

equilibria in cycloalkanes and will serve as a reference group for determining the equatorial and quasi-equatorial preferences of other substituents.

Experimental Section

(*cis*- and *trans*-4-alkylcyclohexyl)methyl bromides were prepared by literature methods.^{12,22} EPR spectra were obtained by photolysis of

(22) Kitching, W.; Olszowy, H.; Adcock, W. *Org. Mag. Reson.* **1981**, *15*, 230-237.

solutions of the bromide (10%), triethylsilane (10%), and di-*tert*-butyl peroxide (10%) in cyclopropane, with light from a 500-W super-pressure Hg arc. At temperatures above ca. 200 K, hexamethylditin was used in place of the silane and *tert*-butylbenzene was the solvent. Spectra were recorded with a Bruker ER 200 D spectrometer. The ratio of the concentrations of the axial and equatorial (4-methylcyclohexyl)methyl bromides [**4a**]/[**4b**] was obtained from the 360-MHz ¹H NMR signals for the bromomethyl groups. At temperatures below coalescence the separate signals were integrated both instrumentally and by planimetry. Above coalescence the ratio was determined from the average value of the chemical shift, the chemical shifts of the axial and equatorial groups being extrapolated from the low-temperature data.^{20,22}

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Registry No. **2a**, 98105-52-3; **2c**, 98105-53-4; **2d**, 64679-52-3; **3a**, 98105-54-5; **3c**, 98105-55-6; *trans*-**4**, 78507-26-3; *cis*-**4**, 78507-33-2; (*cis*-4-*tert*-butylcyclohexyl)methyl bromide, 36293-49-9; (*trans*-4-*tert*-butylcyclohexyl)methyl bromide, 36293-50-2.

Reactivities of Rotameric *ap*- and *sp*-3,5-Dimethyl-2-(9-fluorenyl)phenylnitrenes

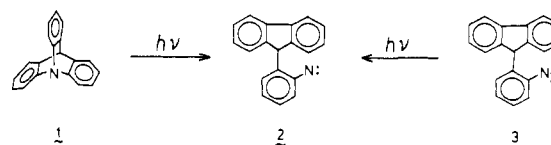
Shigeru Murata, Tadashi Sugawara, and Hiizu Iwamura*

Contribution from the Division of Applied Molecular Science, Institute for Molecular Science, Okazaki 444, Japan. Received February 5, 1985

Abstract: The *ap*- and *sp*-3,5-dimethyl-2-(9-fluorenyl)phenyl azides (**4ap** and **4sp**) have been obtained separately from the corresponding amines **6ap** and **6sp** which in turn were obtained as a mixture by the AlCl₃-catalyzed isomerization of *N*-(9-fluorenyl)-3,5-xylidine and separated by chromatography. Isomerization **4ap** → **4sp** was studied at 40–69 °C to give the kinetic and thermodynamic parameters: $\Delta H^\ddagger = 22.5$ kcal/mol, $\Delta S^\ddagger = -7.6$ eu, $\Delta G^\ddagger_{300} = 24.8$ kcal/mol; $\Delta H^\circ = -1.70$ kcal/mol, $\Delta S^\circ = -0.42$ eu, $\Delta G^\circ_{300} = -1.57$ kcal/mol. Conformationally fixed nitrenes **5ap** and **5sp** were generated independently from **4ap** and **4sp**, respectively, and their spectroscopic and chemical behaviors were scrutinized. When generated in an ESR cavity, **5ap** in the ground triplet state showed the X,Y transition at 6722 G. The resonance field characteristic of the *sp*-nitrene (6745 G) was obtained on the *9-d* derivative **4'sp** of azide **4sp**. The INDO-UHF MO spin-density calculations have been performed on the *ap* and *sp* rotamers of *o*-(9-fluorenyl)phenylnitrene and other model nitrenes. The effect of the *o*-(9-fluorenyl) substitution and its conformation was found to be very small, although the order of the calculated nitrogen spin densities is in parallel with the observed zfs parameters. When photolyzed in an EPA glass, **4ap** showed absorptions at 309 and 340 nm due to **5ap** and azanorcaradiene **8**, respectively. Absorptions at 367, 426, and 554 nm were obtained from **4sp**. These were assigned to dihydroindenoacridine **12** and *o*-quinoid imine **11** from which 10,12-dimethylindeno[*k,l*]acridine (**13**) was isolated after warming up of the matrix, aeration, and chromatography. In fluid solutions of methanol in the presence of a small amount of NaOMe, methoxyamine **14**, 3H-azepine **15** and azepine **16** were obtained in different ratios from **4ap** and **4sp**. The loss of stereospecificity in these reactions was ascribed to the conformational isomerization in the benzazirine intermediate **17**. The rate constants for the formation of **8** and **11** and the decay of **11** were determined by the laser-flash photolysis experiments to be 7.1×10^3 , $>10^8$, and 2.6×10^3 s⁻¹, respectively. The deuterium isotope effect for the hydrogen 1,4-migration in **5sp** was obtained as 1.84 at 25 °C. In diethylamine, **4ap** gave **6ap** and diamine **21**, while **4sp** gave both isomers of **6**, diamine **20** and **21**. Benzazirine **22** is considered to be responsible for the *sp* to *ap* isomerization. Tetracyanoethylene trapped the intermediates to give adducts **24** and **25**. The contrasting spectroscopic and chemical properties of the conformationally restricted nitrenes **5ap** and **5sp** are consistent with the hypothesis that 2-(9-fluorenyl)phenylnitrenes generated from 1-azatriptycene and 2-(9-fluorenyl)phenyl azide by photolysis have the *ap* and *sp* forms, respectively.

We have been interested for some years in the photochemistry of triptycenes in which three benzene rings are fixed at a 120° angle to each other in the molecules of threefold symmetry.¹ In particular we studied in detail the photorearrangement of 1-azatriptycene (**1**) and found a cleavage of the two carbon–nitrogen bonds resulting in the formation of *o*-(9-fluorenyl)phenylnitrene (**2**).² The phenylnitrene derivative **2** was independently generated by the photolysis of *o*-(9-fluorenyl)phenyl azide (**3**), and thus the

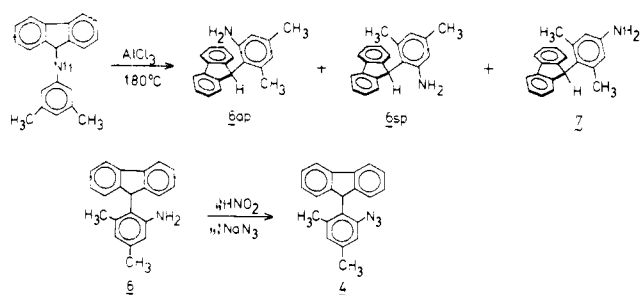
intermediacy of **2** in the photolysis of **1** was unambiguously established.



We noted, however, a slight difference in the behavior of the nitrenes **2** generated from the photolysis of **1** and **3**.² For example, the field positions of the X,Y transition of the triplet nitrenes were slightly different in the ESR spectra obtained at cryogenic temperature. The product distributions in the photoreactions of **1** and **3** in fluid solutions were significantly different. We explained

(1) (a) Iwamura, H.; Yoshimura, K. *J. Am. Chem. Soc.* **1974**, *96*, 2652. (b) Iwamura, H.; Tukada, H. *Tetrahedron Lett.* **1978**, 3451. (c) Kawada, Y.; Tukada, H.; Iwamura, H. *Ibid.* **1980**, *21*, 181. (d) Iwamura, M.; Tukada, H.; Iwamura, H. *Ibid.* **1980**, *21*, 4865. (2) (a) Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1980**, *102*, 7134. (b) Sugawara, T.; Nakashima, N.; Yoshihara, K.; Iwamura, H. *Ibid.* **1983**, *105*, 859. (c) Sugawara, T.; Iwamura, H. *Ibid.* **1985**, *107*, 1329.

Scheme I



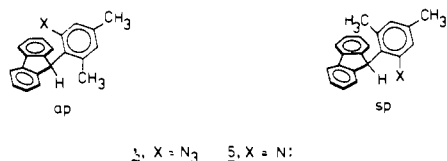
these results in terms of the difference in conformation of the nitrenes **2** generated from the two precursors. From **1**, generation of *ap*-nitrene **2ap** is expected by assuming the least motion principle for the ring opening. On the other hand, from **3**, which is known to have mainly the *sp* conformation in the ground state,³ *sp*-nitrene **2sp** should be produced. In order to confirm this postulate, we attempted the generation of conformationally fixed nitrenes.



The isolation of conformational isomers and investigation of differences in their reactivities are the current topics in organic chemistry.⁴ In 9-arylfluorene systems, Ōki and his co-workers demonstrated that, when the aryl group was either the 2,6-disubstituted phenyl or the 2-substituted 1-naphthyl group, the barrier to rotation about the $\text{C}_9-\text{C}_{\text{Ar}}$ bond was high enough (more than 24 kcal/mol) to provide stable rotational isomers at room temperature.^{4c} Furthermore, the solvolytic reactivities of 9-(2-(bromomethyl)-6-methylphenyl)fluorene⁵ and the carbonyl reactions of 9-(2-formyl-1-naphthyl)fluorene⁶ have been shown to differ between the rotamers.

These results strongly suggest that, if the hydrogen at the other ortho position to the fluorenyl group in phenyl azide **3** is replaced by a suitable substituent, the rotational isomers of the azides would be isolable at room temperature and the conformationally fixed *o*-(9-fluorenyl)phenyl nitrenes would be generated independently.

We wish to report here the preparation of the conformationally fixed azides **4ap** and **4sp** and the generation of the corresponding nitrenes **5ap** and **5sp** which show contrasting behaviors both in the ESR and UV absorption spectra at cryogenic temperature and in the photochemical reactivities in fluid solutions.⁷



Results and Discussion

(A) Conformationally Fixed Azides. Preparation of Conformationally Fixed Azides. 3,5-Dimethyl-2-(9-fluorenyl)aniline (**6**)

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Table I. Isomerization Rates of **4ap** and Equilibrium Constants in Decalin

temp, °C	k , 10^5 s^{-1}	$K = [\text{sp}]/[\text{ap}]$
40.3	3.02	(12.4) ^a
56.7	19.1	10.9
61.2	30.6	10.4
68.8	66.8	9.78
80.2		9.14

^aThis value was obtained indirectly from the other thermodynamic parameters.

Table II. Kinetic and Thermodynamic Parameters for the Conversion of **4ap** to **4sp**

$\Delta H^\ddagger = 22.5 \text{ kcal/mol}$	$\Delta H^\circ = -1.70 \text{ kcal/mol}$
$\Delta S^\ddagger = -7.6 \text{ eu}$	$\Delta S^\circ = -0.42 \text{ eu}$
$\Delta G^\ddagger_{300} = 24.8 \text{ kcal/mol}$	$\Delta G^\circ_{300} = -1.57 \text{ kcal/mol}$
$k_{300} = 5.38 \times 10^{-6} \text{ s}^{-1}$	$K_{300} = 14.0$

was obtained by the Lewis acid catalyzed thermal rearrangement of *N*-(9-fluorenyl)-3,5-xylylidine and separated into the stable rotational isomers, **6ap** and **6sp**, by means of column chromatography on silica gel. They were converted separately to the corresponding azides, **4ap** with mp 121–122 °C and **4sp** with mp 113–114 °C, by the Sandmeyer reaction (Scheme I). Assignment of the conformation of the rotational isomers was readily made by ¹H NMR spectroscopy by considering the ring current effect of the fluorene ring. In **4ap**, the methyl group at the 3-position occupies the deshielding area and, therefore, shows up at δ 2.63. In contrast, since the methyl group in **4sp** is situated in the shielding zone, we observe the signal of this methyl group at δ 1.06. The isomeric purity is kept for months at ambient temperature for the samples of **4ap** and **4sp** in the crystalline state. The interconversion of these rotamers is, however, not unobservable in solution. The rates are, however, slow at room temperature enough to examine the photochemical reactivities of these rotamers independently.

Barrier to Interconversion. The isomerization rates of the azides have been determined in decalin at 40–69 °C, and the results for equilibration starting from *ap*-azide **4ap** are summarized in Table I. The azide group was thermally stable in this temperature range. When the data are treated according to the Eyring equation, we obtain the activation parameters for the conversion of the *ap* isomer to the *sp*, together with the free energy of activation and the calculated rate constant at 300 K as given in Table II.

It is found in Table I that the equilibrium constant, K , is moderately large, meaning that **4sp** is more stable than **4ap**. The significant temperature dependence of the equilibrium constant indicates that this equilibrium is mainly controlled by the enthalpy factor. The thermodynamic parameters obtained according to the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$ are shown together in Table II. The high population of the *sp* conformation is already reported for *o*-(9-fluorenyl)phenyl azide (**3**) and explained in terms of the electronic repulsion between the azide group and the fluorene ring.³

From the rotational barrier, we can calculate that the time required for the conversion of, e.g., 5% of the *ap*-azide to the rotational isomer at 27 °C in solution is $9.1 \times 10^3 \text{ s}$. Since the photoreactions discussed in the subsequent sections were carried out at the temperature below 27 °C and in the very short reaction time, absence of the interconversion of the starting material in the course of the reaction was guaranteed.⁸

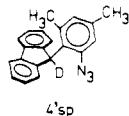
(8) It is indicated that the rates of interconversion of the rotational isomers in 9-arylfluorene systems are accelerated in basic media (ref 6). Moreover, when a solution of **4** in methanol containing sodium methoxide or in diethylamine was allowed to stand in the dark at room temperature, **4** was consumed to give the product derived from the *o*-quinoid imine intermediate (**11**), namely **14** or **20**. This was thought to cause another problem. Though the initial rate of the reaction in the dark was larger than that of rotational isomerization, the reaction was confirmed still to be too slow to compete with the photoreactions carried out under our conditions. Moreover, the barrier to interconversion between the amine rotamers, **6ap** and **6sp**, has been obtained to be ca. 27 kcal mol⁻¹. The conformational stability of **6** is larger than that of **4**.

