Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. **7**, 85613-84-9; **8**, 85613-85-0; **9**, 85613-86-1; **10**, 85613-87-2; **11**, 85613-88-3; **12**, 85613-89-4; **13**, 13025-91-7; **14**, 85613-90-7; **15**, 85613-91-8; **17**, 40015-00-7; $BrCH_2CH(Br)OCH_2CH_2Cl$, 14689-94-2; $LiC{\equiv}CCH_2OLi$, 60851-89-0; 2-(chloroethyl) 2-undecyn-1-yl 2-bromoacetaldehyde acetal, 85613-92-9.

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(15) These monocyclizations were also conveniently performed by using a polystyrene-supported tributyltin hydride first prepared in this laboratory by Gary Tennyson, following essentially the route described for the related dihydride (Weinshenker, N. M.; Crosby, G. A.; Wong, J. Y *J. Org. Chem.* **1975**, *40*, 1966).

Design, Preparation, and ESR Detection of a Ground-State Nonet Hydrocarbon as a Model for One-Dimensional Organic Ferromagnets

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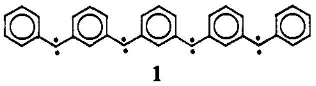
We have succeeded in detecting by electron spin resonance spectroscopy an aromatic hydrocarbon, *m*-phenylenebis((diphenylmethylen-3-yl)methylene) (**1**), which has eight parallel



1

spins, i.e., nonet spin multiplicity ($S = 4$) in the electronic ground state. This is the highest spin multiplicity observed in organic as well as inorganic compounds. The prototype of this molecule, *m*-phenylenebis(phenylmethylene) in the quintet ground state ($S = 2$) was found in 1967 independently by one of us[1] and by Wasserman et al.[2] Some more examples were added to this class of high-spin multiplet hydrocarbons: *m*-phenylenebis(methylene) ($S = 2$),[2] benzene-1,3,5-tris(phenylmethylene) ($S = 3$),[3] 1,3,5-benzenetriyltris(bis(biphenyl-4-yl)methyl) ($S = {}^3/_2$),[4] and biphenyl-3,3′-bis(phenylmethylene) ($S = 0$, 1, and 2).[5]

The molecule **1** is an even alternant hydrocarbon. We assume that one of the unpaired electrons of each divalent carbon atom participates in conjugation with the π system of the benzene rings while the other remains in the nonbonding orbital "n" localized on the divalent carbon atom. The simple molecular orbital theory[6] predicts that the π system has four singly occupied nonbonding MO's, which may be nearly degenerate with the four n orbitals. The meta substitution in **1** is essential for the 4-fold degeneracy of the π MO's, which is dictated by the topological symmetry.[5] Thus, eight parallel spins occupy the eight nearly degenerate orbitals because of Hund's rule as confirmed by the experiment described below. The parallel spins in the π orbitals are delocalized over the whole molecule and are exchange-coupled strongly to the localized spins on the divalent carbon atoms. This interaction resembles closely the one between conducting s electrons and localized d electrons in ferromagnetic transition metals. Therefore, if we consider a long-chain constituted of the unit in **1**, one-dimensional organic ferromagnets may be expected. The possible electronic structure of such polymers was previously discussed by Mataga.[7] The one-dimensional magnetic systems have been a topic in current physics.[8]

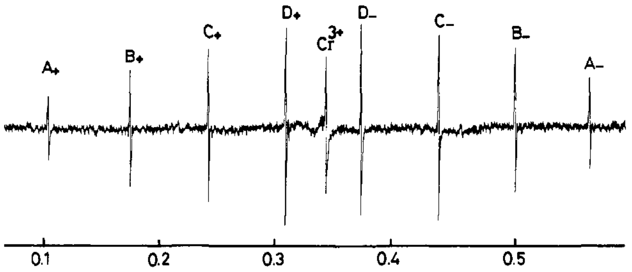
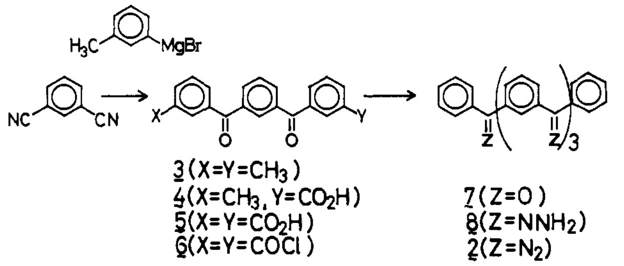


Figure 1. Electron spin resonance spectrum observed after the photolysis at 4.2 K with the magnetic field along the direction 26° from the a axis in the *ab* plane of the host crystal. The microwave frequency is 9550.6 MHz. The central line is due to Cr^{3+} in MgO powder used as a reference substance.

