

irradiated in the Rayonet photoreactor at 254 nm. Gas-chromatographic analysis on the OV-17 column shows that the ratio of the yields of photoproducts 2-(diethylamino)-3*H*-azepine and 2-(di-*n*-butylamino)-3*H*-azepine is ca. 6:4 at each concentration of amines. The results are reported in Table II.

Kinetics of Benzophenone-Excited Triplet Quenching by Phenyl Azide. Solutions of benzophenone (2×10^{-4} M) and varying concentrations of PhN₃ in acetonitrile were prepared and purged with N₂. The samples were irradiated with the Nd-YAG laser at 266 nm, and the time dependence of the benzophenone triplet absorption was monitored at 525 nm. The first-order rate constants for the decay were obtained by least-squares fit and plotted against the PhN₃ concentrations, Figure 2.

Kinetics of Photoproduct Growth with Diethylamine and Di-*n*-butylamine. Solutions of PhN₃ (3.6×10^{-3} M) in hexane with diethylamine (9.6×10^{-2} to 9.30 M) or with di-*n*-butylamine (0.30-5.70 M) were prepared. Laser-flash photolysis with the Nd-YAG laser at 266 nm was

performed by monitoring the rate of growth of the photoproduct at 340 nm. The pseudo-first-order rate constants for the growth at 340 nm were obtained by a computer fit of the data by least squares. The observed rate constants were plotted against the concentration of amine to give Figure 5. The pseudo-first-order rate constants varied from 3.8×10^5 to 9.5×10^6 s⁻¹.

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Registry No. 1, 6798-41-0; **2,** 91202-11-8; PhN₃, 622-37-7; Bu₂NH, 111-92-2; Ph₂C=O, 119-61-9; Et₂NH, 109-89-7; phenylnitrene, 2655-25-6; 2-(di-*n*-butylamino)-3*H*-azepine, 59859-54-0; 2-acetonaphthone, 93-08-3; 1-(diethylamino)-7-azabicyclo[4.1.0]hepta-2,4-diene, 91202-12-9.

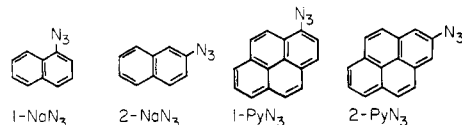
Photochemistry of Naphthyl and Pyrenyl Azides: Chemical Properties of the Transient Intermediates Probed by Laser Spectroscopy

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Abstract: The photochemistry of 1-naphthyl azide, 2-naphthyl azide, 1-pyrenyl azide, and 2-pyrenyl azide was examined in inert (benzene) and reactive (diethylamine) solvents. These studies employ a combination of product analysis, low-temperature spectroscopy, and laser-flash photolysis to reveal the chemical and physical properties of the highly reactive, short-lived intermediates formed in these reactions. In all cases two intermediates account for the observations. One of these is the triplet nitrene and the other is a ground-state singlet transient identified as an azirine. The relationship between these intermediates controls the chemical outcome of the reaction.

Thermolysis or photolysis of polynuclear aromatic azides in some cases leads to products clearly related to those obtained from phenyl azide,¹ and in other circumstances quite different results are observed. The eventual outcome of these reactions is a consequence of the chemical and physical properties of the short-lived intermediates formed when the azide is excited. We report herein results of an investigation of the photolysis of 1-naphthyl azide (1-NaN₃), 2-naphthyl azide (2-NaN₃), 1-pyrenyl azide (1-PyN₃), and 2-pyrenyl azide (2-PyN₃). These findings expose the properties of the intermediates generated in these reactions and permit some useful generalizations about the photochemistry of aromatic azides.

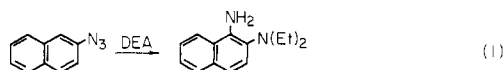


The photochemical and thermal reactions of the polynuclear aromatic azides have been studied for quite some time.² Of this

group 1-NaN₃ and 2-NaN₃ are the most thoroughly characterized. The chemistry of 1-PyN₃ has been examined and applied to photoaffinity labeling and to photoimaging systems.³

Irradiation of 1-NaN₃ in hydrocarbon solvents reveals two reactions. The first is coupling to form azonaphthalene, and the second is reduction to give 1-naphthylamine (1-NaNH₂).⁴ The relative yields of the coupling and reduction products depend on the reaction conditions,⁵ but both are presumed to be characteristic of triplet 1-naphthyl nitrene (1-NaN³).

Photolysis of 1-NaN₃ in diethylamine (DEA) is reported to give low yields of 1-NaNH₂ and azonaphthalene. However, quite in contrast, irradiation of 2-NaN₃ under the identical conditions gives a good yield of 2-(diethylamino)-1-naphthylamine, eq 1.⁶ This product is believed to arise from the trapping of a short-lived, singlet-state intermediate by the nucleophilic DEA. This general



reaction, where substitution by a nucleophile causes regiospecific 1,2-migration of the azide nitrogen, was seen first in the photolysis of 5-benzo[*b*]thiophenyl azide.⁷ It has since become generally observed from photolysis of 2-azido aromatics, but not from the corresponding 1-substituted isomers.⁸⁻¹⁴

(3) Wolf, M. K.; Konisky, J. J. *Bacteriol.* **1981**, *145*, 341.

(4) Reiser, A.; Willets, F. W.; Terry, G. C.; Williams, V.; Marley, R. *Trans. Faraday Soc.* **1968**, *64*, 3265.

(5) Smith, P. A. S.; Boyer, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 2626. Huisgen, R.; Vossius, D.; Appl, M. *Chem. Ber.* **1958**, *91*, 1. Boshev, G.; Dyall, L. K.; Sadler, P. R. *Aust. J. Chem.* **1972**, *25*, 599.

(6) Hilton, S. E.; Scriven, E. F. V.; Suschitzky, H. *J. Chem. Soc., Chem. Commun.* **1974**, 853.

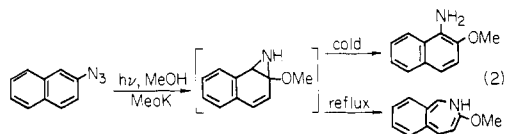
(7) Iddon, B.; Suschitzky, H.; Taylor, D. S. *J. Chem. Soc. Perkin Trans. 1* **1974**, 579. Iddon, B.; Pickering, M. W.; Suschitzky, H. *J. Chem. Soc., Chem. Commun.* **1974**, 759.

(8) Carroll, S. E.; Nay, B.; Scriven, E. F. V.; Suschitzky, H. *Synthesis* **1975**, 710.

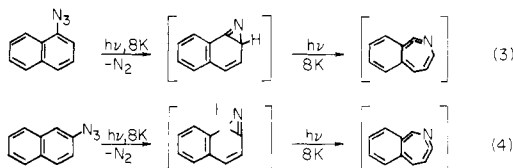
(1) See previous paper in this issue.

(2) The subject has been reviewed periodically: (a) Abramovitch, R. A.; Davis, B. A. *Chem. Rev.* **1964**, *64*, 149. (b) Abramovitch, R. A.; Kyba, E. P. "The Chemistry of the Azido Group"; Patai, S., Ed.; Wiley: New York, 1971; p 256. (c) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Agew. Chem., Int. Ed. Engl.* **1979**, *18*, 900. (d) Boyer, J. H. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley: New York, 1969; Vol. 2, p 296. (e) Smith, P. A. S. In "Nitrenes", Lwowski, W., Ed.; Wiley: New York, 1970. (f) Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980. (g) Lwowski, W. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 1 and 2. (h) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 279. (i) Smith, P. A. S. "Open-Chain Organic Nitrogen Compounds: Derivatives of Hydrazine and Other Hydrinitrogens Having N-N Bonds"; Benjamin-Cummings: New York, 1982. (j) Scriven, E. F. V. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982. (k) Reiser, A.; Wagner, H. M. In "The Chemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971.

