(20 eV). The peak heights with m/e 217 and 218 were compared.

In a control experiment, a mixture of **2**-h and **2**-d was analyzed on the mass spectrometer for the parent peaks m/e 216 and 218. The measured composition, after correction for the small natural abundance of m/e 218 in **2**-h, agreed with the correct value.

Evaluation of Rate Constants and Estimation of Errors. The rate constants of the reactions were evaluated by using a combination of manual treatment, which gave approximative values of $k_{12}' + k_{13}'$ and k_{23}' from plots of ln (mol % starting material) vs. time, and computer simulation. The latter method has been described in detail previously.[6f,g] When starting from pure **1**, the concentrations of **1**, **2**, and **3** are described by the following equations:

$$\text{mol \% }\mathbf{1} = ae^{-m_1t} + (100 - a)e^{-m_2t} \qquad \text{mol \% }\mathbf{2} = be^{-m_1t} - be^{-m_2t}$$

$$\text{mol \% }\mathbf{3} = 100 + ce^{-m_1t} - (100 + c)e^{-m_2t}$$

where

$$a = 100(k_{12}' + k_{13}' - m_2)/(m_1 - m_2)$$

$$b = 100k_{12}'/(m_2 - m_1)$$

$$m_1 = [(k_{12}' + k_{13}' + k_{21}' + k_{23}')^2/4 - k_{12}'k_{23}' - (k_{21}' + k_{23}')k_{13}']^{1/2} + \frac{1}{2}(k_{12}' + k_{13}' + k_{21}' + k_{23}')$$

$$m_2 = -[(k_{12}' + k_{13}' + k_{21}' + k_{23}')^2/4 - k_{12}k_{23} - (k_{21}' + k_{23}')k_{13}']^{1/2} + \frac{1}{2}(k_{12}' + k_{13}' + k_{21}' + k_{23}')$$

All estimated errors are considered to be maximum errors derived from maximum systematic errors and random errors. The maximum errors of the directly measured quantities were thus allowed to propagate as systematic errors into derived quantities, e.g., isotope effects.

Acknowledgment. I am indebted to Professor Heinz Koch for providing me with a preprint of ref 9b and to Professor Per Ahlberg for helpful discussions. The Swedish Natural Science Research Council has financially supported this work.

Registry No. **1**-h, 42271-88-5; **2**-h, 42447-90-5; D_2, 7782-39-0; *p*-NO_2PhO^-, 14609-74-6; PhO^-, 3229-70-7; MeO^-, 3315-60-4; Dabco, 280-57-9; Q, 100-76-5; pyridine, 110-86-1.

Low-Temperature and Time-Resolved Absorption Spectral Studies on the *sp*- and *ap*-2-(9-Fluorenyl)phenylnitrenes Generated from 1-Azatriptycene and 2-(9-Fluorenyl)phenyl Azide

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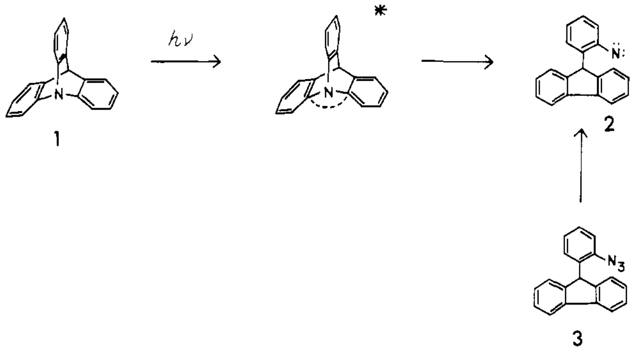
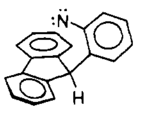
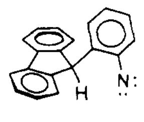
Abstract: Mechanistic details of the photorearrangement of 1-azatriptycene (**1**) have been disclosed by absorption spectroscopic studies on the irradiation of **1** and *o*- and *p*-(9-fluorenyl)phenyl azides (**3** and **4**). At 77 K, **1** developed on irradiation absorption peaks at 290, 302, and 340 nm, while **3** gave strong absorptions at 290, 302, and 314 nm, weak ones at 367 and 384 nm, and a broad band at 507 nm. By comparison with those of **4** and phenylnitrene in the literature, most of the absorptions were found to be due to *o*-(9-fluorenyl)phenylnitrene (**2**) except those at 340 nm from **1** and 507 nm from **3**. These were assigned to azanorcaradiene (**8**), which was presumed to be formed via the singlet **2** and could be considered a key intermediate for a number of the reaction products, and to quinone imine methide (**6**), respectively. The transient absorption spectra at room temperature were obtained after delay times of 100 and 450 ns. The time trace of the absorption intensities at 340 nm showed that **8** was formed by the sum of two kinetic processes with the rate constants of 4 × 10^6 and 1 × 10^6 s^{-1}. Addition of xenon (1.4 atm) suppressed the formation of **8**, while that of triplet **2** was kept almost constant. Combined with the observed rate of disappearance (1.2 × 10^8 s^{-1}) of **1**, a mechanistic scheme is proposed in which the singlet nitrene **2** is in equilibrium with the closed-shell valence isomer. An additional species should intervene before **8** is formed.

