close to that of free spin are consistent with **1** composed of light atoms with small spin-orbit coupling. In addition, the D and E values fall in the range expected from the known high-spin multiplet hydrocarbons.[1-5] It should be mentioned that the observed fine structure and its angular dependence could not be interpreted by superposing spectra of more than one paramagnetic species with $S = 1$, 2 and 3.

In order to determine the lowest energy level, we have also observed ESR spectra in the range 1.8-150 K. No thermally populated triplet, quintet, and septet signals were detected, indicating that the ground state is either nonet or singlet. The latter possibility was excluded by measuring carefully the temperature dependence of the total signal intensity.

In view of these experimental results, we safely conclude that **1** has been obtained in its nonet ground state. It is extremely significant that the spin multiplicity of a hydrocarbon can exceed the highest one (octet) attainable from f orbitals of a transition-metal ion, if its molecular structure is properly designed by considering the topological symmetry.

Registry No. 1, 85566-03-6; **2**, 85566-04-7; **3**, 85566-05-8; **4**, 85566-06-9; **5**, 85566-07-0; **6**, 85566-08-1; **7**, 85566-09-2; **8**, 85566-10-5; isophthalonitrile, 626-17-5; *m*-tolyl bromide, 591-17-3; benzene, 71-43-2.

Contrasting ESR and UV Spectroscopic Properties and Reactivities between the Conformationally Restricted *o*-(9-Fluorenyl)phenylnitrenes at Cryogenic Temperatures

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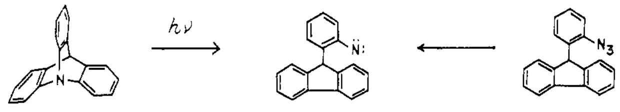
1-Azatriptycene (**1**) undergoes photorearrangement to give



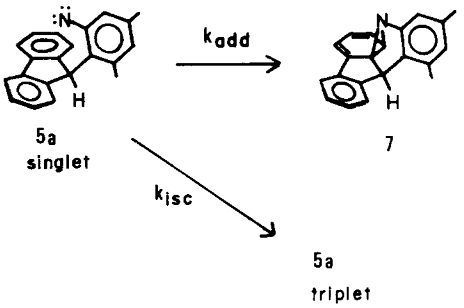
1 2 3

o-(9-fluorenyl)phenylnitrene (**2**). The nitrene intermediate can be generated independently from *o*-(9-fluorenyl)phenyl azide (**3**). The reactions from the two precursors **1** and **3** gave similar spectroscopic and chemical results but differed in some details. The presence of two different conformers, *ap* and *sp* forms (**2a** and **2b**, respectively), from **1** and **2**, respectively, has been postulated.[1] In order to establish the above mechanism, we have prepared the conformationally fixed azides **4a** and **4b**[2] and generated the corresponding nitrenes **5a** and **5b** at cryogenic temperatures. We report here a remarkable contrast of the ESR and UV absorption spectroscopic and chemical behaviors between them.

2a, X=N: R=H
4a, X=N_3 R=CH_3
5a, X=N: R=CH_3

2b, X=N: R=H
4b, X=N_3 R=CH_3
5b, X=N: R=CH_3

Scheme I



9-(2-Amino-4,6-dimethylphenyl)fluorene was prepared by the rearrangement of 3,5-dimethyl-*N*-fluorenylaniline in the presence of aluminum chloride at 180 °C and separated into the stable conformers by column chromatography on silica gel.[3] They were converted separately to *ap*-azide **4a**, mp 121-122 °C, and *sp*-azide **4b**, mp 113-114 °C, by the standard method.[4] Irradiation of **4a** with a high-pressure mercury lamp in methylcyclohexane glass at 4.2 K in an ESR cavity[5] produced the intense X,Y transition of triplet *ap*-nitrene **5a** at 6722 G.[6] No signal characteristic of triplet species was found during the photolysis of **4b** under these conditions. The wanted data were fortunately provided from irradiation of the 9-deuterio derivative (**4b′**)[7] of **4b**; a clear ESR signal due to the X,Y transition appeared at 6745 G. Triplet nitrenes **5a** and **5b′** showed different thermal stability; whereas **5a** decreased only gradually (with the initial first-order decay constant of 8.3×10^{-4} s^{-1}), **5b′** disappeared rapidly (1.2×10^{-2} s^{-1}) at 98 K.