Rigaudy and co-workers¹⁵ discovered that irradiation of 2-NaN₃ in methanol containing concentrated potassium methoxide gives a ring-expanded azepine (analogous to the product obtained from PhN₃)¹ when the reaction mixture is refluxed immediately after irradiation, but it gives 2-methoxy-1-naphthylamine (analogous to the product of irradiation of 2-NaN₃ in DEA) when the reaction mixture is neutralized immediately after irradiation. These findings are used to support the postulate that an intermediate aziridine is formed in these reactions, eq 2.



Further evidence concerning the nature of the intermediates formed from photolysis of 1-NaN₃ and 2-NaN₃ is reported by Dunkin and Thomson.¹⁷ They irradiated these azides in an inert matrix at 8 K and recorded the IR spectrum of the products. Their data show quite clearly that under these conditions both 1-NaN₃ and 2-NaN₃ give first an azirine and that the azirine can be converted to a dehydroazepine by further irradiation, eq 3 and 4.¹⁸ However, there is not doubt that irradiation of either 1-NaN₃



or 2-NaN₃ at 77 K also leads to formation of some of the corresponding triplet nitrenes since their characteristic EPR spectra are readily obtained.¹⁹ It is clear though that EPR is by far the more sensitive technique and that the major primary products, at least at the lower temperature, are the singlet-state compounds observed by Dunkin and Thomson.

Reiser and co-workers²⁰ irradiated 1-NaN₃ in an organic matrix at 77 K and recorded the optical spectrum of the products. They report absorption bands at 223, 367, and 536 nm that are attributed to 1-NaN³. However, in light of the analysis of the IR spectrum mentioned above, and also the instability of the first-formed products to secondary photolysis,¹⁷ this assignment must be considered uncertain.

The photochemistry of 1-PyN₃ has been studied in some detail.²¹⁻²⁴ Irradiation of 1-PyN₃ in degassed benzene solution gives

a high yield of azopyrene, a reaction characteristic of the triplet nitrene (1-PyN³).²¹ When the photolysis is carried out at 77 K an EPR spectrum characteristic of 1-PyN³ is observed and an optical spectrum with maxima at 340 and 420 nm is obtained.²¹ Laser-flash photolysis of 1-PyN₃ in benzene solution²⁴ reveals two short-lived transient products. The first, absorbing at 455 nm, is identified as the singlet nitrene (1-PyN¹) and the other as 1-PyN³ by comparison with the low-temperature spectrum, and by analysis of the kinetics of its formation. However, it should be emphasized again, in light of the matrix IR spectra^{17,25} obtained from photolysis of aromatic azides, that these assignments are uncertain.

We have examined in detail the photolysis of the two isomeric naphthyl azides and the two isomeric pyrenyl azides in both unreactive and reactive (nucleophilic) solvents. These studies employ a combination of product analysis, low-temperature spectroscopy, and laser-flash photolysis to reveal some aspects of the chemical and physical properties of the highly reactive, short-lived intermediates formed in these reactions.

Results

The four azides that we examined fit cleanly into two categories. The chemical and spectroscopic properties of 1-NaN₃ and 1-PyN₃ are similar, and 2-NaN₃ and 2-PyN₃ also have several properties in common. This section is divided along these lines.

A. Products of Photolysis: 1-NaN₃ and 1-PyN₃. The products obtained from irradiation of 1-NaN₃ and 1-PyN₃ depend remarkably on the details of their photolyses. Irradiation of a 3×10^{-3} M solution of 1-NaN₃ in deoxygenated benzene in a Rayonet photoreactor equipped with 350-nm lamps results in the efficient consumption of the azide. Analysis of this reaction mixture by HPLC reveals the formation of 1,1'-azonaphthalene in 24% yield. The amount of azonaphthalene in the reaction mixture increases steadily while the photolysis solution is stored in the dark at room temperature. In a typical case, the yield reaches a maximum of 46% 2 h after the termination of the photolysis. During this time the amount of unreacted 1-NaN₃ in solution remains constant.

When an identical solution of 1-NaN₃ in benzene is irradiated with a nitrogen laser instead of the continuous-light source, a different result is obtained. Photolysis with the high-power pulse source gives 1,1'-azonaphthalene in 52% isolated yield immediately after the irradiation. Analysis of the reaction mixture by HPLC for several hours after the photolysis is complete shows that there is no increase in the yield of the azonaphthalene. It should be noted that 1,1'-azonaphthalene is not stable to either set of reaction conditions, so the yields reported represent lower limits to the actual production of the azo compound.

It is quite clear from the results described above that there are at least two routes to azonaphthalene from the photolysis of 1-NaN₃. To assist in the identification of these paths we irradiated 1-NaN₃ under both high- and low-power conditions in the presence of phenyl azide (PhN₃).

Irradiation of a benzene solution containing 3×10^{-3} M 1-NaN₃ and 1×10^{-2} M PhN₃ in the Rayonet at 350 nm, where most of the light is absorbed by the 1-NaN₃, gives both 1,1'-azonaphthalene and the mixed azo compound 1-naphthylphenyldiazene initially in 24% and 5% yields, respectively.²⁶ The yield of both of these azo compounds increases in the dark after photolysis reaching 38% and 13%, respectively, after 20 h. In contrast, only 1,1'-azonaphthalene is formed when an identical mixture of 1-NaN₃ and PhN₃ in benzene is irradiated at high power with the laser. The initial yield of azonaphthalene is 50%, and it is constant for at least 20 h when the solution is stored in the dark.

Photolysis of 1-NaN₃ in DEA solution shows a related sensitivity to the photolysis conditions. Irradiation of a 9×10^{-3} M solution of 1-NaN₃ at low power gives 1-NaN₂ in 80% isolated yield,

(9) Carde, R. N.; Jones, G. J. *Chem. Soc. Perkin Trans. 1* **1975**, 519.

(10) Iddon, B.; Pickering, M. W.; Suschitzky, H.; Taylor, D. S. *J. Chem. Soc. Perkin Trans. 1* **1975**, 1686.

(11) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1979**, 1837.

(12) Nay, B.; Scriven, E. F. V.; Suschitzky, H.; Khan, Q. U. *Synthesis* **1979**, 757.

(13) Bettinetti, G. F.; Fasani, E.; Minoli, G.; Pietra, S. *Gazz. Chim. Ital.* **1979**, *109*, 175.

(14) Gallagher, P. T.; Iddon, B.; Suschitzky, H. *J. Chem. Soc. Perkin Trans. 1* **1980**, 2362.

(15) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1975**, 3845. Similar observations have been made for 2-azidobiphenyl.¹⁶

(16) Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2439.

(17) Swenton, J. S.; Ikeler, T. J.; Williams, B. H. *J. Am. Chem. Soc.* **1970**, *92*, 3103.

(18) Sundberg, R. J.; Brenner, M.; Suter, S. R.; Das, B. P. *Tetrahedron Lett.* **1970**, 2715.

