Design and Synthesis of a "Starburst"-Type Nonadiazo Compound and Magnetic Characterization of Its Photoproduct

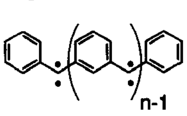
Kenji Matsuda, Nobuo Nakamura, Katsuya Inoue, Noboru Koga, and Hiizu Iwamura*

Abstract: A "starburst"-type nonadiazo compound was designed and synthesized by using the cyclotrimerization of 3,5-dibenzylphenyl ethynyl ketone as a key step. The diazo compound was photolyzed in methyltetrahydrofuran solid solution at cryogenic temperatures and analyzed by means of Faraday magnetometry and EPR spectroscopy. While the *m*-phenylene-connected nonacarbene was predicted to have a nonadecet ($S = 9$) ground state, the magnetic data of the photoproduct was more consistent with a pentadecet ($S = 7$) species. The result was interpreted in terms of the intramolecular cross-linking between the carbene centers by the determination of both the amount and the multiplicity of the spin. In the "starburst"-type polycarbenes with extended branching, the reactive carbene centers are able to approach one another and thus appear to readily recombine. This study highlights one of the limitations of the extension of the carbene network by way of flexible "starburst"-type structures.

Keywords
dendrimers · high-spin molecules · photochemistry · polycarbenes · solid solutions

Introduction

The synthesis and characterization of organic molecules with very high-spin ground states is currently of great interest.[1–3] In typical organic molecules, all the electrons are paired to form singlet ground states, and triplets with two parallel spins are often generated only as lowest excited states. The two singly occupied orbitals in diradicals are often independent, in which case their singlet and triplet states are nearly degenerate, or they overlap weakly to stabilize the singlet relative to the triplet state. When they are orthogonal in space, as in diphenyl carbene, or in terms of topological symmetry, as in *m*-quinodimethane, the triplet becomes the ground state according to Hund's rule.



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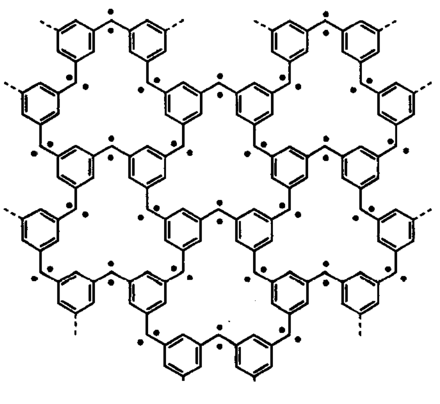
Incorporating the above two structural features within one molecule, Itoh and Wasserman prepared the *m*-phenylene dicarbene **1** ($n = 2$) and demonstrated that it has a quintet ground state ($S = 2$).[4] Linear tri-, tetra-, and pentacarbenes **1** ($n = 3, 4, 5$, respectively) have also been reported. From their EPR fine structures and/or magnetization data these molecules were shown to have ground states with $S = 3$, 4, and 5, respectively.[5]

The linear structure can in principle be extended to poly(*m*-phenylene carbene)s **1** ($n \rightarrow \infty$). In practice, however, there are a number of drawbacks with the linear structures. Firstly, it becomes more and more difficult to produce all the carbene centers without fail and to keep them intact. Once a chemical defect is formed in the middle of the cross-conjugated main chain, the high-spin multiplicity would be halved.[7] Secondly, the linear polyketones, which are key precursors, become less and less soluble in typical organic solvents in which further chemical transformations have to be carried out. Thirdly, one-dimensional alignment of spins is unstable from the point of view of statistical mechanics. Linear magnetic chains, including **1**, are not expected to exhibit spontaneous magnetization at finite temperatures, because the magnitude of the required enthalpy is $2J$ for multiply degenerate lowest excited states, where $2J$ is the exchange coupling parameter between the adjacent spins.[6]

To overcome these problems, construction of a high-dimensional network became an important objective. A rigid structure would also help to reduce the high reactivity of triplet carbene centers, as one-center diradicals, toward recombination, etc. We thus arrived at the network structure **2**



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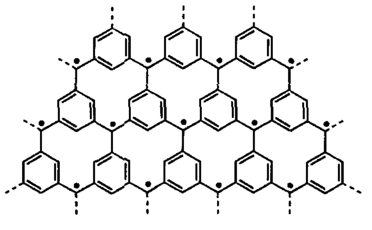
[*] Prof. Dr. H. Iwamura, K. Matsuda
Institute for Fundamental Research of Organic Chemistry
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-81 (Japan)
Fax: Int. code +(92)641-0915
Prof. Dr. N. Nakamura
Department of Material Chemistry, Faculty of Engineering
Hosei University, Kajinocho, Koganei, Tokyo 184 (Japan)
Prof. Dr. N. Koga
Fuculty of pharmaceutical Science, Kyushu University
Maidashi, Higashi-ku, Fukuoka 812-82 (Japan)
Dr. K. Inoue
Department of Chemistry, School of Scienece, Kitasato University
Kitasato, Sagamihara, Kanagawa 228 (Japan)



