[11] and (ii) Reiser has shown that the 1-anthrylnitrene triplet is quenched by the parent azide to give azoanthracene at a rate of ca. 5×10^8 M^{-1} s^{-1}.[19] Since high azide concentrations are needed for flash sensitization, the triplet nitrenes may then be consumed about as rapidly as they are formed. We are aware that Waddell and Co-workers have in contrast postulated that an autocatalytic chain decomposition of phenyl azide is initiated by triplet phenylnitrene, ^{3}**2** + **1** → 2^3**2** + N$_2$,[20] but the present work certainly provides no evidence in favor of their mechanistic proposal, and we disagree with the assignment of their transient spectra as ^{3}**2** and their arguments based on this assignment.[12]

Variable-Temperature Kinetic Flash Photolysis of 1 in the Presence of Diethylamine. Photolysis of **1** in the presence of nucleophiles gives azepine products. In inert solvents only intractable polymers are formed.[1] Sundberg[13] and Schuster[11] report that flash photolysis of **1** in the presence of secondary amines leads to the growth of a secondary intermediate which absorbs strongly in the range 340–370 nm. The rate of growth has been found to be first order in the concentration of amine for [amine] < 0.5 M[11,13] but approached zero order in more concentrated solutions up to neat amine.[11] Both Schuster and Sundberg have identified the growth with the formation of 1*H*-azepine **4**. In our hands, 308-nm flash photolysis of 0.02 M **1** in a 2-methyltetrahydrofuran (MTHF) solution containing 0.5 M diethylamine (DEA) gave a growth lifetime of 550 ns at 293 K. At 193 K, the growth lifetime still amounted to 750 ns, but the yield of **4**, as measured by the total absorbance change after the flash ($A_\infty - A_0$, Table I), was much reduced relative to 293 K. This indicates that the yield of **4** is not diminished due to a high activation energy of the trapping reaction (k_{nuc}, Scheme I) but due to a decreased yield of the reactive azacycloheptatetraene **3**. The trend continued on further cooling, so that the formation of **4** was barely detectable at 173 K.

Product Studies on the Mixture 1/DEA/MTHF Irradiated at Various Temperatures. Broad-band photolysis (350 nm, Rayonet reactor) of a MTHF solution containing 0.04 M **1** and 1 M DEA at ambient temperature gave the 3*H*-azepine **5** in good yield.[21] Only trace amounts of azobenzene (**6**) were formed under these conditions (Table II). Very similar product distributions were obtained down to 233 K. The yield of **5** began to drop at 213 K and was quite low at 173 K. At this temperature an increased yield of azobenzene was obtained. This trend continued on further cooling; at 153 K the yield of azobenzene was still higher and the 3*H*-azepine was formed in only trace amounts.

By extrapolation of the data in Table II one would predict that azobenzene should be the exclusive product formed by photolysis of **1** at 77 K. However, analysis of the products after thawing gave a sizable amount of the 3*H*-azepine **5**. EPR spectroscopy of an irradiated 1 M DEA/MTHF glass confirmed that triplet phenylnitrene (^{3}**2**) is completely stable in the dark for at least 1 h at 77 K. Presumably **3** is also stable under these conditions; it is known to be stable in an argon matrix at 10 K.[8] We assume that, when a sample containing ^{3}**2** and **3** is thawed, the former would dimerize to **6** and the latter would react with DEA yielding first **4** and ultimately **5** (Scheme I). Thus the products formed on annealing the glass should reflect the distribution of ^{3}**2** and **3** in the solid glass.[22]

Table II. Distribution of Products Formed on Photolysis of **1** in MTHF/DEA[a] as a Function of Temperature[b]

T/K	**5**[c]	**6**[c]
293	59	0
273	59	0
253	58	0
233	58	0
213	43	0
193	25	0
173	0	11
153	0	24
77[d]	16	7

[a] 1.0 M DEA and 0.04 M **1** in MTHF, Rayonet RPR 3500 lamps for 2–4 h. [b] Temperature ±2 K. [c] Percent yields are absolute relative to naphthalene internal standard, ±1%. [d] Rigid glass.