(19) Sundberg, R. J.; Heintzelman, R. W. *J. Org. Chem.* **1974**, *39*, 2546.

(20) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499.

(21) There are two possible azirine and dehydroazepine isomers for each azide, we draw only one of each for simplicity.

(22) Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.

(23) Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162.

(24) Reiser, A.; Marley, R. *Ibid.* **1968**, *64*, 1806.

(25) Yamaoka, T.; Kashiwagi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 361.

(26) Tsunoda, T.; Yamoka, T.; Takayama, M. *Nippon Kagaku Kaishi* **1975**, *12*, 2074.

(27) Tsunoda, T.; Yamoka, T.; Osabe, Y.; Hata, Y. *Photogr. Sci. Eng.* **1976**, *20*, 188.

(28) Sumitani, M.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2995.

(29) Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282. Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 334.

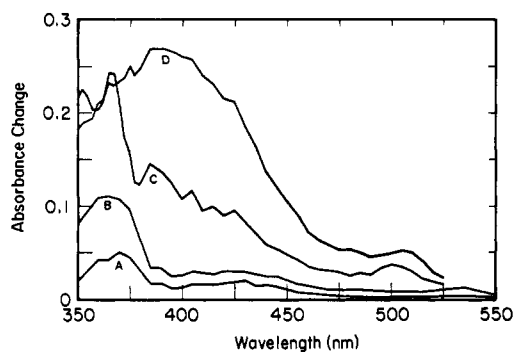


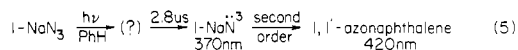
Figure 1. Transient-absorption spectra recorded after pulsed irradiation of 1-NaN₃ in benzene. Spectrum A was recorded 20 ns after the laser pulse, B at 1 μs, C at 10 μs, and D at 90 μs.

but photolysis with the laser gives mainly 1,1'-azonaphthalene and very little 1-NaNH₂.

Quite similar results are obtained from the irradiation of 1-PyN₃. In benzene solution the major product is, as has been previously reported,²⁴ 1,1'-azopyrene. When 1-PyN₃ is photolyzed in a DEA solution with the low-power continuous source, the yield of 1-pyrenamine (1-PyNH₂) is 82%; in contrast, the high-power laser gives 4% of the amine and 1,1'-azopyrene. Additionally, triplet sensitization of 1-PyN₃ with 2-acetonaphthone in benzene containing 1 M DEA at low irradiation power gives 1-PyNH₂ in 55% yield.

The findings described above indicate that short-lived intermediates are formed from photolysis of 1-NaN₃ or 1-PyN₃. The properties of these intermediates are typical of those assigned to triplet nitrenes.² To investigate this further, and to examine the relationship of the triplet nitrenes to the azirines observed at low temperature,¹⁷ we undertook a study of these reactions by laser transient absorption spectroscopy.

B. Transient Spectroscopy of 1-NaN₃ and 1-PyN₃. Irradiation of a 6×10^{-3} M solution of 1-NaN₃ in benzene with an ca. 13-ns, 7-mJ light pulse at 337 nm from a nitrogen laser leads to changes in the absorption spectrum of the solution that occur over a period of ca. 100 μs. We can examine the optical spectrum from ca. 350 nm, where the 1-NaN₃ absorbs strongly, to ca. 650 nm. Spectra taken immediately following the laser pulse show no absorptions in this region. As time proceeds, however, a band with an absorption maximum at 370 nm appears in the spectrum and increases in intensity according to a first-order rate law with a rise time of 2.8 ± 0.2 μs. This species undergoes an additional reaction over a period of ca. 100 μs to give the azonaphthalene that is eventually isolated from this reaction. The rate of growth of azonaphthalene exhibits clean second-order kinetics with a rate constant of 1×10^9 M⁻¹ s⁻¹ and varies as expected with the power of the laser pulse. These findings are shown in eq 5, the spectra are displayed in Figure 1, and the growth of the azonaphthalene is plotted on Figure 2.



The transient product absorbing at 370 nm is identified as 1-NaN^{·3} on the basis of the observation that it is a precursor to the azonaphthalene and the correspondence of the transient absorption spectrum with the spectrum obtained by irradiation 1-NaN₃ at 77 K under conditions where the triplet is shown to be stable by EPR spectroscopy.²⁸ The precursor to 1-NaN^{·3}, the question mark in eq 5, has a lifetime of 2.8 μs in benzene solution, and evidently it does not absorb strongly at wavelengths greater than 350 nm. There are several reasonable choices for the precursor to 1-NaN^{·3}. Among these are 1-NaN₃^{*3}, 1-NaN¹, azirine,

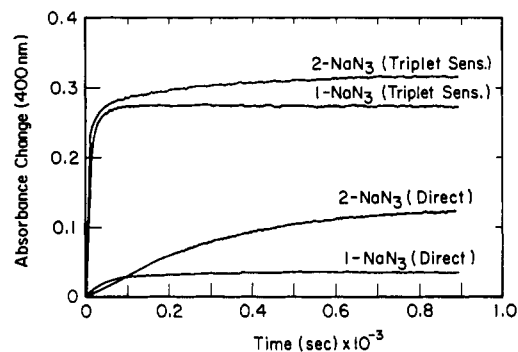
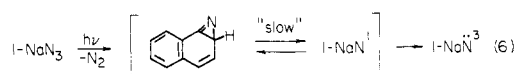


Figure 2. Growth of 1,1'-azonaphthalene and 2,2'-azonaphthalene from the direct and triplet-sensitized pulsed irradiation of the appropriate azide in benzene.

or dehydroazepine (eq 3).¹⁸ Triplet sensitization of 1-NaN₃ should bypass the latter three singlet-state intermediates and help in the assignment of a structure to the question mark in eq 5.

Triplet benzophenone is quenched at nearly the diffusion-limited rate by 1-NaN₃. Laser-flash photolysis of a benzene solution containing 1.5×10^{-2} M benzophenone and 5×10^{-4} M 1-NaN₃ with an ca. 20-ns, 5-mJ pulse at 355 nm (benzophenone absorbs the light) gives transient spectra similar to those observed on direct irradiation of 1-NaN₃. The absorption at 370 nm, identified as 1-NaN^{·3}, is present immediately after the benzophenone is quenched. Significantly, the rise time for this absorption in the triplet-sensitized irradiation is much less than the 2.8 μs observed by direct irradiation. We presume that the precursor to 1-NaN^{·3} in the sensitization experiment is 1-NaN₃^{*3}, and this result therefore eliminates the triplet azide as the major precursor to 1-NaN^{·3} in the direct irradiation.

These findings permit the assignment of the precursor to 1-NaN^{·3} in the direct irradiation of 1-NaN₃ to a singlet-state intermediate. It is nearly inconceivable that 1-NaN¹ has a 2.8-μs lifetime, but this species is almost certainly the immediate singlet precursor to 1-NaN^{·3}. Moreover, the chemical^{5,10,14} and matrix IR spectral evidence¹⁷ clearly implicate formation of an azirine, and this transient intermediate is a reasonable reservoir for 1-NaN¹. Thus, the question mark in eq 5 is assigned to the azirine, and the rise time for 1-NaN^{·3} in the direct irradiation is a consequence of the conversion of azirine to 1-NaN¹, eq 6. Our findings do not indicate whether 1-NaN₃^{*1} loses N₂ to form first 1-NaN¹ or if it goes directly to the azirine. But it is reasonable that 1-NaN¹ can be converted to azirine since thermolysis of aryl azides generally gives products similar to those obtained on photolysis.⁵⁻⁹



The photolysis of 1-NaN₃ in DEA with the laser gives primarily 1,1'-azonaphthalene. The transient absorption spectra observed when 1-NaN₃ is irradiated in DEA are virtually identical with those obtained by irradiation in benzene. This finding helps to confirm the conclusions that the 1-NaNH₂ obtained from low-power irradiations of 1-NaN₃ in DEA comes from reaction of 1-NaN^{·3} rather than from excited azide.²⁹

The transient spectra obtained from flash photolysis of 1-PyN₃ in benzene have been reported previously.²⁴ We repeated these experiments in both benzene and DEA solution and obtained comparable results.