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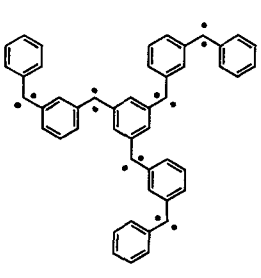
as a long-term goal in our search for strongly magnetic super high spin polycarbenes. This structure is obtained on paper by removing every third benzene ring from Mataga's network polyradical 3.[7c] Previously, we reported the design, synthesis, and characterization of three types of π-conjugated hexacarbenes, namely, 4,[8a, b] 5,[8c] and 6.[8c] Here, we demonstrated that it is not the shape or geometrical symmetry of the molecules, but rather the topological symmetry that is most important in determining the spin multiplicity of the alternating hydrocarbon molecules. Moreover, the nonacarbene 7 was prepared, and its magnetic measurement revealed 7 to be a ground-state nonadecet ($S = 9$).[9] This is the highest spin ever obtained for an organic molecule. However, the network structure 2 remains to be synthesized. In this report, the "starburst"-type dendritic structure 8, which is nearer to a real two-dimensional structure, will be discussed.



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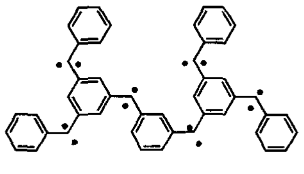

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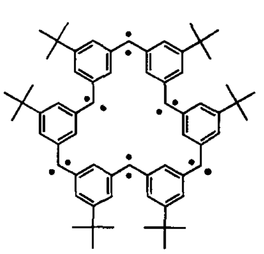

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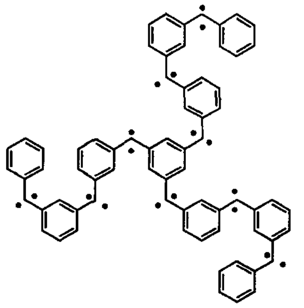

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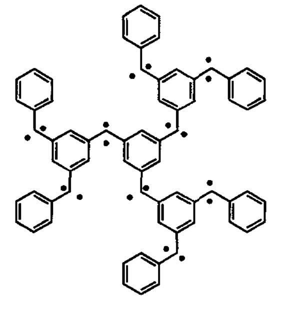

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Results and Discussion

Molecular Design and Synthesis of the Precursors: The "starburst"-type structure as given in Figure 1 is popular as a dendrimer in chemistry and as a Bethe lattice in physics.[10] Ising spins on a Bethe lattice are calculated to show a phase transition at finite temperature. Thus, the number of spins in the system becomes significantly larger as it extends. The most basic dendritic structure in 2 is 8, which is expected to have nonadecet ground state ($S = 9$). The 1,3,5-benzenetriyl unit might be deemed to be as good as or even better than the m-phenylene unit at assembling organic free radical centers in high concentrations within a molecule and aligning those spins parallel to one another.[2b, 11]

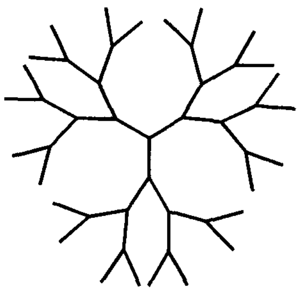
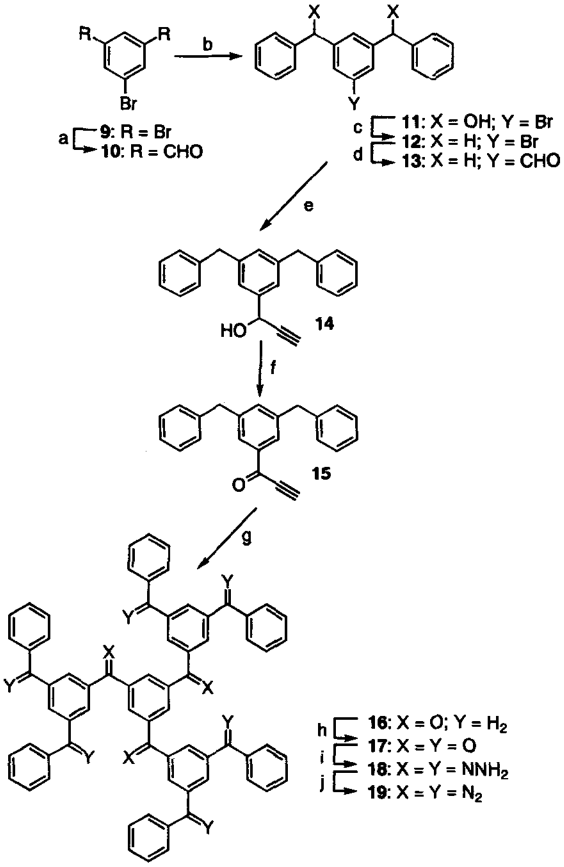


Fig. 1. Dendritic structure or Bethe lattice.