Contrary to the expected di-π-methane rearrangement[1] and the once postulated one-bond cleavage of the C–N bond,[2] 1-azatriptycene (**1**) undergoes photorearrangement in which direct bonding between two of the three benzene rings takes place with expulsion of the bridgehead nitrogen as a monocentric diradical species.[3] The intermediacy of this *o*-(9-fluorenyl)phenylnitrene (**2**) was indicated by the formation of the azepine derivatives and verified unambiguously by the detection of **2** in the triplet state by ESR spectra in matrices at 4 K. Nitrene **2** was independently generated by the photolysis of *o*-(9-fluorenyl)phenyl azide (**3**) in order to confirm the assignment. The observed field positions of **2** in ESR spectra derived from **1** and **3** were 6820 and 6837 G, respectively, showing the presence of slightly different conformations of **2**. Nitrene **2a** from **1** was considered to be in the *ap* conformation, while nitrene **2b** from **3** in the sp conformation, and the interconversion between them could be frozen out in matrices at a cryogenic temperature.[4] A slight difference in the product





2a



2b

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(1) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E.; Viriot-Villaume, M.-L. *J. Am. Chem. Soc.* **1973**, *95*, 1274. (c) Zimmerman, H. E.; Amick, D. R. *Ibid.* **1973**, *95*, 3977. (d) Zimmerman, H. E.; Amick, D. R.; Hemetsberger, H. *Ibid.* **1973**, *95*, 4606.

(2) Wittig, G.; Steinhoff, G. *Liebigs Ann. Chem.* **1964**, *676*, 21.

(3) Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1980**, *102*, 7134.

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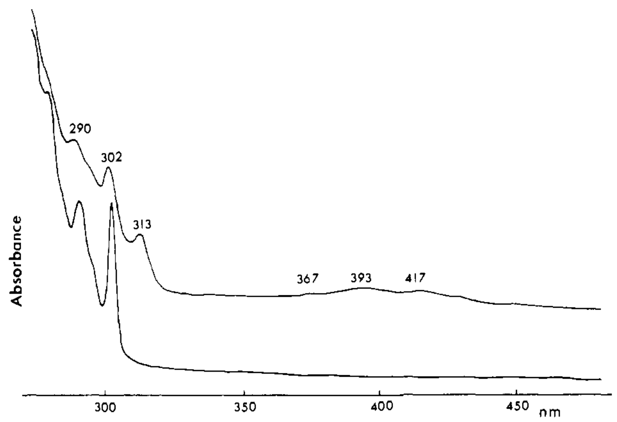
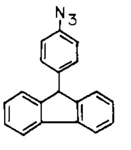


Figure 1. Absorption spectrum of UV-irradiated ethanol–methanol (4:1) matrix containing *p*-(9-fluorenyl)phenyl azide (**4**) at 77 K.

distribution obtained from the photolysis of **1** and **3** was also explained in terms of the different conformations and/or spin states of **2**. In order to get a deeper insight into the difference in the structure and reactivity of **2**, we have examined the photolysis of **1**, **3**, and *p*-(9-fluorenyl)phenyl azide (**4**) both by low-temperature spectroscopy in ethanol–methanol matrices and by time-resolved spectroscopy at ambient temperature.



4

Results and Discussion

Photolysis of *p*-(9-Fluorenyl)phenyl Azide (4). The UV absorption spectrum of the low-temperature photolysate of **4** is shown in Figure 1. The spectrum starting from 280 nm consisted of two main regions: one with strong intensity at 290, 302, and 313 nm, and the other with less distinct absorbances at 367, 393, and 417 nm, respectively. No absorption band was recognized at wavelengths longer than 450 nm. The absorption bands disappeared on warming the sample above 120 K.

Photolysis of *o*-(9-Fluorenyl)phenyl Azide (3). The UV absorption spectrum obtained by the low-temperature photolysis of **3** is shown in Figure 2. Absorption bands with strong intensity at 290, 302, and 314 nm and those with weaker intensity at 367 and 384 nm were observed again. In addition to these, a broad characteristic band at 507 nm was recognized and the irradiated matrices containing the sample turned red at 77 K. The color faded on warming the sample to ambient temperature.

Photolysis of 1-Azatriptycene (1). The absorption spectrum obtained on irradiation of **1** is given in Figure 3. Absorption bands at 290 and 302 nm were recognized, although bands at around 380 nm were shaded by another absorption. A broad band at 340 nm was very characteristic of this system.