Table III. ESR Fields and Zero-Field Parameters for Various Triplet *o*-(9-Fluorenyl)phenylnitrenes at 4.2 K

precursor of nitrene	resonance field, ^a G	shift, ^b G	<i>D</i> , ^c cm ⁻¹
phenyl azide	6824	0	1.012 ^d
1-azatriptycene (1)	6730	-94	0.9764
9-(2-azidophenyl)fluorene (3)	6750	-74	0.9838
ap-3,5-dimethyl-2-(9-fluorenyl)phenyl azide (4ap)	6722	-102	0.9735
sp-3,5-dimethyl-2-(9-deuterio-9-fluorenyl)phenyl azide (4' sp)	6745	-79	0.9823

^aThe microwave frequency was normalized at 9.2196 GHz. ^bThe negative values correspond to downfield shifts relative to the signal position of phenylnitrene. ^c $D = (g\beta H_{xy})^2 / H_0 - H_0$. ^dThe agreement with the literature data¹⁰ is excellent.

(B) Spectroscopic and Chemical Behavior of Nitrenes 5ap and 5sp at Cryogenic Temperatures. Detection of Triplet 3,5-Dimethyl-2-(9-fluorenyl)phenylnitrenes by ESR Spectroscopy. Since Smolinsky and Wasserman reported the first observation of the ESR spectrum of triplet phenylnitrene in 1962,⁹ this technique has proven to be a standard method for studying nitrenes. Irradiation of 4ap with a high-pressure mercury lamp in a methylcyclohexane glass at 4.2 K produced an intense signal at 6722 G in the X-band ESR spectrum. This signal is assigned to the X,Y transition of triplet 3,5-dimethyl-2-(9-fluorenyl)phenylnitrene ($D = 0.9735 \text{ cm}^{-1}$, $E = 0.000 \text{ cm}^{-1}$). Under these conditions, however, no signal characteristic of triplet species was observed in irradiation of 4sp. The starting material was consumed as efficiently as 4ap, but all attempts to detect the triplet 5sp were unsuccessful at several temperatures and in some other matrices. We could observe the triplet nitrene with *sp* conformation in the photolysis of 9-deuterio derivative (4' sp) at 14 K. The effect of



the 9-deuterium substitution on the resonance magnetic field is not conceivable. The signal due to the X,Y transition appeared at 6745 G ($D = 0.9823 \text{ cm}^{-1}$, $E = 0.000 \text{ cm}^{-1}$), which was shifted to higher field by 23 G compared with that of the triplet nitrene with *ap* conformation.

The triplet nitrenes with *ap* (5ap) and *sp* (5' sp) conformations both showed a linear Curie plot in the temperature range 14–85 K, indicating that these species had triplet ground states. Triplet nitrenes 5ap and 5' sp showed different thermal stability; 5ap which survived at 105 K was slightly more stable than 5' sp. The latter disappeared rapidly at 100 K: a stability comparable to that of parent phenylnitrene. The resonance position of the X,Y transition and zero-field parameters for various triplet nitrenes are collected in Table III. Previously we postulated that triplet nitrene 2 with the lower-field X,Y transition generated from 1-azatriptycene had the *ap* conformation and 2 with higher-field transition from the azide 3 had the *sp* conformation.^{2a,2c} This assignment is in agreement with the present results. In order to disclose the origin of such a slight but significant difference of resonance fields between conformational isomers, we attempted the calculations on the *ap* and *sp* rotamers of *o*-(9-fluorenyl)phenylnitrene.

Spin Density Calculation of Rotational Isomers of 2 with the INDO-UHF MO Method. Several workers have undertaken the calculations of spin densities and zero-field splitting (zfs) parameters on phosphorescent triplets,¹¹ biradicals,¹² carbenes,¹³ and

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Table IV. Spin Densities Calculated with INDO-UHF

atom	phenylnitrene	2ap	2sp
N	1.7820	1.7726	1.7760
C ₂	-0.2759	-0.2804	-0.2798
C ₃	0.2963	0.2993	0.2963
C ₄	-0.1528	-0.1561	-0.1558
C ₅	0.2204	0.2216	0.2191
C ₆	-0.1528	-0.1553	-0.1573
C ₇	0.2963	0.2887	0.2905
H ₂₁	-0.0127	-0.0130	-0.0130
H ₂₂	0.0107	0.0110	0.0110
H ₂₃	-0.0093	-0.0095	-0.0094
H ₂₄	0.0107	0.0110	0.0111
fluorenyl group	(-0.0127) ^a	0.0104	0.0111
(C ₈)		-0.0181	-0.0136
(C ₉ , C ₁₅)		0.0113	0.0113
(H ₂₅)		0.0013	-0.0005

^aThe value on hydrogen replaced by the fluorenyl group.

nitrenes.¹⁴ Hutton and Roth carried out HMO and unrestricted Hartree-Fock (UHF) calculations on the geometric isomers of 1- and 2-naphthylmethylenes and obtained a good agreement of the calculated zfs parameters with the experimental values.^{13b} We recently applied a similar method to the calculation of the zfs parameters of 7*H*-benz[*d,e*]anthracen-7-ylidene and obtained an acceptable result.¹⁵ Hall and his co-workers carried out INDO-UHF calculations on a series of 4-substituted phenylnitrenes and showed a good correlation between experimental zfs parameters, *D*, and calculated spin-spin distances.^{14c}

The spin densities calculated with INDO-UHF on phenylnitrene and the rotational isomers of 2 are shown in Table IV. The geometry used in the calculations was adopted from the X-ray crystal structure of related compounds.¹⁶ For simplicity, the plane of the phenylnitrene moiety was assumed to be perpendicular to the fluorene ring.¹⁷ For the C-N bond length, 1.33 Å was used according to the value used by Shillady and Trindle in the calculation of phenylnitrene with MINDO-OPTMO.¹⁸ Since it is known that one-center Coulomb integrals give a dominant contribution to the zfs parameters in nitrenes, the experimental zfs parameters are essentially correlated to the nitrogen spin density as reported in the case of some aryl nitrenes.^{14a,b} It is seen in Table IV that the difference in the spin densities on the nitrenic center of the three compounds is relatively small, though the order of the calculated spin densities is in parallel with that of the experimental zfs parameters. Hall and his co-workers pointed out on 4-substituted phenylnitrenes that the variation of the *D* values was determined by small changes in spin densities on the substituent and the carbon atoms in the ring when the spin density on nitrogen was essentially constant.^{14c} It is expected that, in the case of 2ap, the *p*_x-odd electron interacts with the π system of

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(15) Izuoka, A.; Murata, S.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3526.

(16) Murata, S.; Mori, T.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1970.

(17) In crystals the aryl group of 9-arylfuorenes is twisted by 6–12° from the perpendicular geometry (ref 16). In this calculation, however, there was essentially little change on the results even when the twisted geometry was used.

(18) Shillady, D. D.; Trindle, C. *Theor. Chim. Acta (Berlin)* **1976**, *43*, 137.

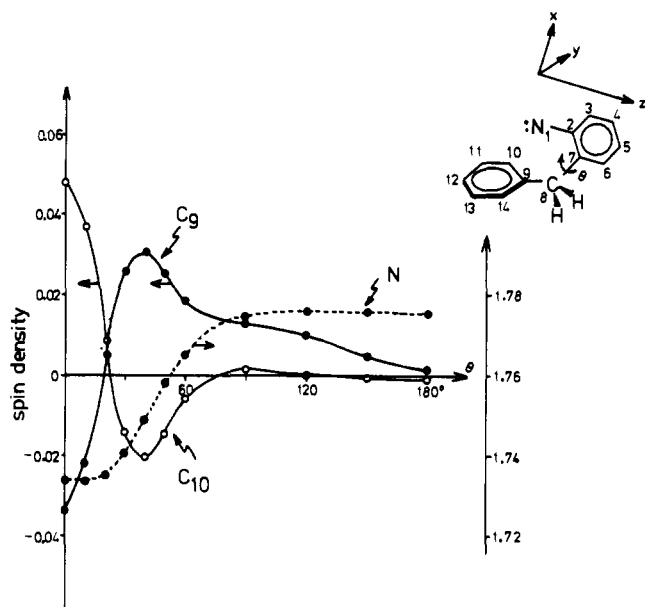


Figure 1. Changes of calculated total spin densities on nitrogen, C₉, and C₁₀ by driving the dihedral angle, θ , in 2-nitrenodiphenylmethane.

the fluorene ring and this through-space interaction will cause a spin delocalization to reduce the zfs parameter. Although the spin densities appear on the aromatic carbons of the fluorene ring in the ap form as shown in Table IV, it is rather small, and we find comparable spin densities on C₉ and C₁₅ even in the sp form. In order to investigate the origin of this unexpected results, we performed a model calculation on the spin delocalization of the nitrenic center in 2-nitrenodiphenylmethane.

Figure 1 shows changes of total spin densities on nitrogen and some aromatic carbons brought about by driving the dihedral angle, θ . From the components of the spin densities on the nitrenic center, the spin density on the p_y orbital is found to be independent of the dihedral angle and it is the p_x -odd electron that interacts with the π system of the benzene ring. Drastic changes of the sign of spin densities¹⁹ on C₉ and C₁₀ indicate that the through-space interaction between the p_x electron on nitrogen and the π orbital on C₉ and C₁₀ reaches a maximum at the dihedral angles of 0° and ca. 40°, respectively. The through-space interaction almost disappears at $\theta = 70$ –80°. In the case of **2ap**, the dihedral angle of the phenylnitrene moiety with each benzene ring of the fluorene unit is ca. 60°, at which the interaction of the two groups is predicted to be relatively small. Moreover, in comparison with 2-nitrenodiphenylmethane, the benzene ring in **2ap** is twisted by ca. 30°, reducing the interaction to some extent.

We then examined an energy level and a shape of occupied molecular orbitals which are constructed for the perpendicular conformation by the correlation of the molecular orbitals of the fluorene and phenylnitrene units, which are shown separately in terms of symmetry about the mirror plane. As seen in Figure 2, the antisymmetric molecular orbital of phenylnitrene, the orbital of the p_y -odd electron, interacts with the highest molecular orbital of fluorene, which is not the case with 2-nitrenodiphenylmethane. This interaction causes the delocalization of the odd electron over the π system of the fluorene ring even in the sp conformation.

Since through-space interaction of the p_x -odd electron with the π system of the fluorene ring is not so favorable in the ap conformation and the p_y -odd electron is delocalized even in the sp conformation, the calculated difference between the rotamers in delocalized spin densities over the fluorene ring becomes negligibly small. It is not known at the present stage if the small differences

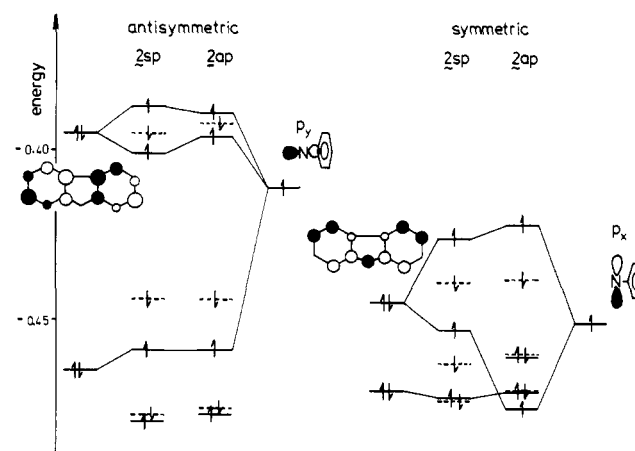


Figure 2. Calculated energy levels of occupied molecular orbitals for the perpendicular conformation of **2ap** and **2sp**. Energy levels described by solid lines are occupied by α spins and those described by dotted lines are occupied by β spins.

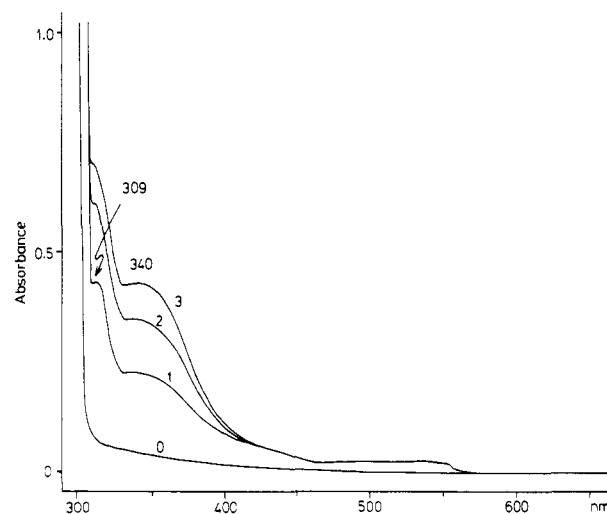


Figure 3. UV absorption spectra obtained by irradiation of **4ap** in an EPA matrix at 77 K. The spectra were recorded at (0) 0, (1) 5, (2) 10, and (3) 16 min after continuous irradiation.

of the total spin density on the nitrenic center and of spatial distributions of spins onto the phenylnitrene moiety might be enough to explain the experimental small difference between the position of the X,Y transition in the phenylnitrene and in rotamers of **2**.