Irradiation of a 1×10^{-4} M solution of 1-PyN₃ in benzene results in the immediate, less than 15 ns, appearance of a transient product with an absorption maximum at 455 nm. This product decays with a half-life of 30 ns as a second transient product with an absorption maximum at 420 nm grows into the spectrum. The second transient product undergoes a second-order reaction over

(26) Mixed azo compounds have been obtained before from photolysis of azides.²⁷ However, in this case the irradiating light was absorbed by both azides.

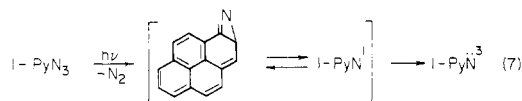
(27) Horner, L.; Christmann, A.; Gross, A. *Chem. Ber.* **1963**, *96*, 399.

(28) The spectrum we obtain at 77 K is similar to that reported previously.²⁰

(29) Abramovitch, R. A.; Challand, S. R. *J. Chem. Soc., Chem. Commun.* **1972**, 964.

a period of ca. 100 μ s to become 1,1'-azopyrene.

In part on the basis of these findings, the transient product absorbing at 420 nm has been assigned to 1-PyN \dot{N}^3 and the first-formed transient absorbing at 455 nm assigned to 1-PyN \dot{N}^1 .²⁴ However, in light of the results described above for 1-NaN \dot{N}_3 and the marked similarity of the chemistry of 1-NaN \dot{N}_3 and 1-PyN \dot{N}_3 , it seems prudent to include the possibility that the intermediate absorbing at 455 nm is actually the azirine, eq 7. One clear



difference between 1-PyN \dot{N}_3 and 1-NaN \dot{N}_3 is the much more rapid rise of 1-PyN \dot{N}^3 indicating that the equilibrium between azirine and singlet nitrene for 1-PyN \dot{N}_3 favors more the singlet nitrene.

C. Products of Photolysis: 2-NaN \dot{N}_3 and 2-PyN \dot{N}_3 . Irradiation of a 2×10^{-3} M solution of 2-NaN \dot{N}_3 in deoxygenated benzene in a Rayonet photoreactor equipped with 350-nm lamps gives 2,2'-azonaphthalene. The yield of the azonaphthalene is 22% immediately after the photolysis, but it grows steadily in the dark to 45% after 20 h. When an identical solution of 2-NaN \dot{N}_3 is irradiated with high-power pulses from the nitrogen laser, the yield of 2,2'-azonaphthalene immediately after irradiation is 95% and it does not increase.

Irradiation of a benzene solution containing 5×10^{-3} M 2-NaN \dot{N}_3 and 1×10^{-2} M PhN \dot{N}_3 in the Rayonet (light absorbed primarily by the 2-NaN \dot{N}_3) gives both 2,2'-azonaphthalene and 2-naphthylphenyldiazene, and the yields of both of these products increase in the dark after irradiation. In contrast, irradiation of an identical solution with the nitrogen laser gives only 2,2'-azonaphthalene. These findings parallel exactly the results obtained for 1-NaN \dot{N}_3 and likewise indicate that there are at least two routes to the azoaromatics.

Photolysis of 2-NaN \dot{N}_3 in benzene containing DEA either with the continuous source or with the laser results in formation of 2-(diethylamino)-1-aminonaphthalene. The yield of the diamine increases as the concentration of DEA increases and reaches a maximum of 94% at 1.45 M. At concentrations below this limit azonaphthalene and 2-NaNH \dot{N}_2 are also generated. This result shows that the diamine is formed from an intermediate in competition with eventual formation of the characteristic triplet nitrene products.

Triplet sensitization of 2-NaN \dot{N}_3 with 2-acetonaphthone in benzene containing 0.3 M DEA does not give any 2-(diethylamino)-1-aminonaphthalene, but it does form the expected azonaphthalene. This experiment confirms the triplet origin for the azo compound, the singlet origin of the diamine, and shows that intersystem crossing from 2-NaN \dot{N}^3 to the singlet intermediates does not compete successfully with other reactions of the triplet.

The photochemistry of 2-PyN \dot{N}_3 is quite similar to that observed for 2-NaN \dot{N}_3 . Irradiation in benzene gives primarily 2,2'-azopyrene. In the presence of DEA, the product is almost exclusively 2-(diethylamino)-1-aminopyrene. The yield of this diamine also follows the concentration of DEA, but in contrast to 2-NaN \dot{N}_3 , it reaches a maximum value (ca. 100%) at only 4×10^{-3} M DEA. This result shows that the singlet intermediate formed from 2-PyN \dot{N}_3 is ca. 1000 times easier to trap than the corresponding intermediate from 2-NaN \dot{N}_3 . Triplet sensitization of 2-PyN \dot{N}_3 with biacetyl or with 2-acetonaphthone, unlike the other azides studied, does not give significant yields of azopyrene. This may be a consequence of reaction of the excited sensitizer with this azide.

D. Transient Spectroscopy of 2-NaN \dot{N}_3 and 2-PyN \dot{N}_3 . Irradiation of a 4×10^{-3} M solution of 2-NaN \dot{N}_3 in benzene with the nitrogen laser leads to changes in the absorption spectrum of the solution. Spectra recorded immediately (within 15 ns) after the laser pulse show no absorptions in the region we can probe (350–650 nm). However, as time proceeds, the absorption of 2,2'-azonaphthalene grows in following a second-order rate law over a period of ca. 1000 μ s (Figure 2). This result takes on added significance when compared with the spectral changes observed for 1-NaN \dot{N}_3 where the triplet nitrene is easily detected and 1,1'-azonaphthalene is

formed ca. 20 times faster than is 2,2'-azonaphthalene.

The triplet nitrene from 2-NaN \dot{N}_3 can be generated and detected by triplet sensitization. Irradiation of a solution containing 1.5×10^{-2} M benzophenone and 4×10^{-4} M 2-NaN \dot{N}_3 at 355 nm generates first triplet benzophenone which in turn is quenched by the azide. As the triplet ketone is quenched, a new product absorbing at 365 nm appears in the spectrum. On a longer time scale the absorptions of 2,2'-azonaphthalene grow into the spectrum, Figure 2. The rate of this growth is much faster than is observed in the direct irradiation of 2-NaN \dot{N}_3 . The transient product absorbing at 365 nm created in the triplet sensitization of 2-NaN \dot{N}_3 is identified as 2-NaN \dot{N}^3 . Irradiation of 2-NaN \dot{N}_3 at 77 K does not give a detectable absorption at 365 nm, but analysis of the EPR spectrum clearly reveals that some of the triplet nitrene has been formed.