UV absorption spectra of triplet phenylnitrene and its derivatives are well characterized by Reiser and co-workers by the low-temperature photolysis of the corresponding azides in matrices.[5] Thus the absorption spectrum of phenylnitrene consists of three regions of bands at 241, 303, and 368 nm. The strongest band at 241 nm (log ϵ 3.7) is assigned to a π–π^* transition on the benzene ring. Because of an open shell structure of the triplet nitrene, two states of almost equal energy are available. One has charge-transfer character from the interaction of nitrogen with the π^* orbitals of the benzene ring, and the other has the opposite CT character derived from the π orbitals on the benzene ring with the nitrogen. These two excited states tend to mix with each other to give two new states (ψ_+ and ψ_-). The remaining two bands at 303 (log ϵ 2.8) and 368 nm (log ϵ 2.5) are assigned to the transition of $\psi_0 \rightarrow \psi_-$ and $\psi_0 \rightarrow \psi_+$, respectively.[5,6]

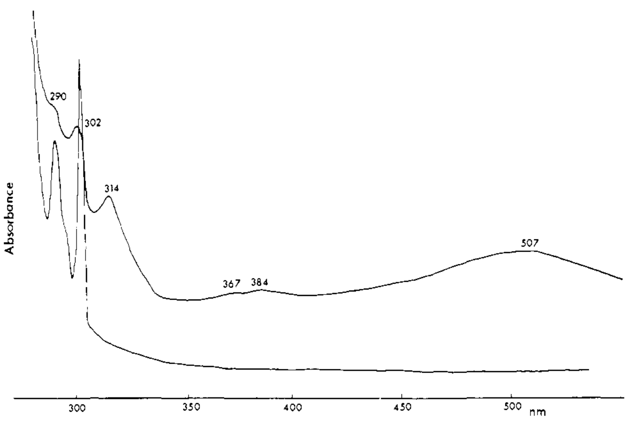


Figure 2. Absorption spectrum obtained by photolysis of *o*-(9-fluorenyl)phenyl azide (**3**) in ethanol–methanol (4:1) matrix at 77 K.

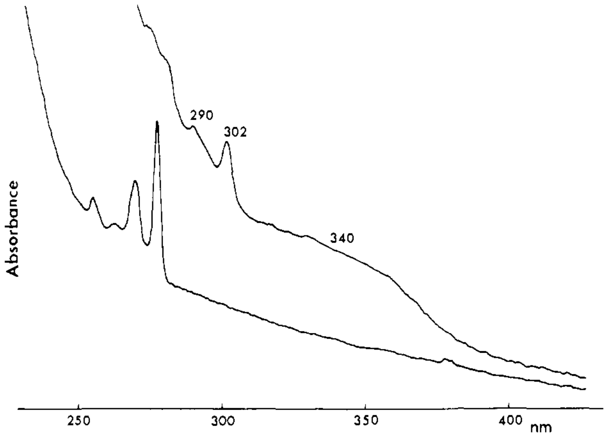


Figure 3. Absorption spectrum obtained by UV irradiation of 1-azatriptycene (**1**) in ethanol–methanol (4:1) matrix at 77 K.

With a knowledge of the UV absorptions of phenylnitrenes, our results can be explained as follows. The absorption spectrum obtained from the irradiation of **4** agrees with that of phenylnitrene and shows the unambiguous formation of *p*-(9-fluorenyl)phenylnitrene. Some typical bands due to a nitrene are also observed in the spectrum obtained for **3**. Since the longest wavelength band at 507 nm was not observed during the low-temperature irradiation either of the para derivative (**4**) or of 1-azatriptycene (**1**), this band should be characteristic of the *sp*-nitrene (**2b**). The key geometrical feature of the *sp* conformation is shown by molecular models to be associated with the close proximity of the hydrogen at C-9 and the monovalent nitrogen. This proton might be responsible for the band at 507 nm. As supporting evidence, the low-temperature irradiation of *o*-(9-methyl-9-fluorenyl)phenyl azide (**5**) showed no absorption at wavelengths longer than 450 nm. The band at 507 nm was therefore ascribed to the *o*-quinoid type tautomer (**6**) of the nitrene formed by hydrogen transfer. The relative intensity of the bands at 507 vs. 314 nm remained constant in the dark at 77 K. This observation excludes the possibility that **6** was formed via the triplet nitrene. Direct formation of **6** via the singlet nitrene seems more likely. The band at 507 nm was also obtained for a sample photolyzed at 4 K. Precedent for the prototropy encountered with the nitrene may be found in the photolysis of *o*-azidotriphenylmethane in which an acridine derivative is efficiently formed.[7]

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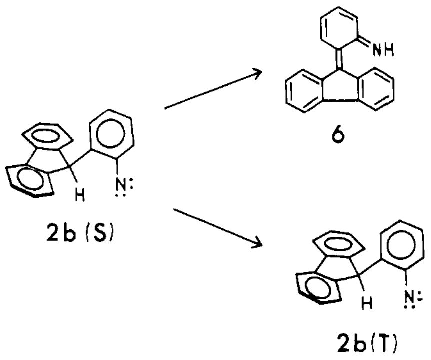
(4) An estimate on the barrier to rotation around the C_9–phenyl bond in **2** may be given by that (13.6 kcal/mol) of *o*-(9-fluorenyl)aniline determined by the DNMR method [Tukada, H.; Iwamura, M.; Sugawara, T.; Iwamura, H. *Org. Magn. Reson.* **1982**, *19*, 78].

(5) (a) Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162. (b) Reiser, A.; Marley, R. *Ibid.* **1968**, *64*, 1806.