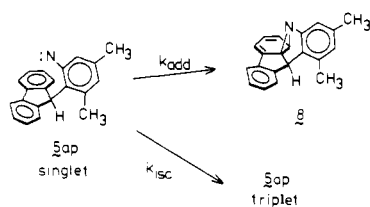
In INDO-UHF calculations, we cannot obtain the evidence that the difference of resonance field between triplet nitrene rotamers, **5ap** and **5sp**, should be due to the delocalization of the p -odd electron at the nitrenic center over the π system of the fluorene ring. In order to obtain more accurate information of the spin distributions on nitrenes **2**, a calculation with more rigorous methods containing geometry optimization and electron configuration mixing would be required.

UV Absorption Spectroscopy during the Irradiation of Rotamers of 3,5-Dimethyl-2-(9-fluorenyl)phenyl Azide at 77 K. In order to detect the triplet nitrenes independently and other singlet intermediary species that were not found by ESR, UV spectra were obtained after irradiation of **4ap** and **4sp** at 77 K with a high-pressure mercury lamp. In the photolysis of **4ap** in an EPA glass, absorptions at 309 and 340 nm increased with irradiation (Figure 3). The band at 309 nm is assigned to the ap -nitrene **5ap**.²⁰ The

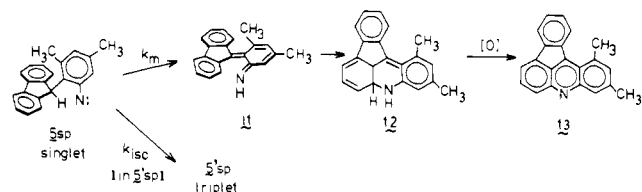
(19) It is indicated theoretically and experimentally that the spin density is transferred to the adjacent atoms in the opposite sign from the atom with an unpaired electron. A spin-ordering problem is discussed by Maynau and his co-workers: Maynau, D.; Said, M.; Malrieu, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5244.

(20) It is well-known that, when irradiated at 77 K, phenyl azide shows a broad absorption between 300 and 420 nm. This band is assigned to triplet phenylnitrene. Recently, Schuster pointed out, however, that the absorption was likely to be due to the singlet intermediate: (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228. (b) Schrock, A. K.; Schuster, G. B. *Ibid.* **1984**, *106*, 5234.

Scheme II



Scheme III



broad absorption at 340 nm is clearly assigned to azanorcaradiene derivative **8**, since this band closely resembles the norcaradiene derivative **9** isolated from the photorearrangement of hydrocarbon triptycene.¹ Moreover, as shown in a subsequent section, this spectrum was observed by the irradiation of **4ap** at room temperature and changed in the presence of base to absorptions assigned to the azepine derivative **10**, which was the isolated product. Azanorcaradiene **8** is thought to be formed by intramolecular addition of the nitrene to the double bond of the fluorene ring lying underneath (Scheme II). These spectroscopic behaviors of **4ap** at 77 K are consistent with that of 1-azatriptycene **1**.^{2b}

On the other hand, in the irradiation of **4sp** under similar conditions, the absorptions at 367, 426, and 554 nm were obtained. The broad band at 554 nm is assigned to the *o*-quinoid imine derivative **11**, which is formed by the hydrogen migration from the 9-position of the fluorene moiety to the nitrenic center. This characteristic band was also observed in the photolysis of *o*-(9-fluorenyl)phenylnitrene **2**,^{2b} in which the position of the band was at 507 nm. A bathochromic shift of 47 nm is noted for the dimethyl derivative **11**. If the *o*-quinoid species essentially had a conformation with a twisted double bond and rather 1,4-biradical character.²¹

When the irradiation was continued, the absorption at 554 nm started to disappear and the intensity of peaks at 367 and 426 nm increased with isosbestic points at 439 and 620 nm (Figure 4). When the sample solution was allowed to warm to room temperature and aerated, it was a bright yellow color with absorptions at 358, 377, and 419 nm. The UV spectrum resembles closely that of indeno[*k,l*]acridine.²² The product could be isolated by means of chromatography and identified as 10,12-dimethyl-indeno[*k,l*]acridine (**13**) as predicted. The *o*-quinoid imine **11** is considered to photocyclize conrotatorily to give dihydroindenoacridine **12** which then was oxidized by air to provide the final product, **13** (Scheme III).

The UV absorption spectrum obtained by the irradiation of **4sp** at 77 K was consistent with that of *o*-(9-fluorenyl)phenyl azide (**3**), indicating the generation of *sp*-nitrene from **3**. In the **4sp**, however, the absorbance of photogenerated *o*-quinoid species was more intense than in the case of **2** and the photocyclization of **11** occurred smoothly. The remarkable reactivity of **5sp** is probably

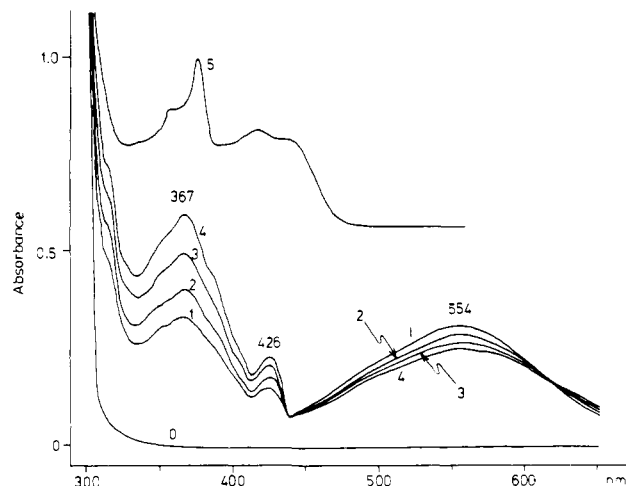


Figure 4. UV absorption spectra obtained by irradiation of **4sp** in an EPA matrix at 77 K. The spectra were recorded at (0) 0, (1) 13, (2) 20, (3) 31, and (4) 46 min after continuous irradiation. Spectrum 5 was recorded after the sample solution was allowed to warm to ambient temperature and aerated. This spectrum is shifted upward by 0.55 of absorbance for clarity.

due to the easy access of the nitrenic center to the 9-hydrogen of the fluorene unit compared with the nitrene generated from **3**. The repulsive nonbonding interaction of the methyl group at the 3-position with the π electron of the fluorene ring appears to be responsible. The irradiation of 9-deuterio derivative **4^{sp}** under these conditions gave essentially the same results as the unlabeled material, although we could not confirm the generation of the triplet nitrene **5^{sp}** in the UV spectrum because of the interference by the broad and intense absorptions due to *o*-quinoid imine **11** and its photocyclized product **12**.

Different Behaviors between Rotamers of 3,5-Dimethyl-2-(9-fluorenyl)phenylnitrenes at Cryogenic Temperature. The conformationally fixed nitrenes generated by the irradiation of **4ap** and **4sp** showed the remarkable contrast of the ESR and UV absorption spectroscopic and chemical behaviors at cryogenic temperatures. The behaviors of the *ap*- and *sp*-nitrenes corresponded to those of the nitrene generated from 1-azatriptycene (**1**) and of *o*-(9-fluorenyl)phenylnitrene, respectively.² Our expectation of two conformations of the nitrenes generated from precursors, **1** and **3**, was now clearly verified. The different behavior between the rotamers is explained in terms of the different competition between the singlet reactions and intersystem crossing to the triplet nitrene in each rotamer. In the singlet **5ap**, the addition to the double bond of the fluorene ring is a favorable reaction path, since the nitrenic center is located right above the fluorene ring. Intersystem crossing to triplet **5ap** can compete with the singlet reaction to give the triplet ESR signals. On the other hand, in the singlet **5sp**, the hydrogen at the 9-position of fluorene is so close to the nitrenic center that the exclusive reaction is a 1,4-migration of the hydrogen.²³ The latter reaction is too rapid for the intersystem crossing process to be competitive. The replacement of the hydrogen with deuterium retards the 1,4-migration and allows intersystem crossing to the triplet to compete with the 1,4-migration. The remarkable isotope effect suggests to us the operation of the tunneling through a potential barrier in this process. Tunneling in proton-transfer reactions in solution has two general features:²⁴ nonlinear Arrhenius plots and

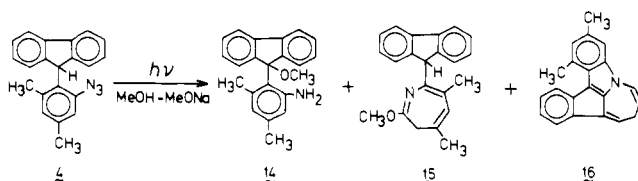
(23) A similar situation is presented for 1-methyl-8-nitrenonaphthalene: Platz, M. S.; Burns, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4425.

(24) Caldin, E. F. *Chem. Rev.* **1969**, *69*, 135. The isomerization of sterically hindered aryl radicals is reported to occur by tunneling. Recently the evidence were presented that the hydrogen atom abstraction by methyl radical and triplet diphenylcarbene from the matrix host took place by this mechanism: (a) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 6803. (b) Sprague, E. D. *J. Phys. Chem.* **1977**, *81*, 516. (c) Le Roy, R. J.; Murai, H.; Williams, F. *J. Am. Chem. Soc.* **1980**, *102*, 2325. (d) Platz, M. S.; Senthilnathan, V. P.; Wright, B. B.; McCurdy, C. W., Jr. *Ibid.* **1982**, *104*, 6494.

(21) Storr and his co-worker obtained the red-colored intermediate in the flash vacuum pyrolysis of 2-aminobenzyl alcohols, though they assigned it not to *o*-quinoid imine but to dihydroacridine: Bowen, R. D.; Davies, D. E.; Fishwick, C. W. G.; Glasbey, T. O.; Noyce, S. J.; Storr, R. C. *Tetrahedron Lett.* **1982**, *23*, 4501.

(22) This compound was reported by Wittig and Steinhoff; λ_{\max} (log ϵ) 349 (3.89), 368 (4.15), 400 (3.94), and 424 nm (3.92): Wittig, G.; Steinhoff, G. *Liebigs Ann. Chem.* **1964**, *676*, 21.

Scheme IV

Table V. Photoproducts in Methanol Containing Sodium Methoxide^a

substrate	yield, %		
	14	15	16
4ap	9	8	70
4sp	40	22	29
4'sp	24	23	32

^a 27 °C, [substrate]₀ = 3.7 × 10⁻⁴ M, [MeONa]₀ = 5.7 × 10⁻³ M.

anomalous isotope effects beyond the classical limitations. The maximum primary isotope effect in the absence of the tunneling mechanism is given by eq 1, where k_H and k_D are the rate constants

$$k_H/k_D = \sqrt{2} \exp(\Delta E/RT) \quad (1)$$

for hydrogen and deuterium abstraction, respectively, and ΔE is the difference in zero-point energy between the C-H and C-D bonding. Assuming that the migration of the hydrogen in **5sp** is expressed as a one-dimensional reaction along a linear path, ΔE is calculated from the difference of stretching frequencies, $\Delta\nu$, between C-H and C-D bonds, $\Delta E = h\Delta\nu N_A/2$, in which h is the Plank constant and N_A is the Avogadro number. If we assume $\Delta E = 350 \text{ cm}^{-1}$ (1.00 kcal/mol), the maximum isotope effect in the absence of tunneling is obtained as 9.8×10^2 even at 77 K. At this temperature the migration of deuterium in 9-deuteriotriene (**5'sp**) must be slow enough to compete with the intersystem crossing, allowing the triplet nitrene to be observed even though in a very weak intensity. The large value of the maximum primary isotope effect calculated without tunneling mechanism at cryogenic temperatures prevents us from concluding that this process occurs by tunneling of the hydrogen atom. The above assumption is, however, not valid in the case of the reaction in fluid solutions at room temperature. As shown in a subsequent section, we estimate the deuterium isotope effect on the migration of 9-hydrogen in **5sp** to be 1.84, which is much smaller than the value, 7.6, calculated with the above equation at 298 K.

Unfortunately, since we have no technique to determine the absolute rate constant of the hydrogen migration in **5sp**, we cannot prove a tunneling mechanism at the present stage.²⁵

(C) Photoreactions of Azides 4ap and 4sp in Fluid Solutions. We have studied the photoreactions of **4** in methanol containing sodium methoxide, in diethylamine, and in acetonitrile in the presence of tetracyanoethylene.²⁶ In this section, the photoreactions are discussed in reference to those of well-documented arylnitrenes²⁷ and the reactivities of the two rotamers are compared.

Photoproducts in Methanol Containing a Small Amount of Sodium Methoxide. A solution of azide **4ap** or **4sp** in methanol containing 8% (v/v) ether for solubility of material was irradiated with a low-pressure mercury lamp under nitrogen atmosphere. In the presence of a small amount of sodium methoxide (5.7×10^{-3} M), three reaction products were obtained after separation

(25) A laser flash photolysis study on the temperature dependence of the isotope effect on the yield of the 550-nm band is planned. The data at 77 K would prove the tunneling interpretation. We thank a referee for pointing this possibility out. These future works will be published elsewhere.

(26) In the absence of the addenda, the photoproducts were too complicated to analyze.