Table III. Distribution of Products Formed on Photolysis of **1** at 77 K as a Function of Photolysis Time[a]

350 Rayonet[b]				366-nm 1000-W Hg–Xe[c]			
time/min	**1**	**5**	**6**	time/min	**1**	**5**	**6**
5	89	0	8	1	95	0	1.0
10	63	7	11	2	93	0	1
15	58	7	12	5	93	1	2
30	56	10	11	15	90	1	2
60	48	21	13	30	83	2.5	1
				63	83	3.8	1

[a] Percent yields are absolute relative to naphthalene internal standard, ±1%. [b] 0.04 M **1** and 1.0 M DEA and MTHF. [c] 0.4 M **1** and 1.0 M DEA and MTHF.

An investigation of the product distribution as a function of photolysis time (Table III) demonstrated the origin of the 3*H*-azepine **5** isolated after photolysis at 77 K. After brief irradiation the only photoproduct was azobenzene. *This shows that triplet phenylnitrene (^{3}**2**) is the only primary photoproduct at 77 K and that the azacycloheptatetraene **3** is formed only by secondary photolysis.* Indeed Chapman has previously concluded that ^{3}**2** can be photolyzed to **3**.[8] At longer irradiation times the yield of **5** matches and eventually surpasses the yield of **6**. The yield of **6** quickly reaches a maximum and then remains constant with increased photolysis times. It has been reported that the photolysis of nitrenes also leads to abstraction of hydrogen from glassy solvents at 77 K; after prolonged photolysis of **1** a small amount of aniline was eventually detected by its phosphorescence.[6] The low overall material balances we observed after photolysis at 77 K (Table II) may be a consequence of polymerization initiated by anilino radicals upon the glass being thawed.

ESR Spectroscopic Monitoring of ^{3}2. The strong and persistent EPR signals[3] observed after photolysis of **1** in MTHF were used as an unambiguous method to monitor relative concentrations of triplet phenylnitrene as a function of the deposited light dose. Identical samples were photolyzed with 365-nm light filtered from a 1000-W Hg–Xe lamp. Each sample was photolyzed for 10 s, but the light intensity was varied by means of neutral density filters. At such low conversions the resulting signal intensities were proportional to the light intensities (Figure 8), confirming that ^{3}**2** is formed by a monophotonic process. In another ex-

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[22] If **3** could in part react to ^{3}**2** via ^{1}**2** upon annealing, the ratio of products **5**/**6** would be smaller than the ratio **3**/^{3}**2** present in the glass. This would introduce a constant correction of the data in Table III but would not change the qualitative trends observed.

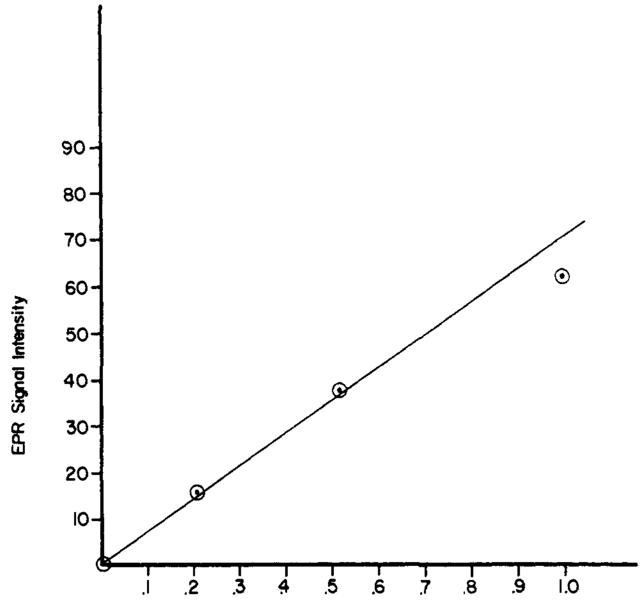


Figure 8. Relative intensity of the EPR spectrum of ^{3}**2** recorded after 10 s of irradiation with various intensities at 77 K (λ > 295 nm, 1000-W Hg-Xe arc lamp shielded by neutral density filters).