(6) Berry, R. S. In "Nitrenes", Lwowski, W., Ed.; Interscience: New York, 1970; Chapter 2.



The absorption bands at 290 and 302 nm, which are obtained after the irradiation of **1**, are assigned to the *ap*-nitrene **2a**. The broad band at 340 nm closely resembles the norcaradiene derivative (**7**), which is the final product obtained from the photorearrangement of hydrocarbon triptycene.[8] Thus the 340-nm band was assigned to azanorcaradiene structure **8**. No band was detected at wavelengths over 450 nm. The relative intensity of the 340- vs. the 302-nm bands remained unchanged in the dark, thereby indicating the direct formation of **8** through the singlet nitrene. The intensity of the band at 340 nm decreased during extended irradiation at 29 K. The remaining bands at 290 and 302 nm should be assigned to the triplet nitrene, as was the case with **3**. Notice that the formation of **8** was only obtained from the *ap*-nitrene **2a**. Molecular models show that the univalent nitrogen of **2a** is sitting right above the benzene ring. The addition reaction to form **8** requires only a slight geometrical change and can occur even at cryogenic temperature in glassy matrices.

The products mentioned above are derived mainly from the singlet state of nitrene **2**. The spectroscopic detection of the triplet nitrene indicates, however, that the intersystem crossing can compete with the intramolecular reactions of the singlet nitrene. The triplet nitrene seems also to add to the benzene ring in much slower rate to give **8** as long as it takes the *ap* conformation. In the case of the photorearrangement of triptycene, both the singlet and triplet states are shown by the xenon perturbation technique to be responsible for the formation of the norcaradiene product in a ratio of 5:1, respectively.[8d] A large difference in rates between the formation of carbazole and the decay of the triplet nitrene from *o*-azidobiphenyl shows that, whereas the both states can contribute to the formation of carbazole, the main route would be from the singlet nitrene.[9]

The *sp*-nitrene **2b** requires the C_9–phenyl bond rotation before adding to the benzene ring internally. The internal rotation may be possible at room temperature, since its rate for the *o*-nitrenophenyl group attached to the fluorenyl system is estimated to be 2×10^3 s^{-1} at 25 °C.[4] Thus, lifetime of the triplet nitrene can compete with the internal rotation. In fact the yield of the azepine derivative from **2** is about 30% at ambient temperature.[3] The value is much larger than the one expected from the conformational equilibrium ($ap/sp = 1/20$) of azide **3**.[4]

The products from irradiation of **1** and **3** at 77 K in frozen matrices contained a large amount of 9-(*o*-aminophenyl)fluorene, which is considered to be formed mainly via the triplet nitrene in the *sp* conformation.[4]

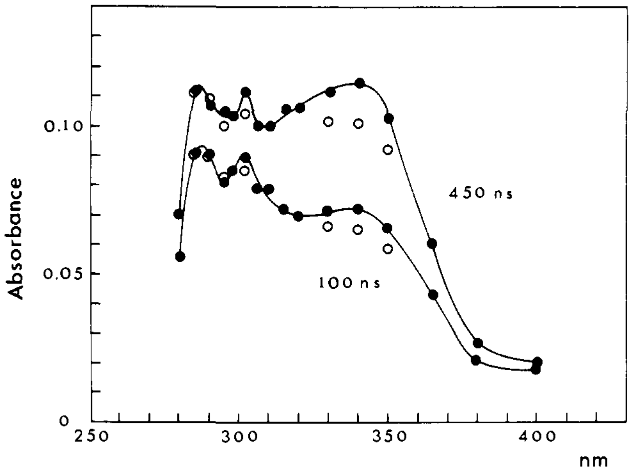


Figure 4. Time-resolved absorption spectra after 100 and 450 ns of UV irradiation of 1-azatriptycene (**1**) in methanol at 23 °C (●). Absorptions in the presence of Xe (1.4 atm) are also given (○).