The UV spectrum obtained by photolysis of **4a** in an EPA glass at 77 K consisted of absorptions at 309 and 340 nm.[8] They are respectively assigned to triplet nitrene **5a** and azanorcaradiene **7** formed by intramolecular addition of the nitrene to the double bond of the fluorene ring in proximity (Scheme I).[1b] It was not possible to find an absorption due to triplet nitrene **5b** among the absorptions at 367, 426, and 554 nm obtained by irradiation of **4b** under these conditions. The broad band at 554 nm assigned to *o*-quinoid tautomer **6** (Scheme II) started to disappear after continued irradiation. The other peaks increased their intensity with isosbestic points at 439 and 620 nm. When the sample solution was allowed to warm to ambient temperatures and aerated, the spectrum changed to absorptions at 358, 377, and 419 nm. The final product was isolated and identified as 10,12-dimethylindeno[*kl*]acridine.[1a,9]

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(1) (a) Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1980**, *102*, 7134. (b) Sugawara, T.; Nakashima, N.; Yoshihara, K.; Iwamura, H. *Ibid.* **1983**, *105*, 858.

(2) Difference in solvolytic reactivities between stable rotamers of 9-(2,6-disubstituted phenyl)fluorenes has been the subject of recent interest and reviewed: Ōki, M. *Top. Stereochem.* **1983**, *14*, 1.

(3) Experimental procedures are practically the same as in ref 1b.

(4) Both **4a** and **4b** gave satisfactory analytical data. Conformational assignments were made by their characteristic ^{1}H NMR spectra: Tukada, H.; Iwamura, M.; Sugawara, T.; Iwamura, H. *Org. Magn. Reson.* **1982**, *19*, 78. The barrier to interconversion between the amine rotamers has been obtained preliminarily to be ca. 27 kcal mol^{-1}. The corresponding value for **4a** and **4b** is slightly lower than this.

(5) Measured on a Varian E-112 EPR spectrometer (9.2196 GHz) equipped with an optical transmission cavity accessory and an Oxford cryostat, the latter being connected with a helium reservoir through a transfer tubing.

(6) For typical ESR data of triplet phenylnitrenes, see: Hall, J. H.; Fargher, J. M.; Gisler, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 2029.

(7) Obtained by the Sandmeyer reaction of the *sp*-amine-*9-d*, which in turn was prepared by treating the *sp*-amine with 9 M excess of butyllithium in ether at 0 °C-room temperature for 10 h and quenching the mixture with D_2O.

(8) The spectrum looked very much like Figure 3 in ref 1b (obtained by UV irradiation of 1-azatriptycene).

(9) Orange granules: mp 124-125 °C; MS, m/e 281 (M^+, 100), 266 ($M^+ - CH_3$, 4); ^{1}H NMR ($CDCl_3$, 399.7 MHz) δ 2.59 (s, 3 H), 3.21 (s, 3 H), 7.36 (s, 1 H), 7.40 (dd, J = 7.6, 7.0 Hz, 1 H), 7.46 (dd, J = 7.3, 7.0 Hz, 1 H), 7.79 (dd, J = 8.5, 6.5 Hz, 1 H), 7.88 (d, J = 6.5 Hz, 1 H), 7.95 (d, J = 7.3 Hz, 1 H), 8.01 (s, 1 H), 8.05 (d, J = 8.5 Hz, 1 H), 8.47 (d, J = 7.6 Hz, 1H); UV (EPA) λ_{max} (log ϵ) 358 nm (3.45), 377 (3.70), 419 (3.50).[1a]