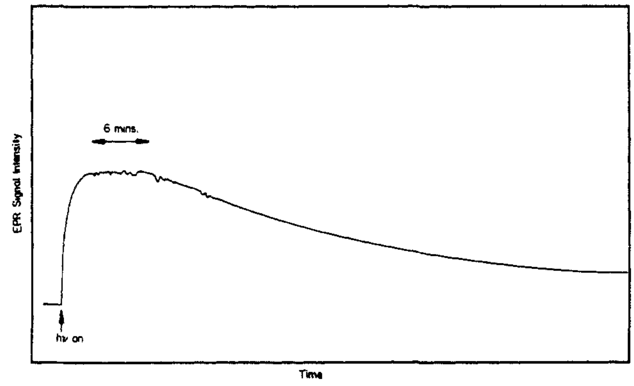


Figure 9. Relative intensity of the EPR signal of ^{3}**2** monitored at 6700 G during irradiation at 77 K (λ > 295 nm).

periment the signal intensity was monitored during 365-nm photolysis at 77 K (Figure 9). The maximum intensity was reached after 3 min; further irradiation led eventually to the complete disappearance of the EPR signal of ^{3}**2**. This provides unambiguous confirmation that ^{3}**2** is quite sensitive to secondary photolysis.

Discussion

Further, to the original arguments put forward by Reiser et al.,[4] we first summarize additional evidence to establish that the photolysis of phenyl azide (**1**) in rigid glasses at 77 K gives essentially a single product, triplet phenylnitrene (^{3}**2**). An attempt is made to assign the electronic spectrum of ^{3}**2** and its derivatives. We then show that a predominant formation of ^{3}**2** at 77 K is quite consistent with earlier work which identified azacycloheptatetraene **3** as a major photoproduct both at ambient[11] and at cryogenic (10 K)[8] temperatures. Finally, we turn to the properties of singlet and triplet phenylnitrene as reactive intermediates.

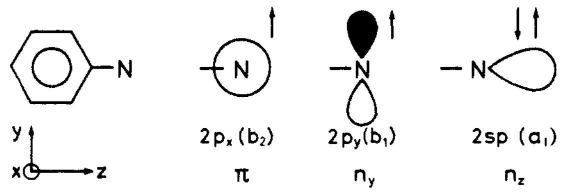
All phenyl azides studied in this work (**1**, **7–10**) gave, after brief photolysis at 77 K, photoproduct absorption spectra which were quite similar in habitus (Figures 1–5). The photoproducts formed from **1**, **7**, and **8** were weakly fluorescent. This was used to confirm that a single photoproduct was observed in each case by absorption spectroscopy, not a mixture of products; the fluorescence emission spectra were independent of the excitation wavelength, and, more important, the fluorescence excitation spectra were in good agreement with the absorption spectra and did not depend on the emission wavelength monitored. The similarity of the photoproduct spectra obtained from **1**, **7**, and **8** is particularly significant, as Dunkin et al. have shown that no azacycloheptatetraenes or benzazirines are formed on photolysis of **7** and **8** in argon at 10 K.[16]

Triplet phenylnitrene (^{3}**2**) has clearly been identified by EPR spectroscopy as a photoproduct of **1** at 77 K, and it was shown that it disappears, upon overirradiation or warming, concomitantly with the optical photoproduct. It may be objected that the EPR signals may arise from trace impurities or a minor side reaction not observed by optical spectroscopy. This was ruled out by analyzing the products isolated after thawing MTHF glasses containing DEA as a trapping agent for **3**: azobenzene, the product expected from ^{3}**2**, was found exclusively after irradiation periods short enough to avoid significant secondary photolysis of ^{3}**2**.