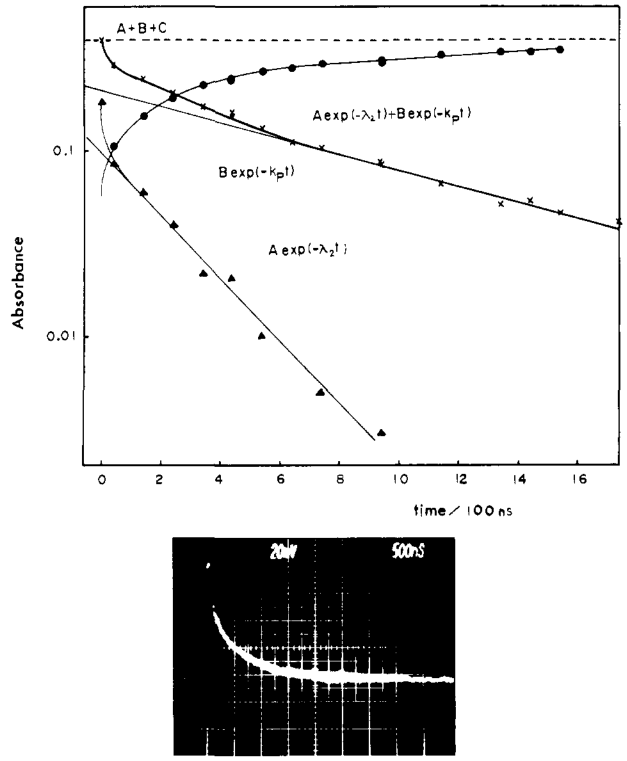


Figure 5. The rise curve of absorptions at 340 nm after irradiation of **1** (7.6×10^{-5} M) in methanol. Analysis based on eq 5 (see text) gave two exponential terms: (●) semilogarithmic plots of the rise curve, (×) A + B + C (denoted as - - -) minus observed values (●), and (▲) × $-B \exp(-k_pt)$. The time trace at 340 nm is also given at the bottom (time axis: 500 ns per division).

Scheme I

$$\begin{tikzcd}
\mathbf{1}^* \arrow[rr] & & S \arrow[rr, shift left, "k_3"] \arrow[dl, "k_1"] \arrow[dr, "k_2"'] & & X \arrow[ll, shift left, "k_4"] \\
& T & & I \arrow[r, "k_p"] & P(=8)
\end{tikzcd}$$

Time-Resolved Absorption Studies on the Photolysis of 1-Azatriptycene (1). Dynamic aspects of the azanorcaradiene formation were investigated by means of the time-resolved spectroscopy of the irradiation of **1**. The irradiation of a methanolic solution of **1** was carried out at ambient temperature on a KrF excimer laser equipped with a xenon flash lamp as a monitor light.[10] The transient spectra obtained after delay times of 100 and 450 ns are reproduced in Figure 4. Any process faster than 50 ns could not be detected due to the fluorescence emission of

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(7) Carde, R. N.; Jones, G.; McKinley, W. H.; Price, C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1211. For another example of hydrogen abstraction of a nitrene from the closely located methyl group, see: Platz, M. S.; Burns, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4425.

(8) (a) Iwamura, H.; Yoshimura, K. *J. Am. Chem. Soc.* **1974**, *96*, 2652. (b) Iwamura, H.; Tukada, H. *Tetrahedron Lett.* **1978**, 3451. (c) Iwamura, M.; Tukada, H.; Iwamura, H. *Ibid.* **1980**, 4865. (d) Tukada, H.; Iwamura, H. to be published.

(9) Sundberg, R. J.; Gillespie, D. W.; DeGraff, B. A. *J. Am. Chem. Soc.* **1975**, *97*, 6193.

(10) Nakashima, N.; Inoue, H.; Sumitani, M.; Yoshihara, K. *J. Chem. Phys.* **1980**, *73*, 5976.

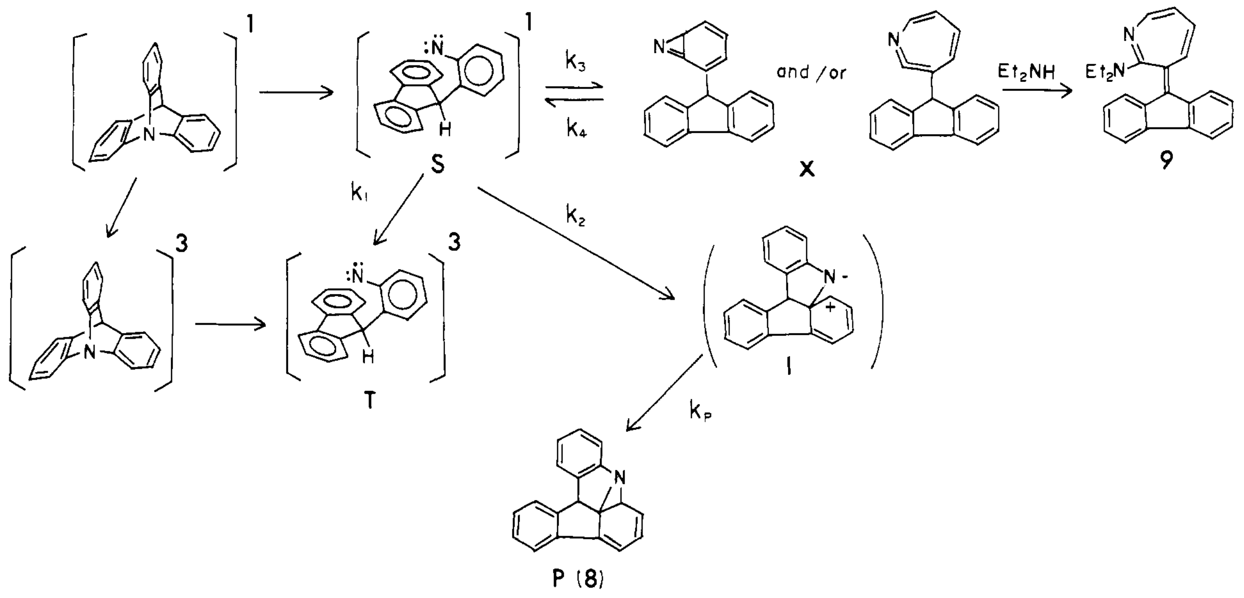

Figure 6. Reaction scheme for the photorearrangement of 1-azatriptycene (**1**).