Direct irradiation of 2-NaN \dot{N}_3 certainly generates 2-NaN \dot{N}^3 since azonaphthalene is a major product. However, the transient concentration of 2-NaN \dot{N}^3 must be much lower than that obtained from direct irradiation of 1-NaN \dot{N}_3 under comparable conditions. The triplet-sensitization results show that the rate constants for dimerization of the two isomeric nitrenes are approximately the same. Thus, the change in steady-state concentration must reflect a slower rate of formation for 2-NaN \dot{N}^3 from its singlet precursor. With the reasonable assumption that the rates for intersystem crossing of 1-NaN \dot{N}^1 and 2-NaN \dot{N}^1 are similar, the slower formation of 2-NaN \dot{N}^3 is traced directly to an increase in the lifetime of expected azirine, eq 9. This finding may explain the profound difference in the photochemistry⁵ between 1-NaN \dot{N}_3 and 2-NaN \dot{N}_3 and is discussed further below.



The transient absorption spectra obtained by irradiating 2-NaN \dot{N}_3 in benzene containing DEA support the reaction scheme shown in eq 8. No additional transient species are observed, but the amount of azonaphthalene formed decreases as the concentration of DEA increases. This is a consequence of interception of the singlet intermediate, presumably the azirine, before it can form 2-NaN \dot{N}^1 and intersystem cross irreversibly to 2-NaN \dot{N}^3 .

The transient absorption spectra obtained from pulsed irradiation of 2-PyN \dot{N}_3 are also quite revealing. Photolysis of a 2×10^{-4} M solution of 2-PyN \dot{N}_3 in benzene leads to the formation of a transient product absorbing at 420 nm. This product is formed within the 15-ns pulse width of the laser. On a longer time scale the absorptions of the 2,2'-azopyrene grow into the spectrum by a second-order process. In concert with the product study, triplet sensitization with 2-acetonaphthone does not lead to any of the transient absorbing at 420 nm or to any azopyrene even though the triplet sensitizer is quenched.

The 420-nm absorption is also formed by irradiation of 2-PyN \dot{N}_3 at 77 K in a 2-methyltetrahydrofuran glass, and EPR spectra taken at 77 K and at 4 K clearly reveal 2-PyN \dot{N}^3 . However, these observations do not unambiguously identify the absorption at 420 nm as due to 2-PyN \dot{N}^3 .

Irradiation of 2-PyN \dot{N}_3 in DEA with the nitrogen laser also causes the immediate appearance of the 420-nm absorbing intermediate. However, under these conditions this species is transformed into a stable product absorbing at 445 nm by a first-order process with a half-life of 2.5 μ s, Figure 3. The spectrum of the stable product is identical with that of the 2-(diethylamino)-1-aminopyrene eventually isolated from this reaction. Thus it appears that the transient product absorbing at 420 nm can become 2,2'-azopyrene (the characteristic triplet nitrene product) in the absence of a nucleophilic reagent, but in the presence of a low concentration of such a trap this same species is converted to the ortho-disubstituted pyrene characteristic of the singlet intermediate.

Discussion

The results described above provide some insight into the factors that affect the reactivity of aromatic azides. In general, there is a clear distinction between the reactions of the triplet intermediates and the singlet intermediates. This distinction breaks

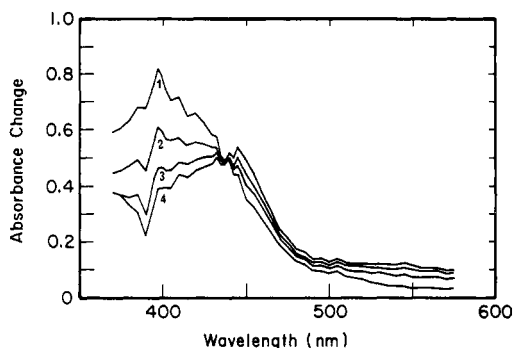
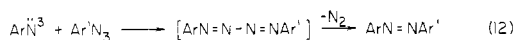
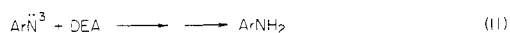
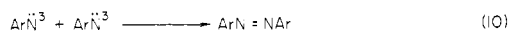
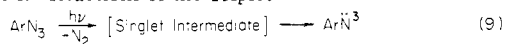
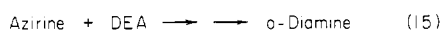


Figure 3. Transient absorption spectra recorded after pulsed irradiation of 2-PyN₃ in DEA. Spectrum 1 was obtained 1.4 μs after the laser pulse, 2 at 3 μs, 3 at 5 μs, and 4 at 20 μs.

Scheme I. Reactions of the Triplet



Scheme II. Reactions of the Singlet Intermediate



down in the case of 2-PyN₃. We discuss first the triplet nitrenes and then turn to the properties of the singlet-state intermediates; the conclusions are summarized in Schemes I and II.

Direct irradiation of each of the azides investigated, under some conditions, leads to the formation of the appropriate triplet nitrene. Once formed, this intermediate has several reaction paths available. Three of the most important are as follows: dimerization to the azoaromatic; combination with ground-state azide; and reduction to give eventually the appropriate aromatic amine. The results show that both the conditions of the reaction and the nature of the azide affect the route selected.

When the azides are irradiated by using the high-power pulsed laser the concentration of transient products is reasonably high. We estimate that the initial concentration in the reaction zone under these conditions is ca. 1×10^{-4} M. In contrast, the steady-state concentration of transient products is ca. 20 000 times less than this under continuous irradiation conditions. The high concentration of triplet nitrenes formed in the pulsed irradiation results in a concomitant increase in the rates of its reactions, of course affecting second-order processes much more than reactions first order in triplet nitrene concentration. Thus, under pulsed irradiation conditions, dimerization of the triplet nitrenes to the azo compounds is the predominant process in both inert and reactive solvents, eq 10, Scheme I. Of course, if the singlet-state transient is intercepted before it can form triplet nitrene, as is the case for 2-NaN₃ and 2-PyN₃ in DEA, then very little azo compound is formed regardless of the irradiation conditions. The rate constant for triplet-nitrene dimerization is ca. 1×10^9 M⁻¹ s⁻¹ which is close to the value expected for a diffusion-limited triplet-triplet reaction.³⁰

Irradiation of the azides at low power permits reactions that are first order in triplet nitrene to compete with their dimerization. One of these reactions is reduction to the aromatic amine by DEA, eq 11, Scheme I. The mechanism of this process is unclear. It may involve initial hydrogen abstraction or first-electron transfer followed by proton migration.

The third reaction of the triplet nitrenes is combination with ground-state azide. This process accounts for the mixed azo compounds when the naphthyl azides are irradiated in the presence of phenyl azide. The increase in the yield of the azo compounds following termination of the irradiation clearly implicates the involvement of a "stable" intermediate in this reaction. We have not isolated or directly detected this species, but we suspect that it is the tetraazine previously suggested to participate in the chain decomposition of PhN₃,³¹ eq 12, Scheme I.

The reactions of the singlet intermediates formed from photolysis of these compounds (Scheme II) depends greatly on the identity of the azide. The results indicate that irradiation leads to an excited singlet state that rapidly loses nitrogen. There is no evidence for an intermolecular reaction involving the excited azide.²⁹ Our findings are entirely consistent with the conclusion that each of these azides first forms an azirine, eq 12. The eventual chemical outcome is determined by the properties of the azirine. The most important properties in this regard are the rate of conversion of the azirine to the singlet nitrene, eq 14, and the rate of return to the azirine by the triplet nitrene, eq 14 and 16.