(27) The photochemistry of arylnitrenes in solutions has been reviewed; for example: (a) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900. (b) Scriven, E. F. V. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982. (c) "Azides and Nitrenes—Reactivity and Utility"; Scriven, E. F. V., Ed.; Academic Press: New York, 1984. (d) Wentrup, C. "Reactive Molecules"; Wiley: New York, 1984; Chapter 4.

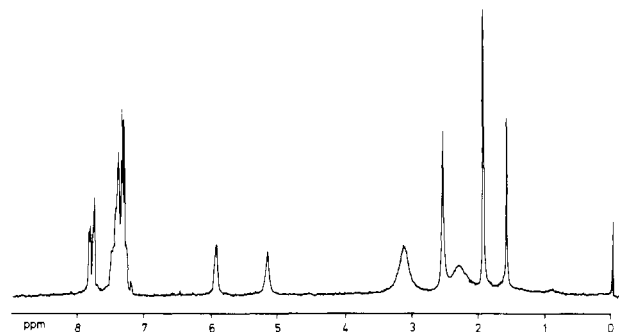
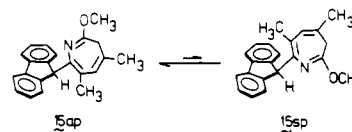


Figure 5. ¹H NMR spectrum (100 MHz) of **15** obtained in CDCl₃ at 25 °C. The sharp peaks at δ 0.0 and 1.6 are due to tetramethylsilane and a contaminating water, respectively.

by chromatography (Scheme IV). The product distribution is shown in Table V. The methoxyamine **14** was characterized by its ¹H NMR spectroscopy, in which the proton at the 9-position of the fluorene ring was absent and the methoxy signal appeared at δ 2.77. In the IR spectrum the antisymmetrical and symmetrical stretching frequencies of the NH₂ group were observed at 3470 and 3360 cm⁻¹, respectively. On the analogy of related compounds,²⁸ the rotational barrier around the bond connecting the fluorene with the benzene ring should be high enough to distinguish the rotational isomers of **14** by ¹H NMR. We could, however, find **14** only in the *sp* conformation at room temperature. Strong intramolecular hydrogen bond of the amino group with the 9-methoxy group seems to favor the *sp* conformation exclusively. The formation of the methoxyamine **14** is rationalized by the conjugate addition of methanol to the *o*-quinoid imine **11**.

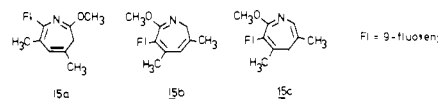
The second photoproduct was identified as the 3*H*-azepine derivative **15**.²⁹ The ¹H NMR spectrum of **15** at room temperature is shown in Figure 5. The line shape of the spectrum was much dependent on temperature. At -40 °C, two sets of



signals due to the presence of two isomers were observed in a 9:1:1 ratio which was hardly dependent on temperature. The conformation of the major and minor isomers is easily assigned by

(28) Rieker, A.; Kessler, H. *Tetrahedron Lett.* **1969**, 1227.

(29) A comment on the assignment of the 3*H*-azepine structure in **15** should be added. Though three possible structures were feasible from the ¹H NMR spectrum, we chose **15a** for the four following reasons. First, the



3*H*-azepine framework as shown in **15c** is rare, although there are some precedents for this type of substitution pattern as reported by Sundberg and his co-workers for the photoproducts of *o*-azidobiphenyl and 2-mesityl-5-methylphenyl azide (ref 31 and 32). There is no report of the isolated 2*H*-azepine derivative like **15b**. Secondly, at -50 °C, though the olefinic proton in **15** was observed at δ 5.95 for the major conformer and at δ 5.66 for the minor conformer in the ¹H NMR, the signals of one methyl group and one methylene group did not separate into those due to each conformer. It indicates that the two groups are situated so nearly on the axis of rotation around the C-fluorenyl bond that the difference of chemical shifts between the rotamers cannot be observable. These results seem to exclude the structure **15c**. For a third, we could obtain the ¹³C NMR at -45 °C to identify the signals of the only major conformer, **15ap**. The methylene carbon appeared at δ 37.8, which was very close to the value of the parent 2-methoxy-3*H*-azepine, δ 33.5 (ref 33). Finally, it is empirically known that the ¹H chemical shift of the 9-hydrogen of the fluorene moiety is sensitive to the substituent lying close. In the minor conformer (**15sp**), the proton was observed at δ 4.78, a value shifted to higher field by 0.41 ppm compared with that of **15ap**. The large high-field shift indicates that in **15sp** there is not such a large substituent as methyl or methoxy group near the hydrogen. This situation is similar to the case of 9-(2-methylphenyl)fluorene (ref 3 and 34). These results support the structure **15a**.

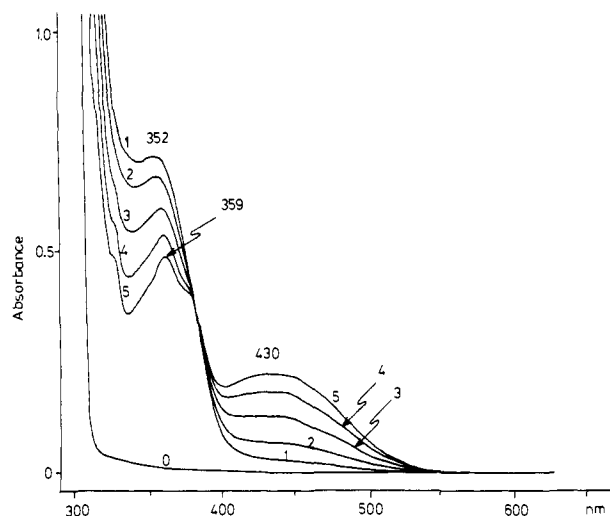
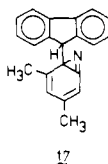


Figure 6. Change of UV absorption spectra obtained by irradiation of **4ap** in methanol-ether (94:6) containing triethylamine at 25 °C. The spectra were recorded (0) before irradiation and after irradiation of 25 s and standing at 25 °C for (1) 5, (2) 16, (3) 43, (4) 89, and (5) 400 min.

considering the ring current effect of the fluorene ring; the methoxy signals of the major and minor isomers are at δ 3.00 and 3.85, respectively. Since these two signals coalesced at 7 °C in the 100-MHz ^1H NMR, the rate and activation energy for the rotational isomerization at the coalescence temperature are estimated as 18.7 s^{-1} and 14.7 kcal/mol .³⁰ This is the first example of measurement of the rotational barrier on the fluorene derivative with a 7-membered ring at the 9-position. The considerable decrease of the barrier height compared with other 9-arylfluorenes is rationalized by the loss of planarity and rigidity of the 3*H*-azepine ring at the 9-position.

The formation of **15** is explained in terms of the well-known "benzazirine" reaction of aryl nitrenes.^{27,35} The intermediate benzazirine leading to **15** should be **17**, which is formed by attack of the nitrenic center to the substituted ortho carbon. This is contrary to the usual tendency that ortho-substituted phenyl azides undergo ring expansion involving migration of the unsubstituted ortho carbon.³²



The other azepine **16** is assigned to the dimethyl derivative of the compound obtained by the photorearrangement of 1-azatriptycene (**1**) under similar conditions.^{2a,c} The ^1H NMR data are consistent with the structure. This product is thought to be derived from the azanocaradiene **8**, which is in equilibrium with 1*H*-azepine **18** to give **16** by the base-promoted isomerization. The rate of the process to the final product **16** was dependent on the kind and concentration of bases. If triethylamine was used instead

(30) The value is for the process from the major to the minor isomer, calculated according to the graphical method of Jaeschke et al.: Jaeschke, A.; Muensch, H.; Schmid, H. G.; Friebohn, H.; Mannschreck, A. *J. Mol. Spectrosc.* **1969**, *31*, 14.

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

(32) Sundberg, R. J.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513.

(33) Though this compound was reported by Vogel et al., we could obtain it by irradiation of phenyl azide under the same condition as that of **4**: Vogel, E.; Erb, R.; Lenz, G.; Bothner-By, A. A. *Liebigs Ann. Chem.* **1965**, *682*, 1.

(34) The chemical shift of 9-hydrogen of this compound appeared at δ 5.30 for the sp conformer and at δ 4.90 for the ap conformer: Nakamura, M.; Nakamura, N.; Oki, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1097.

(35) It is the hot issue which of benzazirine and azacycloheptatetraene should be the stable isomer and reactive intermediates for amines. In this paper, we describe the intermediate tentatively as the benzazirine derivative.

Table VI. Temperature Dependence of the Photoproducts in Methanol Containing Sodium Methoxide^a

substrate	temp, °C	yield, %		
		14	15	16
4ap	27	9	8	70
	0	9	8	78
	-70	<5	5	51
4sp	27	40	22	29
	0	43	24	17
	-70	49	15	8

^a [Substrate]₀ = 3.7×10^{-4} M, [MeONa]₀ = 5.7×10^{-3} M.

Table VII. Dependence of the Photoproducts in Methanol on the Concentration of the Added Base^a

substrate	base	yield, %		
		14	15	16
4ap	none	<5	0	0
	MeONa, 5.7×10^{-4} M	10	5	79
	MeONa, 5.7×10^{-3} M	9	8	70
	MeONa, 4.4×10^{-2} M	<5	16	71
	Et ₃ N, 0.63 M	10	0	70
4sp	none	27	0	0
	MeONa, 5.7×10^{-4} M	36	6	29
	MeONa, 5.7×10^{-3} M	40	22	29
	MeONa, 4.4×10^{-2} M	36	26	24
	Et ₃ N, 0.63 M	37	0	28

^a 27 °C, [substrate]₀ = 3.7×10^{-4} M.

of sodium methoxide in a similar concentration (6.3×10^{-3} M), we could detect the precursor of **16** by means of reversed-phase HPLC, though it could not be isolated. The UV absorption of the precursor was obtained on an almost colorless irradiated solution. The spectrum (λ_{max} 352 nm) closely resembled that of the azanocaradiene **8**, which was obtained in the EPA matrix at 77 K. When the solution was allowed to stand at room temperature, the absorption at 352 nm decreased in the half-life period of ca. 40 min and the peaks at 359 and 430 nm appeared with an isosbestic point at 380 nm (Figure 6). The final spectrum was fully consistent with that of azepine, **16**. From these results it is concluded that the azanocaradiene **8** should be the precursor to **16** though it is not known whether **8** leads to **16** directly or via the short-lived 1*H*-azepine **18**. In the photolysis of phenyl azide in diethylamine, 1*H*-azepine is detected as a relatively long-lived transient,^{20a,36} and as shown subsequently we obtained the adduct of tetracyanoethylene with **18**. The transient spectrum with the peak at 352 nm, however, cannot be assigned **18**, since the 1*H*-azepine derivatives are usually colored to yellow or orange which should have the absorption at longer wavelength.³⁷

It would be reasonable to consider that the azepine **16** was produced specifically from the ap-nitrene **5ap** and the methoxyamine **14** was specifically from the sp-nitrene **5sp** by reference to the UV spectrum at cryogenic temperature. The product distributions shown in Table V, however, are not fully in line with this expectation. The methoxyamine **14** is formed in the photo-reaction of the ap-nitrene **5ap** even though in a low yield, and **16** is obtained in considerable yield from the sp-nitrene **5sp**. It should be emphasized that, in contrast with the stereospecific behaviors at cryogenic temperature, the crossover of the products from **4ap** and **4sp** is observed in the photolysis in a fluid solution at room temperature.

The dependence of the product distributions on the reaction temperature and on the concentration of the base is shown in Tables VI and VII, respectively. The loss of specificity in products is also observed even at low temperature, though the yield of the azepine **16** obtained from the sp rotamer **4sp** is lowered appreciably. It is shown in Table VII that the azepine **15** is formed

(36) DeGraff, B. A.; Gillespie, D. W.; Sundberg, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7491.

(37) (a) Cotter, R. J.; Beach, W. F. *J. Org. Chem.* **1964**, *29*, 751. (b) Sundberg, R. J.; Smith, R. H., Jr. *Tetrahedron Lett.* **1971**, 267.

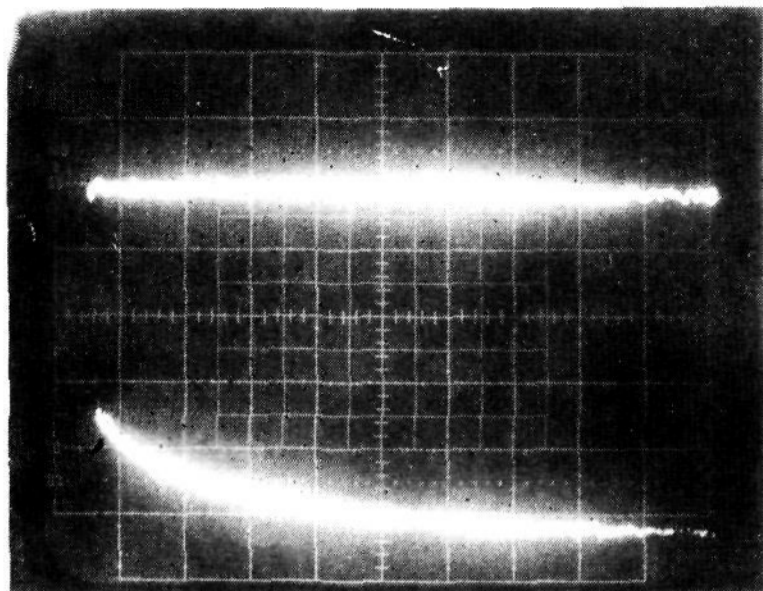


Figure 7. The lower curve represents the rise of an absorption at 340 nm after irradiation of **4ap** in methanol-ether. (One division is 500 ns.) The curve fits the single exponential equation. The upper line shows the I_0 level. The fluctuation of I_0 is less than 1%.