1.[11] The spectrum obtained after 100 ns was almost identical with the one obtained at the cryogenic temperature. Singlet nitrene **2** is considered to be short-lived in this time period and nondetectable.[12] In addition to absorption bands at 290 and 302 nm due to the triplet nitrene **2**, a broad band due to **8** was observed at 340 nm. The latter band considerably increased in intensity after 450 ns. In order to obtain further information on the relation between the spin multiplicity and reactivity of nitrene **2**, the irradiation was carried out under a xenon atmosphere (1.4 atm). Xenon is known to accelerate intersystem crossing by an external heavy atom effect.[13] Addition of xenon quenched the fluorescence of **1** by ca. 20% and at the same time the formation of **8** (absorbance at 340 nm) was suppressed by ca. 20%. The formation of triplet nitrene **2** was almost unaffected (see plots O in Figure 4). In Figure 5 are given the time trace of the absorbance at 340 nm and the semilogarithmic plot thereof. Since the latter plot does not give a straight line, the rise of the absorbance at 340 nm can be expressed by the sum of two processes in which rate constants for the formation of **8** are $k_a = 4 \times 10^6$ s^{-1} and $k_b = 1 \times 10^6$ s^{-1}. All kinetic features of flash photolysis of **1** are rationalized by Scheme I. The singlet nitrene (S) is formed from **1** in the excited singlet state and has three decay processes. The first involves intersystem crossing to the triplet nitrene (T). In the second process, S is converted to intermediate I prior to the formation of product P. Decay of S is generally very fast and, on the basis of the quantum yield of disappearance of **1** ($\phi_r = 0.3$) and the fluorescence lifetime ($\tau_f = 2.4$ ns), the rate of photorearrangement of **1** is calculated to be 1.2×10^8 s^{-1}, while the formation of **8** is in the order of 10^6 s^{-1}. The discrepancy may be rationalized by imposing prior to **8** (=P) intermediate I, which is formed by initial electrophilic attack of the nitrene on the benzene ring. A candidate for I would be a zwitterionic structure.[14] The reported large solvent effect in the formation of carbazole from *o*-azidobiphenyl could be rationalized similarly.[9]

A third process, which serves as a reservoir of S, has to be taken into account to explain the dual process involved in the formation of P. As a candidate for this mechanism, the interconversion between S and its closed shell valence isomer, e.g., azacycloheptatetraene and/or azirine (X), would be mentioned.[15] In fact, X was trapped as **9** in the photolysis of **3** by carrying out the irradiation in the presence of diethylamine.[16] The amine-trapped compounds were not detected in the photorearrangement of **1**, presumably because the intramolecular addition to the neighboring benzene ring might have been too efficient to allow for external trapping. The singlet nitrene S isomerizes to its isomer X with a rate that is determined by the lifetime of S. Structure S is regenerated by a slower process whose rate constant corresponds to k_4. The rate equations 1–4 are thus obtained for S, X, I, and P, respectively. S_0 stands for the rate of formation of S from

$$\dot{S} = S_0 - (k_1 + k_2 + k_3)S + k_4X \qquad (1)$$

$$\dot{X} = k_3S - k_4X \qquad (2)$$

$$\dot{I} = k_2S - k_PP \qquad (3)$$

$$\dot{P} = k_PP \qquad (4)$$

1 in the excited singlet state. The exact solution of eq 1–4 has three exponential terms. As one of these turns out to be too fast to be observed in the nanosecond time resolution, the concentration of P is given by the sum of two rise curves (eq 5) Of the observed

$$P \approx A(1 - e^{-\lambda_2 t}) + B(1 - e^{-k_P t}) + C \qquad (5)$$

$$\lambda_2 = (1/2)[(k_1 + k_2 + k_3 + k_4) - \{(k_4 - k_1 - k_2 - k_3)^2 + 4k_3k_4\}^{1/2}] \qquad (6)$$

two rate constants, k_a and k_b for the formation of P, k_b is considered to correspond to k_P. The reaction scheme would be finalized as shown in Figure 6.

Conclusion

The singlet nitrene **2** derived from the excited singlet azatriptycene (**1***) has three decay processes. The triplet **2** (T) can be formed through intersystem crossing. A direct path from **1** in the excited triplet state to T may also occur. The addition of xenon accelerates the intersystem crossing of azatriptycene or nitrene in the excited singlet state to the corresponding triplet species, resulting in the suppression of azanorcaradiene **8**. On the other hand, the formation of T would not be much affected since T can be supplied both from triplet azatriptycene and S. The reactivity of T must be considerably poorer than S in giving P.[16]

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[11] Previous flash photolysis studies on arylnitrenes[9,17,18] are mainly concerned with slower rate processes ($k \sim 10^3$ s^{-1}). The main scope of this study is to disclose faster processes directly related to shorter lived singlet nitrenes.

[12] Sumitani, M.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2995.

[13] (a) Carroll, F. A.; Quina, F. H. *J. Am. Chem. Soc.* **1976**, *98*, 1. (b) Scully, F.; Nylund, T.; Palensky, F.; Morrison, H. *Ibid.* **1978**, *100*, 7352.