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Scheme II

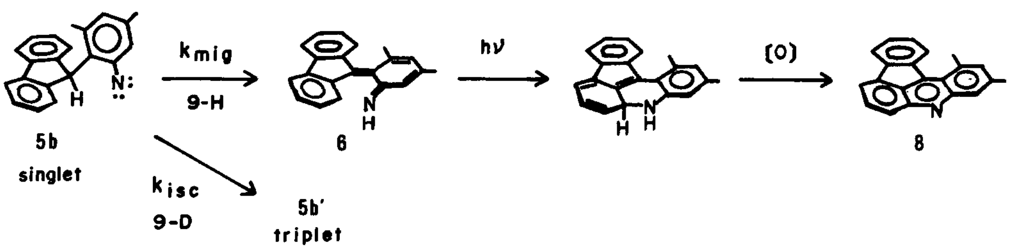

Table I. X,Y Band Positions of Various Triplet *o*-(9-Fluorenyl)phenylnitrenes at 4 K in Methylcyclohexane Glasses

precursor of nitrene	resonance position, G^a	shifts, G
phenyl azide	6824^b	0
1-azatriptycene (**1**)	6730	−94^c
9-(2-azidophenyl)fluorene (**3**)	6750	−74
ap-9-(2-azido-4,6-dimethylphenyl)-fluorene (**4a**)	6722	−102
sp-9-(2-azido-4,6-dimethylphenyl)-9-deuteriofluorene (**4b′**)	6745	−79

^{a} The microwave frequency was normalized at 9.2196 GHz. The band positions were read with the aid of a gaussmeter (a Varian E-500 NMR gaussmeter). ^{b} The agreement with the literature data[6] is excellent. ^{c} The negative values correspond to downfield shifts relative to the signal position of phenylnitrene.

The above results provide, to our knowledge, the first example demonstrating a remarkable difference in reactivity between the well-defined conformers of a nitrene[10] and are explained in terms of the competition between the facile singlet reactions and intersystem crossing to the triplet nitrene in both conformers. In the singlet **5a**, the nitrene center is situated right above the fluorene ring, and therefore the addition to the double bond of the latter ring should be very favorable. Intersystem crossing to triplet **5a** can still compete to some extent. In singlet **5b**, since the hydrogen atom at the 9-position of the fluorene ring is so close to the univalent nitrogen, the 1,4-migration of the hydrogen becomes exclusive.[11] The reaction can be retarded by the deuterium isotope effect at the 9-position,[12] allowing intersystem crossing to the triplet to be competitive with the deuterium migration. *o*-Quinoid tautomer **6** obtained after the hydrogen migration undergoes conrotatory photocyclization to give the dihydro derivative of **8**.

We note that **5a** has the X,Y transition at lower magnetic field by 23 G than **5b′**. The difference corresponds to a slightly smaller zero-field splitting parameter *D*, which in turn indicates the longer average distance between the two odd electrons with parallel spin in **5a**. The probable explanation is that through-space interaction may be operating in delocalizing the p-type odd electron at the nitrenic center over the π-system of the fluorene ring lying underneath.

Turning lastly to a comparison with photochemistry of **1** and **3**, we collected the ESR data in Table I. The previous assignment of triplet nitrene **2** from **1** with low-field X,Y transition to the *ap* conformer and **2** from **3** with high-field signal to the *sp* form is consistent with the present results. The absorption spectral behaviors are also in accord with this assignment.

Registry No. 1, 197-45-5; **2**, 74357-27-0; **3**, 74357-30-5; **4a**, 85681-33-0; **5a**, 85681-34-1; **5b′**, 85681-35-2; **6**, 85681-36-3; **7**, 85681-38-5; **8**, 85681-37-4; phenyl azide, 622-37-7.

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(10) The presence of geometrical isomers in equilibrium is detected by ESR at cryogenic temperatures for naphthyl-, vinyl-, and quinolylcarbenes: (a) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129. (b) Hutton, R. S.; Roth, H. D.; Schilling, M. L. M.; Suggs, J. W. *Ibid.* **1981**, *103*, 5147. (c) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1981**, *103*, 5503.