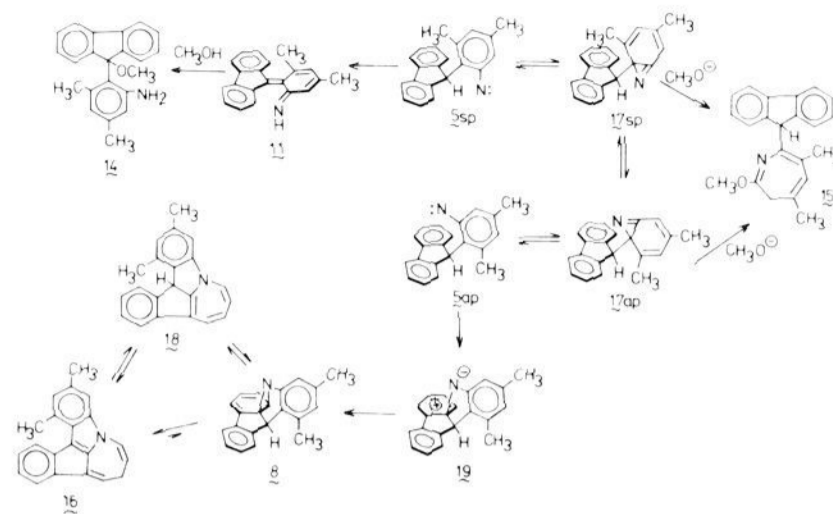
only in the presence of methoxide ion though the yield does not depend on the concentration linearly.³⁸ Irradiation of phenyl azide in methanol is reported to give 2-methoxy-3*H*-azepine in 11% yield.³⁹ A failure to form **15** in the absence of sodium methoxide might be explained in terms of low concentration of the intermediate benzazirine **17** and/or decrease of the rate of formation as a result of the reduced electrophilicity of **17** by the alkyl substituents.

In order to have a clue to disclosing the mechanism for the photoreaction of **4ap** and **4sp** in a methanolic solution, we carried out laser-flash photolysis experiments and determined the absolute rates of some processes.^{7b} In the photolysis of **4ap**, the rate of formation of the azanorcaradiene **8** was found to be $7.1 \times 10^5 \text{ s}^{-1}$ by monitoring the increase of absorbance at 340 nm (Figure 7). No absorption was observed even after 2 μs , at 550 nm where the *o*-quinoid imine **11** should absorb, though the methoxyamine **14** derived from **11** was obtained as a minor product by the preparative photolysis of **4ap** (vide supra). For **4sp**, the absorption at 550 nm was formed at a rate faster than the time resolution (10^8 s^{-1}) of our method and decreased at $2.6 \times 10^3 \text{ s}^{-1}$. The rate of the decay of this absorption is assigned to the reaction of *o*-quinoid imine **11** with methanol to give **14**. When the 9-deuterio derivative **4'sp** was irradiated, though the rate of formation of **11** was still too fast to be measured, the absorbance at 550 nm due to a laser pulse was only 68% of that of **4sp**.²⁵ The deuterium isotope effect on the 1,4-migration of 9-hydrogen of the fluorene ring in **4sp** is concluded to be responsible for the decreased concentration of the *o*-quinoid imine **11**. We note in Table V that, in the product distribution in the irradiation of **4'sp**, the yield of the methoxyamine **14** was extremely diminished. It is reasonable to assume that the concentration of **11** is proportional to the fraction of the 1,4-migration among the whole reaction path, $k_m/(k_m + k_o)$, where k_m shows the rate of the 1,4-migration and k_o means the total rate of the other reactions. Moreover, the value can be regarded as the ratio of **14** to all the reaction products, which is easily obtained from Table V: 0.44 for **4sp** and 0.30 for **4'sp**. The ratio of these two values, 0.68, should indicate the ratio of the concentration of *o*-quinoid imine **11**, which is sufficiently consistent with the value obtained from the difference of the absorbance described above, 0.68. From eq 2, where k_m^H and k_m^D

$$\frac{k_m^D}{k_m^D + k_o} \frac{k_m^H + k_o}{k_m^H} = 0.68 \quad (2)$$

stand for the rates of the 1,4-migration for **4sp** and **4'sp**, re-

Scheme V



spectively, and $k_m^H/(k_m^H + k_o)$ is equal to 0.44, we obtain the deuterium isotope effect for the 1,4-migration at 25 °C as $k_m^H/k_m^D = 1.84$.

In solution chemistry, a wide range of the deuterium isotope effect is reported for the hydrogen-transfer reactions from solvents to radicals⁴⁰ and triplet carbenes.⁴¹ In contrast with the remarkable effect in the matrix, the rather small isotope effect in the hydrogen migration from the 9-position to the nitrenic center was obtained in a fluid solution at room temperature. It seems to indicate the modest breaking of carbon-hydrogen bonds in the transition state.

The mechanism to explain the formation of the three products in the reaction of the conformationally fixed nitrenes, **5ap** and **5sp**, generated from the corresponding azides is summarized in Scheme V. As pointed out previously, we have to explain the crossover of the reaction products, namely, the formation of **14** from **5ap** and of **16** from **5sp**. An interconversion process between the rotational isomers has to intervene in the course of the reaction. Moreover, the rate of interconversion should be comparable to the reaction rate of the nitrenes, that is, in the range 10^5 – 10^6 s^{-1} .⁴²

Since the isomerization of the starting azides under these conditions is negligible as discussed in the first section, there remain four potential intermediates participating in the interconversion process. These are the excited azides **4***, the singlet nitrenes **5**, the *o*-quinoid imine **11**, and the benzazirine intermediate **17**. Since the C_9 - C_{Ar} single bond in question is not involved in the excitation, the rotational barrier should not be different from that of the ground state. Aryl azides do not fluoresce and their excited state potential energy curves are nearly dissociative. Moreover, no isomerization was observed in unreacted azides under irradiation. Therefore an azide in the excited state **4*** is not a good candidate. Though the rotational barrier of the singlet nitrene **5** is thought to be slightly lower than that of the azide **4** for steric reasons, the value should not be lower than 16.4 kcal/mol which is the value of 9-(2-methylphenyl)fluorene.³⁴ Thus the rate of isomerization at room temperature of the singlet nitrenes **5** is expected to be slower than 10^1 – 10^2 s^{-1} . If the isomerization between the rotamers takes place in this time scale, the reaction of the nitrenes should proceed stereospecifically since the rates of the reactions are much faster than that of the isomerization. The singlet nitrenes **5** are therefore excluded from the intermediates responsible for the crossover of the products. If the *o*-quinoid imine **11** is in equilibrium with the singlet nitrene, it is possible for **5sp** to isomerize to the rotational isomer. The yield of the azepine **16** should extremely decrease in the photolysis of the 9-deuterio derivative **4'sp**. It is not the case as shown in Table V. Moreover, this mechanism alone cannot explain the formation of **14** from the *ap*-nitrene (**5ap**).

(40) Engel, P. S.; Chae, W.-K.; Baughman, S. A.; Marschke, G. E.; Lewis, E. S.; Timberlake, J. W.; Luedtke, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 5030.

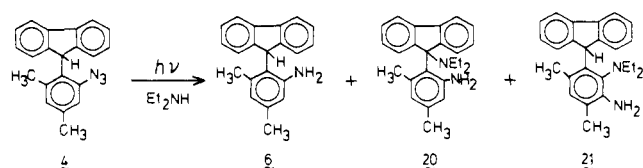
(41) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283.

(42) It is known by the measurement of the rate of formation of 1*H*-azepine in a secondary amine that the singlet nitrene, which is in equilibrium with benzazirine, has a lifetime of the order of microseconds (ref 20a and 36).

(38) The dependence of the rate of 1*H*-azepine formation on the concentration of the added amine was not linear in the reaction of benzazirine intermediate with diethylamine. In high concentration of the amine, the rate was independent of the concentration of the amine (ref 20a).

(39) Sundberg, R. J.; Smith, R. H., Jr. *J. Org. Chem.* **1971**, *36*, 295.

Scheme VI

Table VIII. Photoproducts in Diethylamine^a

substrate	yield, %			
	6ap	6sp	20	21
4ap	65	0	0	16
4sp	11	42	10	15

^a 27 °C, [substrate]₀ = 3.6 × 10⁻⁴ M.

The benzazirine **17** is a much more stable closed-shell isomer of the singlet nitrene **5** and the only intermediate responsible for the crossover of the products. The estimation of the rotational barrier in **17** is difficult, but it is reasonable to expect a considerable decrease of the barrier because of the loss of rigidity in the benzazirine ring and the change of the hybridization of the atom attached to the fluorene ring. The isomerization of **17** would be fast enough to compete with the reactions. It is known that 9-alkylfluorenes have a very low rotational barrier.⁴³

The crossover of the photoreactions of the conformationally fixed azides can now be rationalized by the rotational isomerization of the intermediate benzazirine during the course of the reaction. It should be pointed out that the product distributions are determined not only by the rate of each process but also by the concentrations of the intermediary species, that is the singlet nitrene **5**, the benzazirine **17**, and the *o*-quinoid imine **11**. Therefore, the effect of temperature on the product distribution is complicated, though it appears as shown in Table VI that the crossover of the products decreases probably due to considerable retardation of the isomerization rates of all processes at low temperatures.

It is sometimes inferred that a zwitterionic intermediate intervenes during the addition of a nitrene to double bonds.⁴⁴ If it applies to *ap*-nitrene **5ap** intermediate **19** would be formed, although it cannot be detected. When **5ap** was photolyzed in cyclohexane in the presence of triethylamine, the azepine **16** is obtained only in a trace amount. The solvent effect is presumably due to decreased stability of **19** in a nonpolar solvent.⁴⁵ The zwitterionic intermediate is also assumed in the photoreaction of 1-azatriptycene (**1**) on the basis of the kinetic evidence.^{2b}

We should point out, finally, a remarkable difference of the reaction of the *sp*-nitrene **5sp** in matrices and fluid solutions. While indenoacridine **13** was exclusively obtained in the matrix, it could not be detected at all in the methanolic solution. In solution, the intermediate is estimated to have a short lifetime of ca. 10⁻⁴ s at room temperature, and therefore the photocyclization cannot compete with the capture of **11** by methanol.

Photoproducts in Diethylamine. The photochemistry of aryl azides in secondary amines is well-documented.²⁷ A solution of the azides **4ap** or **4sp** in diethylamine was irradiated with a low-pressure mercury lamp under nitrogen atmosphere. After chromatographic separation, we could isolate three reaction products (Scheme VI). The product distribution and its dependence on the reaction temperature are shown in Tables VIII and IX, respectively.

To our surprise, the main product obtained was the corresponding amines, **6ap** and **6sp**. While the reaction of the *ap*-nitrene **5ap** proceeded stereospecifically, the *ap*-amine was obtained from the *sp*-nitrene. It is generally established that amines

Table IX. Temperature Dependence of the Photoproducts in Diethylamine^a

substrate	temp, °C	yield, %			
		6ap	6sp	20	21
4ap	27	65	0	0	16
	0	59	0	0	31
	-30	37	0	0	51
4sp	27	11	42	10	15
	0	8	36	13	19
	-30	5	15	20	27

^a [Substrate]₀ = 3.6 × 10⁻⁴ M.

are derived from triplet nitrenes. The irradiation of **4** in the presence of oxygen or 1,3-pentadiene in diethylamine gave no or a trace of the amine **6**. The result is not incompatible with the above mechanism.

The second product was obtained only from the photolysis of the *sp*-azide **4sp** and assigned to the diamine **20**. The product is the diethylamino analogue of the methoxyamine **14** obtained in methanol. The diamine **20** was characterized by the lack of the 9-hydrogen of the fluorene ring in its ¹H NMR spectrum and present exclusively in the *sp* conformation probably due to the stabilization by the intramolecular hydrogen bond. The *o*-quinoid imine **11** formed by the 1,4-migration of the hydrogen to the nitrenic center in the *sp*-nitrene **5sp** is considered to have reacted with the solvent to give **20**.

The last product was assigned to the *o*-diamine **21**, of which the ¹H NMR showed a single aromatic proton on the benzene ring at δ 6.55. This compound is expected to have a high rotational barrier around the C₉-C_{Ar} bond enough to isolate the isomers even at room temperature. In the photoreaction products, however, we could find the *o*-diamine **21** only with the *sp* conformation, which showed in the ¹H NMR spectrum a characteristically high field signal of the methyl group experiencing the shielding of the fluorene ring at δ 0.95. *o*-Diamines are also known to be formed from benzazirine intermediates. In general, *o*-diamines are formed on irradiation of condensed aromatic azides in the presence of secondary amines.⁴⁶ The *o*-diamine **21** was the first example, to our knowledge, obtained by the photoreaction of a phenyl azide derivative.⁴⁷ No azepine derived from benzazirine intermediate could be isolated from the photoreaction of the azides **4** in diethylamine; if any were present, the yield should be less than 5%.