Neither 1-NaN₃ nor 1-PyN₃ give significant yields of nucleophile incorporation product even when photolyzed in neat DEA. We trace this result in part to the short lifetime of these azirines compared with the lifetime of the azirine formed from 2-NaN₃ which does give a high yield of nucleophile incorporation product. The lifetime of the azirine from 1-NaN₃ is 2.8 μs, and that for the azirine from 2-NaN₃, while not revealed directly from our experiments, is estimated to be at least 20 times longer on the basis of the observable rates of growth of the azonaphthalenes.

The lifetime of the azirine is likely to be controlled by its rate of isomerization to the singlet nitrene (vide infra). The rate of this process is evidently quite sensitive to structure. This is seen not only in comparison of 1-NaN₃ with 2-NaN₃ but also in the relationship between the naphthyl and the pyrenyl azides. Several factors can influence the rate of this process, not the least of which is the relative energies of the azirine and the singlet nitrene.³²

The nitrogen atom of the singlet nitrene is severely electron deficient. The aromatic nuclei of these aryl nitrenes are relatively electron rich and no doubt donate electron density to the nitrogen. The frontier electron population for the 1-position of naphthalene is much greater than that at the 2-position.³³ This greater electron density may stabilize 1-NaN¹ compared to 2-NaN¹ thereby increasing the rate of azirine isomerization for the 1-isomer and consequently making this azirine unavailable to nucleophiles.

Similar considerations can be employed to explain the observed behavior of 2-PyN₃. This azide gives high yields of the o-diamine even in the presence of low concentrations of DEA. The transient spectroscopy reveals the very rapid formation of a long-lived intermediate absorbing at 420 nm. In the absence of DEA this intermediate exhibits triplet reactivity, and in the presence of DEA it exhibits reactions characteristic of the singlet intermediate. This dichotomy is easily resolved if intersystem crossing from 2-PyN³ back to 2-PyN¹ can compete with the bimolecular reactions of 2-PyN³. In this way the singlet intermediate can behave as if it has the much longer lifetime of the triplet nitrene. The ground state of 2-PyN is shown to be the triplet by the EPR spectrum at 4 K. However, the higher electron-donating capacity of the 2-position of pyrene compared with the 2-position of naphthalene or the 1-position on pyrene may lower the energy of 2-PyN¹ so

(31) Waddell, W. H.; Go, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 5804.

(32) In many reactions a linear free energy relationship holds approximately. Usually, the more exothermic a process the lower the activation barrier.

(33) For a complete discussion of how this electron density affects the reactivity of aromatic hydrocarbons, see: Fleming, I. "Frontier Orbitals and Chemical Reactions"; Wiley: New York, 1976.

(30) Birks, J. B. "Photophysics of Aromatic Compounds"; Wiley: New York, 1970; p 448.

that it can be regenerated from 2-PyN³. Equilibration of the singlet and triplet states of some aryl nitrenes has been suggested previously.³⁴

Conclusions

The photochemistry of the aromatic azides we have investigated is controlled by the chemical and physical properties of the short-lived intermediates formed when N₂ is lost. The keys to understanding these intermediates appear to be the relative energy of the singlet nitrene compared to its isomeric azirine (and/or azepine in the case of PhN₃) and compared to the triplet nitrene. When the energy difference between the azirine and the singlet nitrene is small, the lifetime of the azirine is short, and reactions with nucleophiles do not compete with irreversible formation of the triplet nitrene. When the energy difference between the singlet and triplet nitrenes is small, intersystem crossing is reversible, and the singlet intermediates, in effect, have the longer lifetimes of the triplet nitrene. In this case, nucleophiles are trapped very efficiently.

The observed reactivity patterns for aromatic azides suggest that the ability of the aromatic nucleus to donate electrons controls in part the energy of the singlet nitrenes. We are continuing to test this concept and to apply it in the use of aromatic azides for photoaffinity labeling.³⁵

Experimental Section

General. Proton magnetic resonance (¹H NMR) spectra were recorded on a Varian Associates HR 220 (220 MHz, operated in FT mode) spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Mass spectra (MS) were obtained with Varian MAT CH-5 and 731 mass spectrometers. Electron paramagnetic resonance (EPR) spectra at 77 K were recorded on a Varian Associates E-4 (X-Band) spectrometer. Steady-state ultraviolet-visible (UV-vis) absorption spectra were recorded with a Perkin-Elmer Model 552 spectrophotometer. Analytical gas chromatography (GC) was performed on a Varian Associates Model 3700 or Model 2700 gas chromatograph equipped with a flame ionization detector on 1.5-m glass columns containing 5% SE-30 or 5% Carbowax on DMCS-treated acid-washed Chromosorb W, and with helium at 30 mL/min as the carrier gas. Temperature programs were run with initial temperature at 100 °C increasing to 220 °C at 10 °C/min. High-performance liquid chromatography (HPLC) was performed on a Perkin-Elmer Series 2 liquid chromatograph equipped with a variable wavelength detector with 10- μ m silica columns (0.26 \times 25 cm) with 1% 2-propanol in hexane as the eluant at 1 mL/min. Analytical reverse-phase HPLC was performed on a C8/10 packing (0.46 \times 25 cm) with 25% water in acetonitrile as the eluant at 2 mL/min. All yields are determined on the basis of consumed azide. Nanosecond spectroscopy was performed as previously described.¹

Materials. Benzene (Burdick and Jackson, distilled in glass) was used without further purification. Diethylamine (Aldrich) was distilled under nitrogen. 1-Pyreneamine was prepared by stannous chloride reduction of 1-nitropyrene.³⁶ 2-Pyreneamine was prepared by treatment of 1-bromopyrene with potassium amide in refluxing ammonia.³⁷ 1-Naphthyl azide and 2-naphthyl azide were prepared by decomposition of the diazonium chlorides with sodium azide.³⁸ 1,1'-Azonaphthalene and 2,2'-azonaphthalene were prepared by the procedure of Cohen and Oester,³⁹ with the modification of Shine.⁴⁰ 1-Naphthylphenyldiazene and 2-naphthylphenyldiazene were prepared by the reaction of nitrobenzene and naphthylamine.⁴¹⁻⁴³ 2-(Diethylamino)-1-aminonaphthalene

was prepared by irradiation of 2-naphthyl azide in diethylamine.⁷

Low-Temperature UV-vis Spectra. Low-temperature ultraviolet-visible spectra were obtained with a three-windowed Pyrex optical Dewar filled with liquid nitrogen. The naphthyl (3×10^{-3} M) or pyrenyl azides (1×10^{-4} M) were dissolved in dry 2-methyltetrahydrofuran, placed in a long-necked Pyrex cuvette fitted with a septum, and frozen to an optical glass by being slowly lowered into the Dewar. Spectra before and after irradiation at 350 nm were recorded.