Some comments concerning the electronic spectra of triplet phenylnitrenes follow. All photoproduced spectra exhibited four separate band systems: ①, λ_{max} ca. 500 nm (log $\epsilon \sim 2.5$), ② ca. 400 nm (log $\epsilon \sim 3$), ③ ca. 320 nm (log $\epsilon \sim 3.5$), and ④ ca. 240 nm (log $\epsilon \sim 4$). Bands ④, which overlap with strong absorption by the azide precursors, are not reproduced in Figures 1–5. The numbering ① to ④ is not meant to imply that only one electronic transition contributes to a given band system. The band intensities given above were estimated for those derivatives (**7** and **10**) for which the nitrenes were sufficiently photostable to allow essentially complete conversion.

The electronic spectrum of ^{3}**2** shown in Figure 1 is quite similar to that reported by Reiser et al.,[4] but there are three notable differences. (i) Reiser's estimated band intensities are systematically lower than those given above by ca. 0.5 log unit. Due to the extreme photolability of ^{3}**2**, its absolute extinction coefficient is very hard to estimate and we feel that it is best to rely on the more stable derivatives. (ii) In the original spectrum[4] there is considerable contamination by the secondary photoproduct **3**, which has a broad absorption maximum near 340 nm (Figure 6). At very low conversions the window between bands ② and ③ near 330 nm is much more pronounced than reported previously,[4,6] and the maximum of band ② is at 381 nm, not at 369 nm. (iii) More important, the first, very weak band system ① (λ_{00} = 489 nm) was not reported by Reiser. Thus we have to question previous assignments of the spectrum of ^{3}**2**, since band system ② (λ_{00} = 402 nm) was hitherto associated with the first electronic transition.[4,5] Band ① was reproduced in the spectrum of Smirnov and Brichkin,[6] but these authors attributed systems ① and ② to a single electronic transition. It is obvious from the shapes of the fluorescence emission spectra (mirror image relationship with the first absorption band, Figures 1–3) and from the changes induced by substitution (nitrenes from azides **7–10**) that at least two electronic transitions give rise to band system ①.

The electronic structure of ^{3}**2** has been discussed in terms of MO theory in a review article by Berry.[23] He pointed out that the absorption spectrum should, in addition to the $\pi\pi^*$ absorption bands related to the transitions of the π isoelectronic benzyl radical, exhibit two low-lying, weak but symmetry-allowed (x-polarized) transitions which correspond to the $n_y \rightarrow \pi^*$ (a_2) and π (a_2) $\rightarrow n_y$ charge-transfer excited configurations. The situation is in fact even more complicated, since two additional medium-intensity bands associated with the configurations $n_z \rightarrow n_y$ (y-polarized) and $n_z \rightarrow \pi$ (b_2) (x-polarized) may be expected to lie in the near-UV region. The latter are related to the well-known de-



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generate $A^3\Pi_i$–$X^3\Sigma^-$ transition of ^{3}NH at 336 nm (f = 0.008)[24] which has also been observed as a sharp band in alkylnitrenes at slightly shorter wavelengths.[25] The $n_z \rightarrow n_y$ transition is essentially localized on the monovalent nitrogen atom. It should therefore not be very sensitive to the nature of the substituent and should also be observable as a sharp, medium-intensity ($f \cong 0.01$) peak around 300–350 nm in arylnitrenes.

Experimental band polarizations not being available, we can offer only a very tentative assignment of the observed spectra (Figures 1–5) which is based on qualitative considerations of the band shapes and intensities and of the band shifts upon substitution. We propose that the very weak, long wavelength features ① are due to the charge-transfer-type $n_y \rightarrow \pi^*$ (a_2) and π (a_2) $\rightarrow n_y$ transitions. On the basis of PPP SCF CI calculations and in agreement with Reiser and others,[4-6] we attribute the main part of systems ②, ③, and ④ to the $\pi\pi^*$ transitions observed similarly in the benzyl radical. Finally, we feel that the sharp, isolated peak near 320 nm found in the fluorinated nitrenes derived from **7** and **9** is due to the localized $n_z \rightarrow n_y$ transition. In the other nitrenes this transition is probably part of band system ③.