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

(12) Precedents for the isotope effect in the hydrogen abstraction reaction of biradicals and carbenes in matrices are found in the following: (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688. (b) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1980**, *102*, 7637.

Migration of Tricarbonylchromium Groups in Phenylanthracenes

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There are few reported examples of metal migration from one site on a coordinated organometallic ligand to another. Deprotonation of (fluorene)tricarbonylchromium [$C_{13}H_{10}Cr(CO)_3$] leads to an equilibrium mixture of the η^5 and η^6 complexes of the fluorenyl anion,[1] $C_{13}H_9Cr(CO)_3^-$. (η^6-Fluorene)tricarbonylmanganese cation, η^6-$C_{13}H_{10}Mn(CO)_3^+$, on deprotonation, gives η^6-$C_{13}H_9Mn(CO)_3$, which rearranges irreversibly to η^5-$C_{13}H_9Mn(CO)_3$.[2] We report the migration of a tricarbonylchromium group between two nonadjacent six-membered rings in phenylanthracenes.

(Anthracene)tricarbonylchromium (ATC) is a deep-purple complex in which the $Cr(CO)_3$ group bonds to a terminal ring.[3] (Biphenyl)tricarbonylchromium is yellow.[4] 9-Phenylanthracene incorporates biphenyl and anthracene systems in a single molecule. A refluxing solution of 9-phenylanthracene and $Cr(CO)_6$ in dioxane became purple. This solution, on standing overnight in the dark, turned yellow; heating to reflux temperature caused the solution again to become purple. From the cooled yellow solution were isolated yellow crystals of structure IIa[5] (Chart I). A solution of IIa in dioxane slowly became dark brown when heated to 100 °C, indicating a mixture of the yellow and purple compounds.

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(1) Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andre, S.; Ustynyuk, Yu. A.; Novikova, L. N.; Luzikov, Yu. N. *J. Organomet. Chem.* **1978**, *154*, 45–63. Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko, Yu. F.; Roznyatovsky, V. A.; Luzikov, Yu. N.; Ustynyuk, Yu. A. *Ibid.* **1980**, *202*, 279–289.

(2) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749–753. Treichel, P. M.; Fivizzani, K. P.; Haller, K. *Organometallics* **1982**, *1*, 931–934.

(3) Willeford, B. R.; Fischer, E. O. *Naturwissenchaften* **1964**, *51*, 38; *J. Organomet. Chem.* **1965**, *4*, 109–113. Deubzer, B.; Fischer, E. O.; Fritz, H. P.; Kreiter, C. G.; Kriebitzsch, N.; Simmons, H. D.; Willeford, B. R. *Chem. Ber.* **1967**, *100*, 3084–3096. Hanic, F.; Mills, O. S. *J. Organomet. Chem.* **1968**, *11*, 151–158.

(4) Fischer, E. O.; Kriebitzsch, N.; Fischer, R. D. *Chem. Ber.* **1959**, *92*, 3214–3222.

(5) Anal. Calcd for $C_{23}H_{14}CrO_3$: C, 70.77; H, 3.61; O, 12.30. Found: C, 70.57; H, 3.56; O, 12.52. Mass spectrum, *m/z* 390 (M^+), 334 [$(M - 2CO)^+$] 306 [$(M - 3CO)^+$], 254 [$(M - Cr - 3CO)^+$], 52 (Cr^+, base peak), 28 (CO^+); ^1H NMR (60 MHz, CD_2Cl_2) δ 8.32 (s, 1 H), 7.60 (m, 9 H), 6.58 (m, 1 H), 6.15 (m, 1 H), 5.73 (m, 2 H); ^{13}C NMR (50.31 MHz, CD_2Cl_2) δ 138.4, 136.1, 133.2, 131.5, 130.8, 130.6, 128.7, 128.3, 127.9, 126.8, 126.6, 126.3, 105.7, 105.2, 93.2, 93.0, 90.9, 89.3.

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