[14] (a) Cadogan, J. I. G. *Acc. Chem. Res.* **1972**, *5*, 303. (b) Iddon, B.; McCohn, O.; Scriven, E. F. V.; Suschizky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900.

[15] (a) Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 6245. (b) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499. Dunkin et al. reported IR absorption spectra of UV-irradiated azidonaphthalene in Ar matrix at 12 K. They detected a photolabile precursor that would be assigned to azirine derivative.

[16] Details will be published elsewhere.

The behavior of phenylnitrene[17] and *o*-biphenylylnitrene[9,18] was previously investigated by a flash photolysis technique.[11] Especially in the latter case, the reaction scheme was proposed to account for the carbazole formation and trapping of an azepine by a secondary amine. Two separate intermediates were proposed, an amine–trappable intermediate forming the azepine derivative and a nontrappable intermediate giving the carbazole directly. The structure of these intermediates was, however, not explicitly stated. Our results are not compatible with these previous mechanisms and may warrant a further mechanistic study of the parent phenylnitrene with the aid of nanosecond spectroscopy.

Experimental Section

Materials. Methanol and ethanol (Dotite luminasol) were purchased from Wako Pure Chemical Industries, Ltd. 1-Azatriptycene (**1**) was prepared according to literature methods.[2]

***o*- and *p*-(9-Fluorenyl)anilines.** A mixture of 3.8 g (0.155 mol) of 9-(*N*-phenylamino)fluorene,[19] 7 g of aniline, and 0.5 g of anhydrous aluminum chloride was heated at 180 °C for 11 h under an argon atmosphere. The cooled reaction mixture was treated with 20 mL of 5% aqueous sodium hydroxide and the organic materials were extracted with benzene. The solvent and excess aniline were removed under reduced pressure to give 3.1 g of crude product. Chromatography on a silica gel column (Merck, Kieselgel 60) with hexane–benzene (1:1) gave 1.1 g of the ortho isomer (yield 29%): mp 158–159.5 °C (from hexane–benzene, 1:1); NMR ($CDCl_3$) δ 2.8 (2 H, bs), 5.05 (1 H, s), 6.5–7.5 (10 H, m), 7.7–7.9 (2 H, m); IR (Nujol) 3470, 3390, 1620, 1380, 760 cm^{-1}. Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.73; H, 5.86; N, 5.59. Elution with benzene gave 1.2 g (31%) of the para isomer: mp 174–174.5 °C (from hexane–benzene, 1:1); NMR ($CDCl_3$) δ 3.3 (2 H, bs), 4.90 (1 H, s), 6.44, 6.54, 6.79, 6.88 (4 H, q), 7.1–7.4 (6 H, m), 7.7–7.9 (2 H, m). Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 89.04; H, 5.83; N, 5.43.

***o*-(9-Fluorenyl)phenyl Azide (3).** To the cooled paste containing 200 mg (0.68 mmol) of *o*-(9-fluorenyl)anilinium chloride (obtained by passing anhydrous hydrogen chloride into a solution of *o*-(9-fluorenyl)aniline in benzene) in 2 mL of concentrated HCl was added at 0–5 °C a solution of 110 mg of sodium nitrite in 3 mL of water. The mixture was stirred for 10 min in an ice bath to obtain a homogeneous solution. A cooled solution of 140 mg of sodium azide in 3 mL of water was added to the diazonium salt solution. The mixture was warmed at 40–50 °C for 10 min to complete the reaction. Recrystallization from methanol and ether gave 164 mg (85%) of colorless needles: mp 140.5–141 °C; NMR ($CDCl_3$) δ 5.52 (1 H, s), 6.58 (1 H, d), 6.9 (1 H, m), 7.2–7.5 (8 H, m), 7.7–7.9 (2 H, m); IR (Nujol) 2110, 2070, 1590, 1380, 1290, 1280 cm^{-1}. Anal. Calcd for $C_{19}H_{13}N_3$: C, 80.55; H, 4.62; N, 14.83. Found: C, 80.55; H, 4.51; N, 14.60.

***p*-(9-Fluorenyl)phenyl Azide (4).** In the manner described for 2-azidobiphenyl,[20] diazotization of *p*-(9-fluorenyl)aniline followed by reaction with sodium azide gave needles (89%): mp 100–101.5 °C (from methanol); NMR ($CDCl_3$) δ 5.00 (1 H, s), 6.85, 6.97, 7.03, 7.10 (4 H, q), 7.2–7.5 (6 H, m), 7.77, 7.83 (2 H, d); IR (Nujol) 2070, 2100, 1600, 1570, 1375, 1290 cm^{-1}. Anal. Calcd for $C_{19}H_{13}N_3$: C, 80.55; H, 4.62; N, 14.83. Found: C, 80.85; H, 4.41; N, 14.74.