The primary photoproduct observed by spectrographic flash photolysis of **1** in solution has an absorption spectrum which, although superficially similar, is significantly different from that of ^{3}**2** at 77 K (Figure 6). The difference is quite obvious for the pair of spectra obtained from the dimethyl derivative **8** (Figure 7). That these differences are not simply due to a solvent and/or a temperature effect on the electronic spectra of triplet nitrenes is seen from the two spectra produced similarly from the tribromo derivative **10** (Figure 5), which does cleanly give the triplet nitrene under both conditions. Therefore there is no real conflict in having different assignments for the two spectra from **1**, namely, ^{3}**2** for the spectrum at 77 K[4-7] and **3** for the transient spectrum at ambient temperature.[11,13]

Why then should azacycloheptatetraene **3** be the major photoproduct of **1** both at ambient and at cryogenic temperatures? In order to link the work on fluid solutions and on rigid glasses, we studied the photochemistry of **1** in MTHF containing DEA as a trapping agent at various temperatures in the range 293–77 K. Both kinetic flash photolysis (Table I) and product analysis (Table II) consistently showed that the yield of **3** gradually drops to zero in favor of ^{3}**2** as the temperature is lowered. These results are best interpreted in terms of Scheme I. Photolysis of **1** gives singlet phenylnitrene (^{1}**2**) which can either ring expand (k_1) to **3** or intersystem cross (k_{isc}) to the ground state ^{3}**2**. The results are easily explained if the ratio k_{isc}/k_1 is temperature dependent with $k_1 \gg k_{isc}$ at 273 K and $k_{isc} \gg k_1$ at 77 K. It is quite reasonable to assume that the rearrangment ^{1}**2** → **3** should be a thermally activated process, whereas the photophysical intersystem crossing rate should be essentially independent of temperature. It has been reported that the lifetime of isc in 1-pyrenylnitrene increases only slightly from 22 to 34 ns by lowering the temperature from ambient to 77 K.[26]

There is no continuous experimental connection between a rigid glass at 77 K and an inert gas matrix at 10 K. However, we can offer two reasonable arguments, either or both of which may be responsible for the fact that **3** is again observed as a major photoproduct of **1** in the matrix work.[8] First, as pointed out by Chapman et al., excess heat dumping is likely to be quite slow in inert gas matrices, and the matrix work may therefore reflect "high-temperature chemistry going on in a locally super-heated region of the argon".[8] Second, IR detection is somewhat less sensitive than optical spectroscopy. As Reiser already noted,[4] ^{3}**2** is extremely sensitive toward secondary photolysis. In this work, the light sensitivity of ^{3}**2** was consistently observed by EPR (Figure 9), absorption, and fluorescence spectroscopies. Preparative analyses as a function of irradiation time (Table III) proved that the main photoproduct of ^{3}**2** is **3**, in agreement with previous observations by Chapman et al.[8] Therefore it is quite possible that all of the matrix-isolated **3** is formed by secondary photolysis of the primary photoproduct ^{3}**2**; this is certainly true for rigid glasses at 77 K.

Dunkin et al. have concluded from matrix photolysis of the azides **7** and **8** that these ortho, ortho′-disubstituted derivatives decompose cleanly to the corresponding nitrenes and are relatively stable to further irradiation.[16] We found this to be true also for **7**–**10** in rigid glasses at 77 K. Note, however, that the substituents seem to prohibit mainly the photochemical conversion from triplet nitrene to azacycloheptatetraene. Only **10** gives the triplet nitrene cleanly at ambient temperature, and this is likely due to an acceleration of k_{isc} by an internal heavy-atom effect rather than an inhibition of k_1. Compound **10** may thus be of interest if one wishes to study the chemistry of an authentic triplet arylnitrene at ambient temperature. Compared with polynuclear aromatic azides,[27] it has the advantage that the triplet nitrene is formed directly within (probably much less than) 20 ns. Flash photolysis of 10^{-4} M **10** in acetonitrile gave a clean second-order decay at 530 nm which was not noticeably affected by the presence of atmospheric oxygen. On the conventional flash photolysis system (cell path length d = 10 cm), the decay occurred on a millisecond time scale ($^2k\epsilon^{-1}d^{-1} = 1.1 \times 10^5$ s^{-1}, i.e., log (^2k M^{-1} s^{-1}) $\cong$ 8.5 ± 1). Thus the reaction rate of the triplet nitrene with $^3O_2$ must be less than 1×10^6 M^{-1} s^{-1}.