It is well-known that photolysis of ortho-substituted aryl azide in diethylamine leads to oxidizable intermediates and gives pyridine derivatives and 2*H*-azepin-2-ones.³² From the photolysis under similar conditions of *o*-(9-fluorenyl)phenyl azide (**3**) we could indeed obtain the corresponding pyridine derivative.^{2c} In the reaction of the azides **4**, however, we were not able to obtain any product derived from an oxygen-sensitive intermediate. These results are in agreement with the reactions of 2-mesityl-5-methylphenyl azide and ascribed to a large steric effect.³²

The azepine **16** formed by the internal addition of the *ap*-nitrene **5ap** to the fluorene ring was not obtained in diethylamine. It is probably due to the lowered polarity of the solvent which would cause the destabilization of zwitterionic intermediate **19** described in the previous section. The intersystem crossing to the triplet nitrene becomes relatively efficient, and its reaction to the corresponding amine predominates in diethylamine.

As indicated in the photoreaction in methanol, crossover of the reaction products was also noted; formation of the *ap*-amine **6ap** from the *sp*-azide **4sp** took place in diethylamine and the reaction was one-way from the side of the *sp* conformation. It may be reasonable to assume that the intermediate responsible for the crossover of the products should be benzazirine which has a

(43) Rieker and Kessler reported that the rotational barrier of 9-*tert*-butylfluoren-9-ol was 9.4 kcal/mol at -85 °C. The corresponding hydrocarbon should have a lower barrier than the alcohol (ref 28).

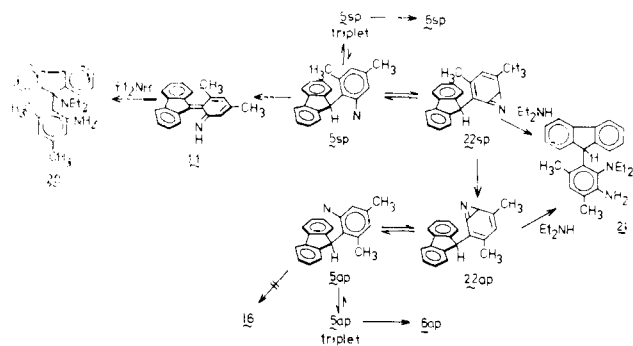
(44) Cadogan, J. I. G.; Kulik, S. *J. Chem. Soc. C* **1971**, 2621.

(45) A large solvent effect on the rate of formation of carbazole from *o*-azidobiphenyl is reported: Sundberg, R. J.; Gillespie, D. W.; DeGraff, B. A. *J. Am. Chem. Soc.* **1975**, *97*, 6193.

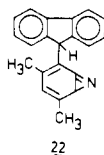
(46) (a) Carroll, S. E.; Nay, B.; Scriven, E. F. V.; Suschitzky, H. *Synthesis* **1975**, 710. (b) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1975**, 3845.

(47) The orthodiamines derived from phenyl azide derivatives are seldom known; 7-(diethylamino)-3-methyl-6-mesityl-4*H*-azepine obtained on irradiation of 2-mesityl-5-methylphenyl azide in diethylamine is converted to the corresponding orthodiamine on heating at 175 °C (ref 32).

Scheme VII



relatively low rotational barrier. The benzazirine intermediate leading to the *o*-diamine **21** should now be **22**, which has a different structure from that in methanol, **17**. The benzazirine **22**



formed from the singlet *sp*-nitrene **5sp** seems to be much less stable than that from the *ap*-nitrene because of a serious steric repulsion between the fluorene ring and the methyl group. Therefore, the rate of interconversion of the *sp* conformer of **22** to the *ap* conformer should be much faster than the back-reaction. In the reaction in diethylamine, the interconversion along the faster direction alone can compete with the electrophilic reaction of **22** with diethylamine, which is presumably the reason why the crossover of the photoreaction products was observed only in the *ap*-azide **4ap**. On the whole, the crossover observed in the reaction in diethylamine was less than that in methanol containing a small amount of sodium methoxide. The trend is thought to be partially due to the higher rotational barrier of **22** than that of **17**, though we should also consider the difference of the reaction rate of the benzazirines with the nucleophile.

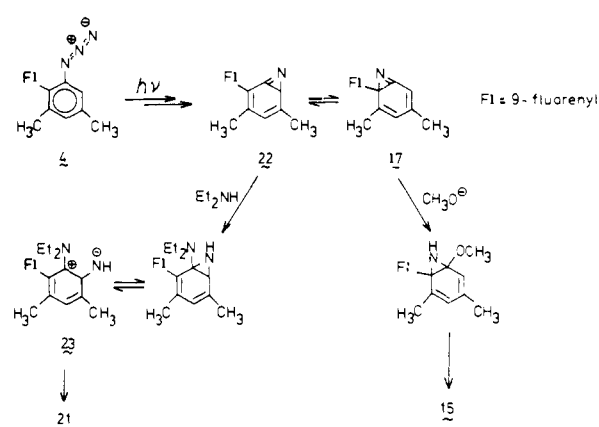
We have found an interesting temperature dependence of the product distributions as shown in Table IX. The yield of the diamines **20** and **21**, which were derived from the singlet nitrene, increased considerably at low temperature at the expense of the amines **6** (vide infra).

As shown above, the nitrenes **5** showed remarkably different reactivities in diethylamine from those in methanol. The reaction scheme for the formation of the products is shown in Scheme VII. In reference to other arylnitrenes, the reactivity of **5** in diethylamine differs considerably from that in methanol in the presence of sodium methoxide. The results appear to be explained by assuming that the steady-state concentration of the singlet nitrene, which is in equilibrium with the benzazirine, is higher in methanol than in diethylamine. There are three possible bases for the assumption. One is a lower reactivity of the triplet nitrene **5** in methanol and the presence of an equilibration of the singlet and triplet nitrenes.^{48,49} The alkyl substituents on the benzene ring may lower the energy of the singlet nitrene because of their electron-donating ability, and therefore the singlet state can be in equilibrium with the triplet state. The second basis is the effect of solvent on the energy level of the singlet state and the rate of intersystem crossing. It is established that the use of lone-pair carrying solvents such as tetrahydrofuran and dioxane results in stabilization of the singlet nitrene in equilibrium with a benz-

(48) The presence of equilibrium of the singlet and triplet states in aryl-nitrenes was already suggested, ref 20b and the following: (a) Reiser, A.; Wagner, H.; Boves, G. *Tetrahedron Lett.* **1966**, 2635. (b) Lindley, J. M.; McRobbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2194.

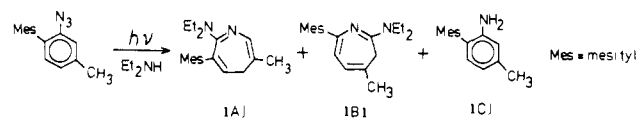
(49) Recently the triplet-singlet energy splitting of phenylnitrene in the gas phase has been reported as 4.3 kcal/mol: Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443.

Scheme VIII



azirine.^{46b,50} The solvent polarity effect on the rate of intersystem crossing is studied for a similar monocentric diradical, diphenylcarbene, where the rate is higher in the less polar solvents.⁵¹ For a third is mentioned the slightly higher nucleophilicity of diethylamine than methoxide ion, though it may be questionable to apply the order of nucleophilicity in S_N2 reactions to the nucleophilic reactions with a benzazirine intermediate.

The singlet nitrene in methanol is, therefore, thought to have such a long lifetime that the benzazirine intermediate of structure **22** can isomerize to **17**. Moreover, the strong nucleophile, diethylamine, attacks **22**, while methoxide ion reacts selectively with **17** for stereochemical reasons. As discussed by Sundberg and his co-workers, it would be reasonable to consider that the initially generated benzazirine has the structure **22** as the result of this predominant conformation in the precursor azide **4**.³² An interesting solvent effect on the benzazirine structure which reacts with amines is reported in the photoreaction of 2-mesityl-5-methylphenyl azide in diethylamine. In this solvent 4*H*-azepine **A**, which is derived from the benzazirine formed by the attack of the nitrenic center to the unsubstituted ortho carbon atom, is obtained in a 47% yield, and the 3*H*-azepine **B** formed by the attack at the substituted carbon is obtained in a 10% yield with the corresponding amine **C** in a 16% yield. However, in diethylamine-tetrahydrofuran (1:9) **B** is exclusively obtained in a 39% yield with the amine in a 19% yield.



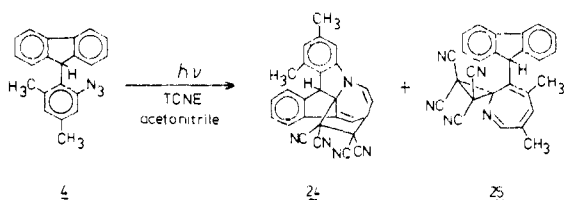
Once the attack of nucleophiles occurs and the benzazirine ring is expanded to the azepine derivative, the product structure is determined from its stability since azepines are believed to be the products of kinetic control.^{27a,b} It would be reasonable to think that the serious nonbonded repulsion between the fluorene ring and the diethylamino group in the azepine derived from **22** with diethylamine results in shifting the equilibrium toward the zwitterion **23** to give the *o*-diamine **21** (Scheme VIII).

Finally we have to refer to the reactivity of the triplet nitrenes **5** in two solvents. The low reactivity in methanol is rationalized by two reasons. First the availability of abstractable hydrogens in this solvent molecule may be so low that the process to the corresponding amine is unfavorable. Second the rate of dimerization to the azo compound, which is a usual reaction of triplet nitrenes in methanol, would be seriously reduced in the azide **5**

(50) (a) Scriven, E. F. V.; Thomas, D. R. *Chem. Ind. (London)* **1978**, 385. (b) Takeuchi, H.; Kinoshita, K.; Abdul-Hai, S. M.; Mitani, M.; Tsuchida, T.; Koyama, K. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1201. (c) Takeuchi, H.; Kasamatsu, Y.; Mitani, M.; Tsuchida, T.; Koyama, K. *Ibid.* **1978**, 780. (d) Takeuchi, H.; Igura, T.; Mitani, M.; Tsuchida, T.; Koyama, K. *Ibid.* **1978**, 783. (e) Senda, S.; Hirota, K.; Suzuki, M.; Asao, T.; Maruhashi, K. *J. Chem. Soc., Chem. Commun.* **1976**, 731. (f) Senda, S.; Hirota, K.; Asao, T.; Maruhashi, K. *J. Am. Chem. Soc.* **1977**, *99*, 7358.

(51) Sitzmann, E. V.; Langan, J.; Eissenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868.

Scheme IX

Table X. Photoproducts in Acetonitrile in the Presence of Tetracyanoethylene (TCNE)^a

substrate	yield, %	
	24	25
4ap	44	24
4sp	12	11

^a 27 °C, [substrate]₀ = 4.0 × 10⁻⁴ M, [TCNE]₀ = 1.2 × 10⁻³ M.

since the reaction center is sterically covered against the approach of another bulky attacking reagent. In diethylamine, it is well-known that triplet nitrenes are effectively reduced to the corresponding amines, though the mechanism of this process is not entirely established.⁵² Though the alkyl substitution on the benzene ring of phenylnitrene has a tendency to increase the yield of the corresponding amine,⁵³ the reason for the extremely high yield of the amine from **5** is not known at the present stage. The decrease of the yield of the triplet product at lower temperature as shown in Table IX would be explained by the retardation of this process and the decrease of the triplet concentration because of the shift of the equilibrium of the singlet nitrene to the benzazirine.

Photoproducts in Acetonitrile in the Presence of Tetracyanoethylene (TCNE). The photolysis of a solution of azide **4ap** or **4sp** in the presence of 3 equiv of TCNE under nitrogen atmosphere gave two adducts (Scheme IX) to which structure **24** and **25** were assigned. They are the dimethyl derivatives of the adducts obtained by the irradiation of *o*-(9-fluorenyl)phenyl azide (**3**) under similar conditions.²⁶ In Table X, the yields of the two adducts obtained in the photoreaction of **4ap** and **4sp** are shown. In this reaction, we obtained no photoproduct derived from the *o*-quinoid imine intermediate **11**, indicating that **11** could not be externally trapped by TCNE.⁵⁴ The low yields of the adducts in the photolysis of **4sp** seemed to indicate that **11** reacted with TCNE to give no isolable products.

The adduct **24** is regarded as the 1*H*-azepine derivative **18** trapped externally with TCNE. Though **24** should be formed from the *ap*-nitrene **5ap**, it was also obtained in large amount by the irradiation of **4sp**. The other adduct **25** is the analogue of the TCNE adduct of 2-nitrenobiphenyl, for which the structure has recently been determined by the X-ray crystallographic analysis in these laboratories.⁵⁵ Though this adduct appears to be formed via the isomerization of singlet nitrene to azacycloheptatetraene rather than benzazirine, the mechanism has not been fully explored yet. We could find the adduct **25** only in the *sp* conformation, which showed in ¹H NMR a signal of the methyl group at δ 1.02.

Note that in the photoreaction in acetonitrile containing TCNE the product crossover between the rotational isomers was also observed as was the case in methanol and in diethylamine.

Conclusions

The conformationally fixed nitrenes generated by the photolysis of rotamers of 3,5-dimethyl-2-(9-fluorenyl)phenyl azide, **4ap** and

4sp, showed a remarkable contrast not only at cryogenic temperature but also in fluid solutions at room temperature. These results provided, to our knowledge, the first example demonstrating differences in spectroscopic behaviors and reactivities between the defined conformers of a nitrene.⁵⁶

The behaviors of the *ap*- and *sp*-nitrenes, **5ap** and **5sp**, were parallel to those of the nitrenes generated from 1-azatriptycene (**1**) and *o*-(9-fluorenyl)phenyl azide (**3**), respectively. Thus we were able to obtain evidence for the assumption that the nitrenes generated from the two precursors, **1** and **3**, differed conformationally.