***o*-(9-Methyl-9-fluorenyl)aniline.** A mixture of 1.1 g of *N*-(9-methyl-9-fluorenyl)aniline[16] (obtained by the reaction of methyllithium with *N*-fluorenylideneaniline), 2 g of aniline, and 0.3 g of anhydrous aluminum chloride was heated at 135 °C for 5 h under an argon atmosphere. Workup and chromatography (elution with hexane-benzene (5:1)) as described for 9-fluorenylanilines gave 0.3 g (27%) of the ortho isomer: mp 130–131 °C (from hexane–benzene 5:2); NMR ($CDCl_3$) δ 1.74 (3 H, s), 2.69 (2 H, bs), 6.25, 6.34 (1 H, d), 6.6–7.4 (8 H, m), 7.73, 7.81 (3 H, d). Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.32; N, 51.6. Found: C, 88.61; H, 6.22; N, 5.05.

***o*-(9-Methyl-9-fluorenyl)phenyl Azide (5).** In the manner described for 2-azidotriphenylmethane,[7] *o*-(9-methyl-9-fluorenyl)aniline was converted to the azide: mp 120.5–121.5 °C (from hexane–benzene 5:2); NMR ($CDCl_3$) δ 1.76 (3 H, s), 6.8–7.5 (9 H, m), 7.76, 7.87 (3 H, d); IR (Nujol) 2060, 2110 cm^{-1}. Anal. Calcd for $C_{20}H_{15}N_3$: C, 80.78; H, 5.09; N, 14.13. Found: C, 80.94; H, 5.02; N, 14.20.

UV Absorption Spectral Measurements at 77 K. Samples (**1–5**) were dissolved in a mixture of ethanol and methanol (4:1, v/v) to make ca. 4 $\times 10^{-5}$ mol/L solutions. The solution was transferred to a quartz cell of 1.0-cm optical length. Dissolved oxygen was removed by three freeze–pump–thaw cycles. UV irradiation with a 4-W low-pressure mercury lamp was carried out in a liquid nitrogen Dewar vessel with a transparent window that was placed in the sample chamber of a Cary 17 absorption spectrophotometer. The spectra were recorded at several intervals after irradiation.

Product Analysis of the Samples Irradiated at 77 K. The sample solutions of the above experiments obtained after extended irradiation and melting of the frozen matrices were analyzed by high performance liquid chromatography on a Waters Model 600 A apparatus. The retention time of *o*-(9-fluorenyl)aniline was 5.8 min when eluted with methanol–water (5:1) from a μ-Bondapak C_{18} column. Yields of the aniline based on the reacted **1** (47% conversion) and **3** (79%) were 41 and 27%, respectively.

Time-Resolved Spectral Measurements on 1. An undegassed methanol solution of **1** (7.6×10^{-5} M) was irradiated in a 1 × 1 × 4 cm quartz cell with a 248-nm pulse from a KrF excimer laser (Lambda Physik EMG 500) with a pulse width of 10 ns (fmhw) and output energy if 60 mJ/cm^2. The monitoring light source for the transient absorption spectra was an EG & G FX-265 UV xenon lamp. The monitoring light was divided into two beams, one of which was used for normalization of the transient absorption. The sample solution was renewed at every shot.

Measurement of Fluorescence Lifetime. A sample solution was excited with a mode-locked Nd-YAG laser (the fourth harmonic 266-nm light with 0.5 mJ) and the fluorescence lifetimes were measured with a biplanar photodiode (HTV R1328U-02) and an 1-GHz oscilloscope (Tektronix 7104).

Measurements of Quantum Yields of Photorearrangements. Quantum yields of the photorearrangement of **1** were determined with the monochromatic light (an Ushio UXL-500D 500-W xenon lamp and a Shimadzu 33-86-25 monochrometer) of the dispersion of 5 nm. The energy of the absorbed light was measured by a power meter (International Light, Inc., IL 700A) in an integral mode as the difference of the transmitted light energy between the solution and the solvent. The power meter was calibrated by the photolysis of phenyl azide in hexane at 25 °C for which $\Phi = 0.53$ at 254 nm.[5b] The conversion of the photochemical reactions was determined by high performance liquid chromatography (a Waters Model ALC/GPC 244 apparatus) on a μ-Bondapak C_{18} column with methanol–water (4:1) elution.

Registry No. **1**, 197-45-5; **2**, 74357-27-0; **3**, 74357-30-5; **4**, 84108-33-8; **5**, 84108-37-2; **6**, 84108-36-1; **8**, 74357-28-1; phenylnitrene, 2655-25-6; 5-(9-fluorenyl)-7-azabicyclo[4.1.0]hept-6-ene, 84108-34-9; 3-(9-fluorenyl)azacyclohepta-1,2,4,6-tetrene, 8108-35-0; xenon, 7440-63-3; *o*-(9-fluorenyl)aniline, 75819-53-3; *p*-(9-fluorenyl)aniline, 84108-38-3; *o*-(9-fluorenyl)anilinium chloride, 84108-39-4; aniline, 62-53-3; 9-(*N*-phenylamino)fluorene, 31859-87-7; *N*-fluorenylideneaniline, 10183-82-1; *N*-(9-methyl-9-fluorenyl)aniline, 39194-36-0; *o*-(9-methyl-9-fluorenyl)-aniline, 84108-40-7.

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