Some time ago, Huisgen and Appl suggested that nitrogen elimination from **1** might proceed synchronously with ring expansion.[28] To our knowledge, the temperature dependence attributed to k_1 is the first, if indirect, piece of evidence that singlet phenylnitrene (^{1}**2**) is a true intermediate. The energy gap $E(^1\mathbf{2}) - E(^3\mathbf{2})$ = 4.3 ± 0.4 kcal/mol was recently determined by electron photodetachment from $^2\mathbf{2}^-$.[29] Analysis of the temperature-dependent data given in Tables I and II on the basis of the reaction mechanism given in Scheme I should yield the lifetime of ^{1}**2** as a function of temperature. In practice, the quality of the data and the possibility of systematic errors[22] allow only the following very crude estimate.

We assume that both reactions ^{1}**2** → **3** (k_1) and ^{1}**2** → ^{3}**2** (k_{isc}) are irreversible in the presence of DEA and further that only k_1 is a function of temperature. This leads to the simple relation

$$\frac{\phi(\mathbf{3})}{\phi(^3\mathbf{2})} = \frac{\phi(\mathbf{5})}{\phi(\mathbf{6})} = \frac{k_1}{k_{isc}} = C\exp(-E_a/RT)$$

The data in Tables I and II indicate that the isokinetic temperature ($k_1 = k_{isc}$) is in the range of 210 ± 20 K and that the ratio k_1/k_{isc} changes by a factor of 2 over a temperature interval of 20 ± 5 K. From the latter we find that E_a = 3 ± 1 kcal/mol. If we assume a normal A factor of ca. 10^{13} s^{-1} for the rate of rearrangement k_1, we arrive at $k_{isc} = k_1$ (210 K) = $10^{10\pm1}$ s^{-1}. For the decay rate of ^{1}**2** at room temperature we obtain $\tau^{-1}(^1\mathbf{2}) \cong k_1$ (293 K) = $10^{11\pm1}$ s^{-1}. The preliminaries for a picosecond flash photolysis study of phenyl azide are thus available.

In conclusion, the rate of ring expansion from singlet phenylnitrene (^{1}**2**) is strongly dependent on temperature and substituent effects. The competing process of intersystem crossing to triplet phenylnitrene (^{3}**2**) is favored at low temperature. Experimental knowledge about the branching ratio from singlet arylnitrenes, such as that provided here for compounds **1** and **7**–**10**, will be essential for successful applications of aryl azide photochemistry. The fate of the singlet intermediate **3** in the absence of trapping agents such as DEA has not been firmly established due to the formation of intractable product mixtures. In con-

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centrated solutions of **1** it may be responsible for the autocatalytic chain decomposition reaction discovered by Waddell and coworkers.[30] In highly dilute solutions or viscous media the formation of **3** may be reversible and eventually give rise to a delayed formation of ^{3}**2**.[11,27]

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Registry No. 1, 622-37-7; **2**, 2655-25-6; **7**, 1423-15-0; **8**, 26334-20-3; **9**, 102284-85-5; **10**, 13125-57-0.

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Vacuum Ultraviolet Circular Dichroism of Dermatan Sulfate: Iduronate Ring Geometry in Solution and Solid State

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Contribution from the Department of Chemistry, State University of New York, Binghamton, New York 13901, Department of Food Research and Technology, Cranfield Institute of Technology, Silsoe College, Silsoe, Bedford MK45 4DT, U.K., and National Institute for Medical Research, Mill Hill, London NW7 1AA, U.K. *Received June 7, 1985*

Abstract: The circular dichroism of dermatan sulfate was measured to 170 nm in solution and 155 nm in films. A previously unobserved CD band is found near 175 nm. The CD spectra of solutions and films are essentially identical, indicating no significant conformational change on drying. A quadrant rule for the 175-nm band in polysaccharides is proposed that rationalizes the large data bank of CD spectra in this wavelength region. The positive sign of the 175-nm band in dermatan sulfate indicates that the $^1C_4$ iduronate ring conformation is predominant in both solution and films.