In matrices at cryogenic temperatures, the *ap*- and *sp*-nitrenes showed fully stereospecific behaviors. In fluid solutions, however, the photoproduct derived from **4ap** by addition of the nitrene to the double bond of the fluorene ring was obtained in the photolysis of **4sp**, and that derived from **4sp** by a conjugate addition of solvent to the *o*-quinoid imine **11** was detected in the irradiation of **4ap**. We concluded that the crossover of the photoreactions was due to the rotational isomerization of the intermediate benzazirine during the course of the reaction in fluid solutions.

In addition, we should point out some interesting reactivities of the nitrene **5** in view of aryl nitrene and different behaviors of **5** in methanol in the presence of sodium methoxide and in diethylamine, for example, an extremely high yield of the aniline **6** in diethylamine and a difference of the structure of the benzazirine intermediate in the two solvents. Though we explained these matters in terms of the larger stabilization of the singlet nitrene in methanol than in diethylamine, we could not satisfactorily demonstrate them at the present stage. We are continuing work to elucidate these problems.

Experimental Section

Spectral Measurements and Chromatography. ¹H NMR spectra were recorded on a Varian EM-390 spectrometer (90 MHz), a JNM-FX-100 spectrometer, and a JNM-GX-400 spectrometer. ¹³C NMR spectra were obtained with a JNM-GX-400 spectrometer operating at 100.5 MHz. IR and UV spectra were recorded on a Hitachi 295 spectrometer and a Cary 17 absorption spectrophotometer, respectively. Low- and high-resolution mass spectra were obtained with a JEOL D-300 machine. ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100 kHz field modulation) equipped with an optical transmission cavity and an Oxford cryomagnetic system or on Air Products LTD-3-100 liquid helium transfer system. The microwave frequency was measured with a Takeda Riken 5201M frequency counter and the X,Y band positions of triplet nitrenes were read with the aid of a Varian E-500 NMR gaussmeter. Time-resolved absorption spectra were obtained by the use of an excimer laser (Lambda Physik EMG 500) and the monitoring light source for the transient absorption spectra (an EG & G FX-265 UV xenon lamp). In analyses, a Waters M-6000A high-pressure liquid chromatograph was used. In preparative experiments, LC-08 gel permeation liquid chromatography (Japan Analytical Industry Co., Ltd.) and medium-pressure liquid chromatography (a Duramat pump, 76 Schutzart IP 31 and an ALTEX-MS UV monitor) on silica gel columns (Merk, LiChroprep Si60) were used.

Photolysis. Irradiation in the ESR and UV measurements was carried out with an Ushio USH-500D 500-W high-pressure mercury lamp. The UV absorption spectra at 77 K were obtained by the irradiation of the sample which was cooled in a liquid nitrogen Dewar vessel with a transparent window and placed in the sample chamber of a spectrometer. Preparative photolysis in fluid solution was carried out with a NORMAG TNN 15/32 15-W low-pressure mercury lamp or an sp-3 3-W "penlight" containing mainly 254 nm (SEN Tokushu Kogen Co., Ltd.).

Chemicals. 3,5-Xylydine was purchased from Tokyo Kasei Kogyo Co., Ltd. and distilled from potassium hydroxide. Methanol and methylcyclohexane were purchased from Wako Pure Chemical Industries, Ltd. Diethylamine was distilled from potassium hydroxide and stored over potassium hydroxide. Acetonitrile was distilled from phosphorus pentoxide. Tetracyanoethylene (TCNE) was purified by sublimation. Deuterium oxide was from Commissariat à l'Énergie Atomique (CEA), and an isotope enrichment of the material was 99.8%. Nitrogen gas used in photolysis in fluid solutions was purchased from Japan Oxygen Co., Ltd.,

(52) The mechanism involving hydrogen abstraction or electron transfer followed by proton migration is proposed: ref 20b.

(53) In the irradiation in diethylamine, the reported yields of the corresponding amines are 13%, 35%, and 29% for 2-methyl-, 2,4-dimethyl-, and 2,4,6-trimethylphenyl azides, respectively: ref 32.

(54) It is reported that the *o*-quinoid imine generated from [*o*-((trimethylsilyl)alkylamino)benzyl]trimethylammonium halide cannot be externally trapped: Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 5250.

(55) Murata, S.; Sugawara, T.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1198.

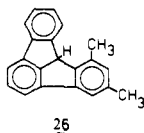
(56) The presence of geometrical isomers in equilibrium is detected by ESR at cryogenic temperatures for naphthyl-, vinyl-, and quinoly-carbenes—ref 13a and the following: (a) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129. (b) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1981**, *103*, 5503.

and its purity was more than 99.9995%.

***N*-(9-Fluorenyl)-3,5-xylyldine.** To a solution of 3.0 g (12.2 mmol) of 9-bromofluorene⁵⁷ in 30 mL of 2-propanol was added 1.9 g (15.7 mmol) of freshly distilled 3,5-xylylene and 1.2 g (14.6 mmol) of sodium acetate. The mixture was refluxed with stirring for 30–40 min. After rapid filtration of the hot suspension followed by cooling, the colorless precipitate was collected by filtration, washed with cold 2-propanol, and dried to afford 3.0 g (86%) of *N*-(9-fluorenyl)-3,5-xylylene as colorless granules: mp 126–127 °C; ¹H NMR (CDCl₃) δ 2.25 (6 H, s), 3.85 (1 H, br s), 5.67 (1 H, s), 6.48 (2 H, s), 7.2–7.8 (8 H, m); IR (KBr disk) 3360 cm⁻¹; MS found M⁺ 285.1524. C₂₁H₁₉N requires M⁺ 285.1517.

3,5-Dimethyl-2-(9-fluorenyl)anilines (6ap and 6sp). A mixture of 1.0 g (3.50 mmol) of *N*-(9-fluorenyl)-3,5-xylylene, 1.0 g of anhydrous aluminum chloride, and 10 mL of 3,5-xylylene was heated at 180 °C for 20 h under an argon atmosphere. To the cooled reaction mixture was added 20 mL of 5% aqueous sodium hydroxide. The organic material was extracted with benzene, and the extract was washed and dried over magnesium sulfate. The solvent and excess 3,5-xylylene were removed under reduced pressure. The residue was developed on a silica gel column (Wakogel C-200) with hexane–benzene (1:1). The *ap* form (6ap), 420 mg (42%), was eluted first and the *sp* form (6sp), 130 mg (13%), followed. The *ap* form: oil; ¹H NMR (CDCl₃) δ 2.17 (3 H, s), 2.48 (2 H, br s), 2.57 (3 H, s), 5.40 (1 H, s), 6.10 (1 H, s), 6.56 (1 H, s), 7.2–7.9 (8 H, m); IR (KBr disk) 3450, 3350 cm⁻¹; MS found M⁺ 285.1524. C₂₁H₁₉N requires M⁺ 285.1517. The *sp* form: colorless granules; mp 137–138 °C; ¹H NMR (CDCl₃) δ 1.05 (3 H, s), 2.21 (3 H, s), 3.83 (2 H, br s), 5.28 (1 H, s), 6.29 (1 H, s), 6.57 (1 H, s), 7.2–8.0 (8 H, m); IR (KBr disk) 3360, 3300 cm⁻¹; MS found M⁺ 285.1492. C₂₁H₁₉N requires M⁺ 285.1517. Elution with benzene gave 3,5-dimethyl-4-(9-fluorenyl)aniline (7) as colorless needles: mp 138–139 °C; ¹H NMR (CDCl₃) δ 0.99 (3 H, s), 2.56 (3 H, s), 3.29 (2 H, br s), 5.37 (1 H, s), 6.15 (1 H, s), 6.50 (1 H, s), 7.2–7.9 (8 H, m); IR (KBr disk) 3410, 3320 cm⁻¹; MS found M⁺ 285.1517. C₂₁H₁₉N requires M⁺ 285.1517.

3,5-Dimethyl-2-(9-fluorenyl)phenyl Azides (4ap and 4sp). To a cooled solution of 500 mg (1.75 mmol) of *ap*-3,5-dimethyl-2-(9-fluorenyl)aniline (6ap) in 22 mL each of dioxane and 6 N sulfuric acid was added in portions at 0–5 °C a solution of 125 mg (1.81 mmol) of sodium nitrite in 4 mL of water. The reaction mixture was stirred for 15 min at this temperature to obtain a yellow homogeneous solution. The cooled diazonium salt solution was added dropwise to a solution of 1.5 g of sodium azide in 8 mL of water warmed to 40–50 °C in advance. After the addition, the reaction mixture was allowed to stand for 10 min and cooled. The organic materials were extracted with ether and the extract was washed with dilute aqueous sodium hydroxide and dried on magnesium sulfate. The solvent was removed under reduced pressure with the temperature below 50 °C to avoid extensive isomerization of the product. The residue was developed on a silica gel column with hexane. After elution of 36 mg (7%) of isomeric *sp*-azide 4sp (see below), the *ap* form was eluted. The yield was 300 mg (55%): colorless granules; mp 121–122 °C; ¹H NMR (CDCl₃) δ 2.27 (3 H, s), 2.63 (3 H, s), 5.24 (1 H, s), 6.63 (1 H, s), 6.94 (1 H, s), 7.2–7.9 (8 H, m); IR (KBr disk) 2090 cm⁻¹; MS, *m/z* (%) 311 (M⁺, 21), 283 (M⁺ – N₂, 71), 282 (100), 268 (45); found M⁺ 311.1415. C₂₁H₁₇N₃ requires M⁺ 311.1421. 1,3-Dimethylindeno[*j,k*]fluorene (26) was obtained (44 mg, 9%) as a byproduct which was eluted between the *ap*- and *sp*-azides in the chromatography.



When an aqueous sodium azide solution was added to the diazonium salt solution, 26 was obtained in a larger amount at the expense of the azides. 26: colorless granules; mp 61–62 °C; ¹H NMR (CDCl₃) δ 2.41 (3 H, s), 2.78 (3 H, s), 5.16 (1 H, s), 6.95 (1 H, s), 7.2–8.0 (8 H, m); ¹³C[¹H] NMR (CDCl₃) δ 21.3, 21.5, 55.5, 118.6, 118.7, 120.1, 121.9, 126.2, 126.6, 127.2, 128.9, 129.8, 134.8, 137.4, 139.3, 139.6, 143.3, 144.8, 145.1, 147.3, 160.7; MS, *m/z* (%) 268 (M⁺, 77), 253 (M⁺ – CH₃, 100); found M⁺ 268.1271. C₂₁H₁₆ requires M⁺ 268.1252.

Aniline 6sp afforded *sp*-3,5-dimethyl-2-(9-fluorenyl)phenyl azide (4sp) as a sole product in a 40% yield: colorless powder; mp 113–114 °C; ¹H NMR (CDCl₃) δ 1.06 (3 H, s), 2.31 (3 H, s), 5.74 (1 H, s), 6.57 (1 H, s), 6.97 (1 H, s), 7.2–7.9 (8 H, m); IR (KBr disk) 2110 cm⁻¹; MS found M⁺ 311.1418. C₂₁H₁₇N₃ requires M⁺ 311.1421.

Deuteration of 3,5-Dimethyl-2-(9-fluorenyl)aniline (6). To a solution of 620 mg (2.17 mmol) of the amine 6⁵⁸ in 35 mL of dry ether was added

slowly 12 mL (19.6 mmol) of *n*-butyllithium solution in hexane (1.60 M) at 0 °C. After the addition, the reaction mixture was stirred for 15 h at room temperature, cooled in an ice bath, and quenched by the slow addition of 10 mL of deuterium oxide. The organic layer was separated, and the water phase was extracted with ether. The combined extract was washed with water, dried on magnesium sulfate, and evaporated to give *sp*-3,5-dimethyl-2-(9-deuterio-9-fluorenyl)aniline (6'sp) in a quantitative yield. The Sandmeyer reaction of 6'sp as described above gave the *sp*-azide-9-*d*, 4'sp, in which the deuterium isotope purity was found by an NMR integration of the remaining 9-*h* compound to be higher than 98.5%.

Rates of Rotational Isomerization. The pure *ap*-azide 4ap was dissolved in decalin (3.2 × 10⁻³ M), and the solution was transferred into glass capillaries and then sealed. The solution was heated in an appropriate boiling solvent bath. The decrease of 4ap and the increase of 4sp were monitored by HPLC on a μ-Porasil column with hexane–dichloromethane (5.5:1) elution. The equilibrium constant, *K*, was obtained at each temperature by heating the solution for a long time (at least 50 half-lives). Assuming the first-order reaction, the rate constant, *k*, was obtained by the following equation,

$$kt = \frac{K}{K+1} \ln \left(\frac{1+x}{1-x/K} \right)$$

where *x* is the ratio of the amount of 4sp to that of 4ap at time *t*. The plot gave good straight lines. Putting *k*'s into the Eyring equation, we obtained the activation parameters.

Photolysis at Cryogenic Temperatures. (A) ESR Measurements at 4 K. The azides were dissolved in methylcyclohexane (ca. 5 × 10⁻³ M) and the solution was degassed in a quartz cell by 3 freeze–thaw cycles. The sample was cooled in a precooled ESR cavity and irradiated.