Preparation of 2-Pyrenyl Azide. A slurry of 300 mg (1.38 mmol) of 2-pyreneamine in 15 mL of 12 M HCl was refluxed for 15 min and then 15 mL of glacial acetic acid was added. The solution was cooled to 0–5 °C and 95 mg (1.38 mmol) of NaNO₂ in 5 mL of H₂O was added dropwise to the stirred solution. After 30 min of additional stirring at 0–5 °C, 180 mg (2.76 mmol) of sodium azide in 5 mL of H₂O was added. The resulting dark slurry was stored at 0 °C for 6 h and then extracted 3 times with 50 mL of ether. The combined solutions were washed twice with 50 mL of brine and then 3 times with 50 mL of saturated NaHCO₃. The ether solution was dried over anhydrous magnesium sulfate, filtered, and evaporated at room temperature on a rotary evaporator. The residue was chromatographed on silica gel eluting with 10% benzene in petroleum ether. The product was recrystallized from petroleum ether/benzene at –20 °C yielding 135 mg (40%) of colorless needles: mp 129–130 °C dec; IR (CHCl₃) 2111, 1600, 1440, 1309, 1289, 875, 860, 842, 815, 710 cm⁻¹; UV (benzene) 340 nm log ϵ = 4.41; NMR (CDCl₃) δ 8.21–7.96 (m, 7 H), 7.80 (s, 2 H); mass spectrum, *m/e* 243.0796 (calcd for C₁₆H₉N₃ 243.0796).

Preparation of 1-Pyrenyl Azide.⁴⁴ A slurry of 500 mg (2.3 mmol) of 1-pyreneamine, 20 mL of *p*-dioxane, and 20 mL of 4 N H₂SO₄ was stirred and cooled to 0–5 °C in an ice-brine bath. To this solution was added 142 mg (2.1 mmol) of NaNO₂ in 3 mL of H₂O. After 30 min, 200 mg (3.1 mmol) of NaN₃ in 3 mL of H₂O was added in one portion. The mixture was stirred for an additional 30 min and then stored at 0 °C for 6 h. The reaction mixture was extracted 3 times with 30 mL of ether. The combined ether extracts were washed twice with 50 mL of H₂O, dried over MgSO₄, filtered, and evaporated at room temperature on a rotary evaporator. The residue was chromatographed on neutral alumina eluting with CCl₄. Recrystallization from benzene/pentane gives 110 mg (20% yield) of off-white plates: mp 119–120 °C⁴⁴ dec; IR (Nujol) 2110 cm⁻¹; ¹H NMR (CDCl₃) δ 8.2–7.95 (m).

2-(Diethylamino)-1-aminopyrene. A solution of 50 mg (0.21 mmol) of 2-PyN₃ in 25 mL of DEA was purged with nitrogen for 5 min and then irradiated in a Rayonet photoreactor at 350 nm for 15 min. The solvent was removed, and the residue was chromatographed on a silica thick-layer plate, eluting with 5% ether in benzene to give the diamine in 84% yield: NMR (CDCl₃) δ 7.82 (d, 1 H, *J* = 8 Hz), 7.70–7.2 (m, 6 H) 6.98 (d, 1 H, *J* = 9 Hz), 3.5 (q, 4 H), 1.2 (t, 6 H); the amino hydrogens are observed in some spectra at 4.65; mass spectrum found *m/e* 288.1625 (calcd for C₂₀H₂₀N₂ 288.1627).

Preparation of 2,2'-Azopyrene. A solution of 25 mg (0.1 mmol) of 2-PyN₃ in 50 mL of benzene was purged with N₂ and irradiated at 350 nm for 30 min. The red solution was evaporated to low volume in the dark and chromatographed on a silica gel thick-layer plate, eluting with toluene. The red band was extracted with THF, filtered, and evaporated under dim red lights to give 2,2'-azopyrene: 2 mg; mp 260 °C; mass spectrum, *m/e* 430.1471 (calcd C₂₂H₁₅N₂ 430.1470).

Direct Irradiation of 1- and 2-Naphthyl Azide in Benzene with and without Phenyl Azide. Solutions of 1-NaN₃ or 2-NaN₃ (5×10^{-3} M) and PhN₃ (1×10^{-2} M or none) in benzene were purged with nitrogen and then irradiated either with a Rayonet photoreactor equipped with 350-nm lamps or a nitrogen laser at 337 nm and 2 Hz. The naphthyl azides absorbed greater than 90% of the light in the solutions containing phenyl azide. The samples were analyzed by reverse-phase HPLC eluting with 25% water in acetonitrile immediately after photolysis and then stored in the dark at room temperature. Periodic analysis of the stored samples showed an increase in yields of the azoaromatics for the solutions photolyzed in the Rayonet, but no increase for the solutions irradiated with the laser. The conversion of the naphthyl azides was kept below 20% to minimize photolysis of the azonaphthalenes which absorb strongly at the irradiation wavelengths.

Photolysis of 1-Naphthyl Azide in Diethylamine. A solution of 1-NaN₃ (6×10^{-3} M) in neat DEA was purged with nitrogen and irradiated at 350 nm. The product, 1-naphthylamine, was isolated in 80% yield by thin-layer chromatography on silica gel, eluting with benzene, and identified by comparison with an authentic sample. A similar solution of 1-NaN₃ (4×10^{-3} M) in DEA was irradiated with the nitrogen laser at 337 nm and 2 Hz. After photolysis, diethyl phthalate was added as an internal standard and the yields of products were determined by

(34) Reiser, A.; Wagner, H.; Bowes, G. *Tetrahedron Lett.* **1966**, 2635. Lindley, J. M.; McRobbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc. Perkin Trans. 1* **1977**, 2194.

(35) Schrock, A. K.; Schuster, G. B. *Photochem. Photobiol.*, to be submitted.

(36) Goldschmiedt, G. *Monatsh. Chem.* **1881**, 2, 580.

(37) Streitwieser, A.; Lawler, R.; Schwaab, D. *J. Org. Chem.* **1965**, 30, 1470.

(38) Boshev, G.; Dyall, L. K.; Sadler, P. R. *Aust. J. Chem.* **1972**, 25, 599.

(39) Cohen, S.; Oesper, R. E. *Ind. Eng. Chem., Anal. Ed.* **1936**, 8, 306.

(40) Shine, H. J. *J. Am. Chem. Soc.* **1956**, 78, 4807. Neitski, R.; Goll, O. *Chem. Ber.* **1885**, 18, 297.

(41) Ramart-Lucas, P.; Guilmar, T.; Marytnoff, M. *Bull. Soc. Chim. Fr.* **1947**, 424.

(42) Warning: Detonation hazard, see "Methoden de Organischen Chemie" 10/3, 345.

(43) Marytnoff, M. *Bull. Soc. Chim. Fr.* **1951**, 214.

(44) Yamaoka, T.; Kashiwaga, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1972**, 45, 361.

reverse-phase HPLC, eluting with 25% water in acetonitrile. The yield of 1-naphthylamine is less than 4%, and the yield of 1,1'-azonaphthalene is 50% at 10% conversion of 1-NaNH₂.

Photolysis of 1-Pyrene Azide in Diethylamine. A solution of 1-PyN₃ (4×10^{-3} M) in neat DEA was purged with nitrogen and irradiated at 350 nm. The product, 1-pyreneamine, was isolated in 82% yield by thin-layer chromatography on silica gel, eluting with benzene, and identified by comparison of its spectral data with those of an authentic sample. A similar solution of 1-PyN₃ (2×10^{-4} M) was irradiated with the nitrogen laser at 337 nm and 2 Hz. After photolysis, diethyl phthalate was added as internal standard. The solvent was removed and the sample analyzed by HPLC, eluting with 1% 2-propanol in hexane. The yield of 1-pyreneamine in this case was 4%.