Glycosaminoglycans are components of animal connective tissue found mainly in the extracellular matrix. They are unbranched polysaccharide chains composed of repeating disaccharide units. In the hyaluronate–chondroitin–dermatan family of glycosaminoglycans, the disaccharide unit consists of a hexosamine and a uronic acid, with glycosidic linkages alternately (1→3) and (1→4). The hexosamine in both chondroitins and dermatans is 2-acetamido-2-deoxy-β-D-galactose (β-D-GalNAc). The uronic acid in chondroitins is β-D-glucuronic acid (β-D-GlcA); in dermatans it is α-L-iduronic acid (α-L-IdA). The hexosamine occurs sulfated at the 4-position in chondroitin 4-sulfate (chondroitin A) and dermatan sulfate (chondroitin B), and at the 6-position in chondroitin 6-sulfate (chondroitin C). Structural heterogeneity exists such that the degree of sulfation is variable, and in dermatans, β-D-GlcA occurs to varying extents as a minor component, partially replacing α-L-IdA. The primary structures, available crystallographic data, and biological functions of glycosaminoglycans have recently been reviewed.[1] Figure 1 shows the predominant repeating disaccharide unit of dermatan sulfate.

In the $^4C_1$ ring conformation of β-D-GlcA residues in chondroitins, the linkage oxygens [O(1), O(4)], the hydroxyl groups at O(2) and O(3), and the carboxylate substituents at C(6) all occupy equatorial locations, well separated from each other around the periphery of the sugar ring, giving rise to a particularly stable chair geometry. On C(5) epimerization to α-L-Ida (as in dermatan sulfate), the $^4C_1$ conformation is destabilized by placing the bulky carboxylate group in a sterically crowded axial position. C(6) can be shifted to an equatorial location by ring inversion to the $^1C_4$ chair conformation, but this is accompanied by conversion of the equatorial arrangement of the other four substituents [O(1), O(2), O(3), O(4)] to axial, which again induces severe steric crowding. Thus, both chair forms of α-L-IdA are far less stable than the $^4C_1$ conformation of β-D-GlcA, and the conformational preference of the ring is delicately balanced between them. The conformation of iduronate residues in dermatan sulfate is, in particular, an area of current controversy.

Studies of conformational equilibria in model idopyranosides favor the $^1C_4$ form [C(6) equatorial],[2] and the proton NMR of dermatan sulfate solutions also indicates adoption of this ring geometry.[3] The susceptibility of dermatan sulfate solutions to periodate oxidation,[4] however, has been interpreted as indicating a predominance of the $^4C_1$ form in which the hydroxyl groups at C(2) and C(3) are trans-diequatorial, rather than trans-diaxial as in the $^1C_4$ conformation indicated by NMR. This apparent discrepancy can be resolved[5] by invoking the Curtin-Hammett principle, according to which the reaction pathway for a molecule that exists as an equilibrium mixture of two different conformers is independent of their relative abundance if conformational interconversion is rapid in comparison with subsequent chemical reactions. Thus, a minor conformer ($^4C_1$) could determine the course of periodate oxidation, with the major conformer ($^1C_4$) acting solely as an unreactive reservoir.

A second aspect of the controversy is that X-ray fiber diffraction evidence[6] is incompatible with standard $^1C_4$ geometry for the L-iduronate ring and instead favors the alternative $^4C_1$ conformation. In view of the small energy difference between the two chair forms, conformational rearrangement in response to packing constraints in the solid state is entirely feasible. However, direct investigation requires techniques applicable to both the solid and solution states. Chiroptical methods allow such comparison.

In the present work we have reinvestigated the conformation of the iduronate ring in dermatan sulfate solutions, using NMR at 500 MHz to confirm the conclusions from the original study at 270 MHz, and have made a direct comparison of the circular dichroism (CD) of dermatan sulfate in solutions and in solid films. CD originates from temporal correlations between the electric

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