(B) UV Absorption Spectral Measurements at 77 K. The azides were dissolved in EPA (ca. 1.1 × 10⁻⁴ M), and the solution was transferred to a quartz cell of 1.0-cm optical length and degassed by 3 freeze–thaw cycles. The spectra were recorded at an appropriate interval after irradiation. The preparative experiment was carried out in a similar manner. The degassed solution of 2.5 mg (8 μmol) of 4sp in 5 mL of EPA was irradiated in a quartz cell at 77 K. The solution was colored immediately to red-violet and the irradiation was continued until the color completely disappeared to give a blue-green fluorescent solution (for 40–60 min). After the irradiation, the sample was allowed to stand overnight at ambient temperature on exposure to air. The obtained yellow solution was evaporated and the residue separated by the use of GPLC with chloroform eluant to give 36% of the recovered starting material and 10,12-dimethylindeno[*k,l*]acridine (13) in a 29% yield based on the reacted material. 13: yellow needles; mp 148–149 °C; ¹H NMR (CDCl₃) δ 2.59 (3 H, s), 3.21 (3 H, s), 7.36 (1 H, s), 7.40 (1 H, dd, *J* = 7.6, 7.0 Hz), 7.46 (1 H, dd, *J* = 7.3, 7.0 Hz), 7.79 (1 H, dd, *J* = 8.5, 6.5 Hz), 7.88 (1 H, d, *J* = 6.5 Hz), 7.95 (1 H, d, *J* = 7.3 Hz), 8.01 (1 H, s), 8.05 (1 H, d, *J* = 8.5 Hz), 8.47 (1 H, d, *J* = 7.6 Hz); UV (EPA) λ_{max} (log ε) 358 nm (3.45), 377 (3.70), 419 (3.50); MS, *m/z* (%) 281 (M⁺, 100), 266 (M⁺ – CH₃, 4); found M⁺ 281.1223. C₂₁H₁₅N requires M⁺ 281.1205.

Photolysis in Fluid Solutions. Solutions of the azide in the concentration of ca. 4 × 10⁻⁴ M were prepared and purged with nitrogen for 5–10 min. Irradiation was carried out under a nitrogen atmosphere. The reaction was monitored by HPLC on a μ-Porasil column with hexane–dichloromethane (5:1) or on a μ-Bondapak C₁₈ column with methanol–water (5:1) elution. The irradiation was stopped when 80–90% of the material was consumed. Yields of the products based on the reacted material were determined by HPLC after the correction of absorptivities. The resulting solution was worked up by the following procedures.

(A) In Methanol in the Presence of Sodium Methoxide. A solution for the photoreaction was prepared by the addition of 150 mL of methanol containing 20 mg of dissolved sodium to the solution of 20 mg (64 μmol) of azide 4 in 12 mL of ether. The photolyzed solution was concentrated under reduced pressure and diluted with chloroform. The solution was washed with water until the water phase was neutral, dried over magnesium sulfate, and evaporated. The residue was separated by the use of GPLC to give three products, which were further purified by Lobar column chromatography with dichloromethane eluants. The yield of products is shown in Table V. 9-(2-Amino-4,6-dimethylphenyl)-9-methoxyfluorene (14): oil; ¹H NMR (CDCl₃) δ 1.16 (3 H, s), 2.15 (3 H, s), 2.77 (3 H, s), 6.12 (1 H, s), 6.45 (1 H, s), 7.2–7.7 (8 H, m); IR (Nujol) 3470, 3360 cm⁻¹; MS, *m/z* (%) 315 (M⁺, 67), 283 (86), 282 (100); found M⁺ 315.1612. C₂₂H₂₁ON requires M⁺ 315.1622. 4,6-Dimethyl-7-(9-fluorenyl)-2-methoxy-3H-azepine (15): oil; ¹H NMR

(58) A material used for deuteration was not required to be separated to each rotational isomer since in the course of the reaction the amine isomerized to the *sp* conformer to give the *sp*-amine-9-*d* exclusively.

(CDCl₃) (at 22 °C) δ 1.92 (3 H, s), 2.37 (3 H, br s), 2.51 (2 H, s), 3.07 (3 H, br s), 5.15 (1 H, s), 5.91 (1 H, s), 7.2-7.8 (8 H, m); ¹H NMR (CDCl₃) (at -50 °C) δ 1.92 (3 H, br s), 2.40/0.81 (3 H, s), 2.51 (2 H, br s), 3.00/3.84 (3 H, s), 5.19/4.78 (1 H, s), 5.95/5.66 (1 H, s), 7.2-7.8 (8 H, m) (the signals for the major and minor conformers are indicated before and after the slant lines, respectively); ¹³C{¹H} NMR (CDCl₃) (at -45 °C) δ 20.1, 23.8, 37.8, 51.6, 53.9, 119.5, 119.6, 124.2, 126.6, 126.6, 126.8, 126.9, 141.4, 142.6, 147.3, 151.1; MS, *m/z* (%) 315 (M⁺, 100), 300 (M⁺ - CH₃, 26), 284 (M⁺ - OCH₃, 15); found M⁺ 315.1615. C₂₂H₂₁ON requires M⁺ 315.1622. 1,3-Dimethyl-4b-aza-7*H*-benz[*a*]-indeno[*c,d*]azulene (**16**): orange granules; mp ca. 115 °C dec; ¹H NMR (CDCl₃) δ 2.37 (3 H, s), 2.76 (3 H, s), 3.70 (2 H, ddd, *J* = 4.7, 4.7, 1.8 Hz), 4.57 (1 H, tdd, *J* = 9.9, 4.7, 0.8 Hz), 6.14 (1 H, td, *J* = 4.7, 0.8 Hz), 6.58 (1 H, td, *J* = 1.8, 9.9 Hz), 6.69 (1 H, s), 6.82 (1 H, s), 6.8-7.6 (4 H, m); UV (CH₃OH-CH₂Cl₂, 9:1) λ_{max} (log ε) 325 nm (3.39), 359 (3.46), 375 (sh) (3.40), 424 (3.14); MS found M⁺ 283.1317. C₂₁H₁₇N requires M⁺ 283.1361.

(B) In Diethylamine. The photoreaction in diethylamine was carried out in a small photoreaction vessel (12 mL) with a pen-light under nitrogen bubbled continuously through the solution. The irradiated solution was evaporated and the residue was treated in the same manner described in methanol to give three photoproducts. The yield is shown in Table VIII. The amines **6** were identified by comparing with the authentic samples. 9-(2-Amino-4,6-dimethylphenyl)-9-diethylaminofluorene (**20**): oil; ¹H NMR (CDCl₃) δ 0.92 (6 H, t, *J* = 7.0 Hz), 1.08 (3 H, s), 2.14 (3 H, s), 2.16 (2 H, m), 2.69 (2 H, m), 6.05 (1 H, s), 6.39 (1 H, s), 7.2-7.8 (8 H, m); ¹³C{¹H} NMR (CDCl₃) δ 16.1, 20.5, 23.5, 44.8, 79.3, 116.3, 119.5, 120.5, 123.1, 126.2, 127.1, 128.0, 136.5, 138.0, 140.9, 147.4, 149.9; MS, *m/z* (%) 356 (M⁺, 26), 284 (M⁺ - Et₂N, 100), 282 (43); found M⁺ 356.2270. C₂₅H₂₈N₂ requires M⁺ 356.2253. 9-(3-Amino-2-(diethylamino)-4,6-dimethylphenyl)fluorene (**21**): colorless needles; mp ca. 235 °C dec; ¹H NMR (CDCl₃) δ 0.95 (3 H, s), 1.24 (6 H, t, *J* = 7.2 Hz), 2.15 (3 H, s), 3.33 (4 H, m), 4.13 (2 H, br s), 5.67 (1 H, s), 6.55 (1 H, s), 7.2-7.9 (8 H, m); ¹³C{¹H} NMR (CDCl₃) δ 15.7, 17.2, 17.8, 49.5, 49.5, 119.9, 121.3, 124.1, 126.6, 127.1, 127.5, 131.0, 136.5, 137.3, 140.9, 142.8, 148.1; MS, *m/z* (%) 356 (M⁺, 100), 327 (M⁺ - Et, 12), found M⁺ 356.2268. C₂₅H₂₈N₂ requires M⁺ 356.2253.

(C) In Acetonitrile in the Presence of TCNE. A solution of 20 mg (64 μmol) of the azide and 26 mg (200 μmol) of TCNE in 160 mL of

acetonitrile was irradiated. The photolyzed solution was evaporated and the residue was extracted with a small amount of chloroform. The extract was filtered through the tube packed with cotton. The two adducts, **24** and **25**, were obtained by separation and purification in the same manner as described for methanol. The yield of the adducts shown in Table X was determined by the integration of ¹H NMR in the crude reaction mixture, based on the reacted material determined by HPLC. 1,3-Dimethyl-4c,7-tetracyanoethano-4c,12b-dihydro-4b-aza-7*H*-benz[*a*]indeno[*c,d*]azulene (**24**): colorless needles; mp ca. 190 °C dec; ¹H NMR (CDCl₃) δ 2.27 (3 H, s), 2.67 (3 H, s), 3.63 (1 H, dd, *J* = 8.5, 7.6 Hz), 4.97 (1 H, dd, *J* = 8.5, 8.5 Hz), 5.34 (1 H, s), 6.41 (1 H, s), 6.59 (1 H, d, *J* = 8.5 Hz), 6.70 (1 H, s), 6.86 (1 H, d, *J* = 7.6 Hz), 7.4-7.7 (4 H, m); MS, *m/z* (%) 411 (M⁺, 12), 284 (36), 283 (M⁺ - TCNE, 100), 282 (69), 268 (25); found M⁺ 411.1480. C₂₇H₁₇N₅ requires M⁺ 411.1483. 6,8-Dimethyl-9-(9-fluorenyl)-1,1,2,2-tetracyano-4-spiro[2,6]nona-4,6,8-triene (**25**): colorless granules; mp ca. 205 °C dec; ¹H NMR (CDCl₃) δ 1.02 (3 H, s), 2.28 (3 H, s), 4.96 (1 H, s), 6.79 (1 H, br s), 7.1-7.8 (8 H, m), 8.21 (1 H, d, *J* = 1.8 Hz); MS, *m/z* (%) 411 (M⁺, 54), 347 (44), 346 (M⁺ - HC(CN)₂, 100), 282 (35); found M⁺ 411.1455. C₂₇H₁₇N₅ requires M⁺ 411.1483.

Time-Resolved Absorption Spectroscopy. An undegassed solution of the azide (4.8 × 10⁻⁵ M) in methanol-ether (92:8) was irradiated at 25 °C in a 1 × 1 × 4 cm quartz cell with a 248-nm pulse from an excimer laser with a pulse width of 12 ns and output energy of 50 mJ/cm². In the observation of decomposition rate of the *o*-quinoid species **11**, a steady light source was used as a monitor light.

Calculation of Spin Densities with the INDO-UHF Method. Calculations were carried out on a Hitachi-M-200H computer of the Computer Center of the Institute for Molecular Science. The program used was the following, CNINDO: CNDO and INDO molecular orbital program (FORTRAN IV), which was originally programmed by J. A. Pople, D. L. Beveridge, and P. A. Dobosh (QCPE No. 141).

Registry No. **4**, 85681-33-0; **4'**, 98128-22-4; **6**, 98128-18-8; **6'**, 98128-21-3; **7**, 98128-19-9; **13**, 85681-37-4; **14**, 91481-73-1; **15**, 98128-23-5; **16**, 98128-24-6; **20**, 98128-25-7; **21**, 98128-26-8; **24**, 98170-00-4; **25**, 98128-27-9; **26**, 98128-20-2; TCNE, 670-54-2; D₂, 7782-39-0; 9-bromofluorene, 1940-57-4; 3,5-xylydine, 108-69-0; *N*-(9-fluorenyl)-3,5-xylydine, 98128-17-7.

Methyl-Substituted Poly(vinylnaphthalene) as a Reversible Singlet Oxygen Carrier

Isao Saito,* Ryu Nagata, and Teruo Matsuura

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. Received March 29, 1985

Abstract: Methyl-substituted poly(vinylnaphthalenes) (**5a-c**) were prepared by radical polymerization of the corresponding vinylnaphthalenes **4a-c**. Polymers **5a** and **5b** have been shown to bind and release singlet molecular oxygen (¹O₂) reversibly at temperatures between 0 and 35 °C. Methylene blue sensitized photooxygenation of polymers **5** at 0 °C produced the corresponding polymer endoperoxides **6** in nearly quantitative yields. Generation of ¹O₂ from the thermolysis of polymer endoperoxide **6b** at 35 °C was confirmed by trapping experiments using typical ¹O₂ acceptors. Kinetic parameters for the thermolyses of **6a** and **6b** were compared with those for the corresponding monomer endoperoxides. The yield of ¹O₂ generated from polymer **6b** was determined to be as high as 66 ± 5%. The synthetic utility of these polymeric endoperoxides as a ¹O₂ source has been demonstrated in the oxidation of a series of representative substrates. Advantages of using these polymer ¹O₂ sources are the following: (1) the mild condition for generation of ¹O₂, (2) utility in nonsolvent systems, and (3) easy removal and reuse.

Since singlet oxygen (¹O₂) was shown to be involved in a variety of chemical and biochemical phenomena, there has been a surge of interest in chemical methods of producing ¹O₂.¹ One major advantage of the use of chemical ¹O₂ sources over the photosensitization method is to avoid secondary interactions of photoexcited sensitizers with substrates or products which sometimes complicate

the mechanisms of photosensitized oxygenations.² Mechanistically less complicated chemical ¹O₂ sources that can generate ¹O₂ at ordinary temperature are extremely useful for ¹O₂ reactions of organic substrates and biological systems, particularly for their

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