Scheme I



1 was generated by UV irradiation of the corresponding diazo compound **2**, which in turn was prepared as shown in Scheme I. Isophthalonitrile was allowed to react with *m*-tolylmagnesium bromide, and the mixture was hydrolyzed with HCl to give diketone **3**, mp 101–102 °C, in 80% yield. Heating of **3** under reflux with $Na_2Cr_2O_7$ in acetic acid produced in quantitative yield monocarboxylic acid **4**, mp 321–326 °C, which then gave dicarboxylic acid **5**, mp 328–334 °C, in 80% yield with $KMnO_4$ in aqueous alkaline conditions. Treatment of **5** with thionyl chloride gave dichloride **6** as an oil, which was reacted with anhydrous $AlCl_3$ in benzene to give tetraketone **7**, mp 219.0–219.5 °C, in 78% yield. Tetrahydrazone **8**, mp 105–113 °C, was obtained in 79% yield by the reaction of **7** with hydrazine hydrate in boiling ethanol. Treatment of **8** with active MnO_2 in anhydrous ether in the absence of light and air gave **2**, mp 113 °C dec: IR 2040 cm^{-1}; UV 290 nm (91 600), 522 (416).[9]

The diazo precursor **2** was oriented in single crystals of benzophenone, the concentration being 0.05 mol %. Figure 1 shows the ESR spectrum observed at 4.2 K after photolysis by the 405-nm mercury line.[10] The eight observed lines were found to be the fine structure due to the following $\Delta M_S = \pm 1$ allowed transitions: $A_\pm$ ($M_S = \pm 4 \leftrightarrow \pm 3$), $B_\pm$ ($M_S = \pm 3 \leftrightarrow \pm 2$), $C_\pm$ ($M_S = \pm 2 \leftrightarrow \pm 1$), and $D_\pm$ ($M_S = \pm 1 \leftrightarrow 0$). The relative separations are nearly $(A_- - A_+):(B_- - B_+):(C_- - C_+):(D_- - D_+) = 7:5:3:1$, and the relative integrated intensities are nearly $A_\pm:B_\pm:C_\pm:D_\pm = 4:7:9:10$ as expected of $S = 4$ in the high-field approximation. The magnetic field is approximately parallel to the Z principal axis of the fine-structure tensor, the deviation being 9.8°, which gives the largest fine-structure splittings.

The angular dependence of the resonance fields and of the signal intensities of the eight lines is well reproduced by the spin Hamiltonian

$$\mathcal{H} = g\beta \mathrm{H}\cdot\mathrm{S} + D[S_Z{}^2 - {}^1\!/_3 S(S+1)] + E(S_X{}^2 - S_Y{}^2)$$

where $S = 4$, $g = 2.003$, $D = +0.0332$ cm^{-1}, and $E = -0.0031$ cm^{-1}. Higher terms in S group theoretically allowed for $S = 4$ are negligibly small. This fact and the nearly isotropic g value

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(1) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235.

(2) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(3) Takui, T.; Itoh, K. *Chem. Phys. Lett.* **1973**, *19*, 120.

(4) Brickman, J.; Kothe, G. *J. Chem. Phys.* **1973**, *59*, 2807.

(5) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251.

(6) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.

(7) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372.

(8) Steiner, M.; Villain, J.; Windsor, C. G. *Adv. Phys.* **1976**, *25*, 87.

(9) Satisfactory elemental analyses and ^{1}H and ^{13}C NMR spectra were obtained for all new compounds.

(10) A JEOL 3BX ESR spectrometer equipped with a home-made cavity (TE_{102}, $Q = 6000$) and an OSRAM high-pressure mercury lamp (500 W) was used.

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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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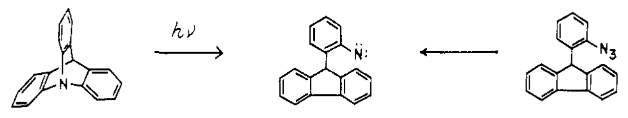
1-Azatriptycene (**1**) undergoes photorearrangement to give *o*-(9-fluorenyl)phenylnitrene (**2**). The nitrene intermediate can be generated independently from *o*-(9-fluorenyl)phenyl azide (**3**). The reactions from the two precursors **1** and **3** gave similar spectroscopic and chemical results 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.

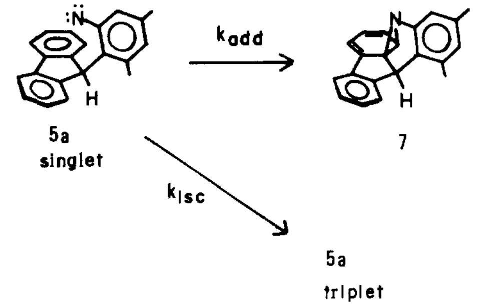


1 2 3

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$_2$O.

[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]