Triplet Sensitization of 1-Pyrenyl Azide in 1 M Diethylamine. A solution of 1-PyN₃ (4×10^{-4} M), 2-acetonaphthone (2.1×10^{-2} M), and DEA (1.0 M) in benzene was purged with nitrogen and irradiated with a 200-W Hg lamp filtered through a Corning 0-51 glass plate. After photolysis diethyl phthalate was added as an internal standard, and the solvent was removed. The residue was diluted with benzene and analyzed by HPLC, eluting with 1% 2-propanol in hexane. The yield of 1-pyreneamine is 55%. To insure that the 1-pyreneamine was stable to the reaction conditions, a solution of 1-pyreneamine (3×10^{-4} M), 2-acetonaphthone (2.1×10^{-2} M), and 1 M DEA was treated exactly as above. HPLC analysis shows that on prolonged irradiation only a small amount of the 1-pyreneamine is consumed.

Triplet Sensitization of the 2-Aryl Azides. A solution of 2-NaN₃ (1×10^{-3} M), 2-acetonaphthone (1.5×10^{-2} M), and DEA (1.0 M) in benzene was purged with nitrogen and irradiated with the frequency-tripled Nd-YAG at 355 nm and 2 Hz or in the Rayonet photoreactor at

350 nm. The sensitizer absorbs more than 95% of the light under these conditions. After photolysis, diethyl phthalate was added as an internal standard. The sample was analyzed by analytical reverse-phase HPLC for the yield of 2,2'-azonaphthalene and by gas chromatography on an OV-101 column for the yields of 2-(diethylamino)-1-aminonaphthalene and 2-naphthylamine. A similar solution of 2-pyrene azide (3.4×10^{-4} M), 2-acetonaphthone (2×10^{-2} M), and diethylamine (1 M) was treated as above and analyzed by HPLC for 2-pyreneamine and 2-(diethylamino)-1-aminopyrene. Also, a similar sample of 2-PyN₃ without DEA was treated as above. The sample was monitored by UV-vis for 2,2'-azopyrene at 600 nm.

Acknowledgment. This work was supported by grants from the National Science Foundation and from the National Institutes of Health. Some preliminary experiments were performed by Dr. Keith Horn.

Registry No. DEA, 109-89-7; 1-NaNH₂, 134-32-7; 2-NaNH₂, 91-59-8; 1-PyNO₂, 5522-43-0; 1-PyNH₂, 1606-67-3; 2-PyNH₂, 1732-23-6; 1-NaNH₂⁺Cl⁻, 3177-49-9; 2-NaNH₂⁺Cl⁻, 20893-80-5; 1-PyN₂⁺, 41070-21-7; 2-PyN₂⁺, 91110-56-4; 1-PyBr, 1714-29-0; 1-NaN₃, 6921-40-0; 2-NaN₃, 20937-86-4; 1-PyN₃, 36171-39-8; 2-PyN₃, 91110-61-1; 1-NaN, 3315-52-4; 2-NaN, 3315-51-3; 1-PyN, 36171-40-1; 1-NaN=NNa-1, 487-10-5; 2-NaN=NNa-2, 582-08-1; 1-NaN=NPh, 2653-70-5; 2-NaN=NPh, 2653-77-2; 2-PyN=NPY-2, 91110-57-5; K⁺NH₂⁻, 17242-52-3; Na⁺N₃⁻, 26628-22-8; PhNO₂, 98-95-3; PhN₃, 622-37-7; 2-(diethylamino)-1-aminonaphthalene, 54922-17-7; 1aH-naphthaleno[1,2-b]azirine, 91110-58-6; 7bH-naphthaleno[1,2-b]azirine, 91110-60-0; 1aH-pyreno[1,2-b]azirine, 91110-59-7; 2-acetonaphthone, 93-08-3.

Carbon-13 Spin-Lattice Relaxation Studies of G_{D1a} Micelles. Limited Segmental Motion of Head Group Saccharide Units¹

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Abstract: Measurements of ¹³C spin-lattice relaxation times (*T*₁) for G_{D1a} micelles have been made. The results indicate that the head group is relatively immobile with no overall anisotropic axis of rotation. There is evidence, however, for a small gradient of internal rotation for the individual saccharide units. Significant differences in relaxation were observed between the two sialic acid residues of G_{D1a}. The relaxation data show that carbons in the periphery of the saccharide rings (i.e., saccharide C-6 carbons and the sialic acid glycerol chains) exhibit relaxation behavior similar to the related system, neuraminylactose (Czarniecki, M. F.; Thornton, E. R. *J. Am. Chem. Soc.* 1977, 99, 8279-8282). These phenomena are explained in terms of models derived for neuraminylactose when possible. The relatively low mobility observed for Cer C-2 and C-3 lent support to the existence of a hydrogen bond in the region of these two carbons. Interestingly, Cer C-1 was found to be significantly more mobile than surrounding carbons.

We wish to report the first complete carbon-13 NMR spin-lattice relaxation time (*T*₁) measurements for ganglioside micelles. These measurements provide important information regarding conformational mobilities and interactions of gangliosides, which are very significant lipid constituents of neuronal membranes.

Gangliosides, such as G_{D1a} (1), are membrane glycosphingolipids in which a sphingosine, usually *trans-D-erythro-2-amino-1,3-dihydroxyoctadec-4-ene*, is *N*-acylated with a fatty acid and linked glycosidically at C-1 to an oligosaccharide containing at least one sialic (NeuAc) acid residue. Variations among gangliosides mainly involve the oligosaccharide region, in which the number of residues and types of linkages can differ.³

(1) (a) Supported in part by the National Institutes of Health (Grant GM-22,647). (b) For further details, cf.: Nerz-Stormes, M. Ph.D. Dissertation in Chemistry, University of Pennsylvania, Philadelphia, to be submitted.

(2) Czarniecki, M. F.; Thornton, E. R. *J. Am. Chem. Soc.* 1977, 99, 8279-8282.

Gangliosides are found in the outer leaflet of most mammalian cell membranes.⁴ The oligosaccharide chains extend into the intercellular space where they can act as receptors for a variety of proteins and cations such as Ca²⁺.^{5,6} Of particular interest

(3) Svennerholm, L. *J. Neurochem.* 1963, 10, 613-623.

(4) (a) Ledeen, R. W. In "Complex Carbohydrates of Nervous Tissue"; Margolis, R. U.; Margolis, R. K., Eds.; Plenum Press: New York, 1979; pp 1-23. (b) Ledeen, R. W.; Yu, R. K. In "Glycolipid Methodology"; Witting, L. A., Ed.; American Oil Chemists Society: Champaign, IL, 1976; pp 187-214.

(5) (a) Dreyfus, H.; Louis, J. C.; Harth, S.; Mandel, P. *Neuroscience* 1980, 5, 1647-1655. (b) Yamakawa, T.; Nagai, Y. *Trends Biochem. Sci. (Pers. Ed.)* 1978, 3, 128-131. (c) Kohn, L. D.; Consiglio, E.; DeWolf, M. J. S.; Grollman, E. F.; Ledley, F. D.; Lee, G.; Morris, N. P. In "Structure and Function of Gangliosides"; Svennerholm, L., Mandel, P., Dreyfus, H., Urban, P.-F., Eds.; Plenum Press: New York, 1980; pp 487-503. (d) Hollenberg, M. D. *Pharmacol. Rev.* 1978, 30, 393-410.

(6) Behr, J.-P.; Lehn, J.-M. *FEBS Lett.* 1973, 31, 297-300.