The polycarbene 8 was obtained by photolysis of the corresponding diazo precursor 19. The preparation of the diazo precursor was carried out in an usual way from the corresponding ketone 17, which in turn was synthesized from 9 by using the cyclotrimerization of the ethynyl ketone 15 as a key step (Scheme 1).[12]

Tribromobenzene (9) was lithiated and then allowed to react with N,N-dimethylformamide to give 3,5-diformylbromobenzene (10). Phenyllithium was added to 10, and the product 11 was then reduced to give bromo compound 12. Lithiation and followed by treatment with N,N-dimethylformamide gave the aldehyde 13. Lithium monoacetylide was added to 13 to give 14, which was then oxidized by Jones reagent to ethynyl ketone 15. Cyclotrimerization catalyzed by a secondary amine followed by oxidation gave nonaketone 17.[12]

Ketone 17 was characterized by ^{1}H NMR, ^{13}C NMR, IR, and FAB mass spectroscopy. The ^{1}H NMR spectrum of 17 shows singlets at $\delta = 8.42$, 8.46, and 8.55, and a mono-substituted benzene pattern at $\delta = 7.50$



Scheme 1. Reagents and Conditions: a) 4 equiv of tBuLi, ether, and then DMF, 84%; b) PhLi, THF; c) $LiAlH_4/AlCl_3$, ether, 47%, 2 steps; d) nBuLi, THF, and then DMF; e) HC≡CLi/TMEDA, THF; f) CrO_3/H_2SO_4, acetone, 70%, 3 steps; g) Et_2NH, toluene, 86%; h) $Na_2Cr_2O_7$, AcOH, 43%; i) N_2H_4, $N_2H_4 \cdot HCl$, DMSO, 93%; j) HgO, EtOK, Et_2O, CH_2Cl_2, 11%.

(t), 7.60 (t), 7.84 (d) (Fig. 2). The ^{13}C NMR shows ten signals corresponding to aromatic carbons ($\delta = 128.7$, 130.1, 133.4, 133.9, 134.6, 135.0, 136.2, 136.7, 133.7, and 138.7) and two signals for carbonyl carbons ($\delta = 192.8$ and 194.4). In the FAB mass spectrum there is a peak at $(m+1)/z = 1015$ (calculated, 1015.3).

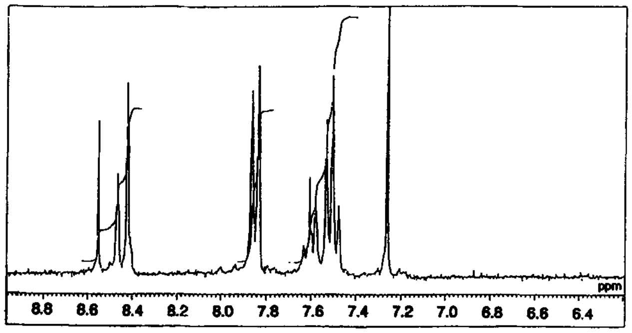


Fig. 2. ^1H NMR (270 MHz, $CDCl_3$) spectrum of nonaketone **17**.

Ketone **17** was converted to the corresponding hydrazone **18**. The oxidation reaction with yellow mercury oxide was carried out in the dark and monitored by thin-layer chromatography (TLC) on alumina. The diazo compound **19** was purified by column chromatography on alumina (activity IV) in the dark. Its IR spectrum shows an absorption at 2037 cm^{-1} characteristic of the diazo group. The UV/Vis spectra of **19** has an absorption maximum at 516 nm attributable to the n–π* absorption and at 289 nm assigned to the π–π* absorption. The molar absorptivity (ε) of the former is 954, a value nearly nine times as large than that of diphenyldiazomethane; this indicates that the molecule had nine cross-conjugated diazo groups.

Magnetization of Photoproducts: The photolysis was carried out at 2 K in the sample room of a Faraday magnetic balance. The light ($400 < \lambda < 500$ nm), from a Xe lamp with a combination of a band-pass filter and a cold mirror, was introduced through a quartz light guide installed for irradiation of the precursor.[13] After the photolysis, the field dependence of magnetization of the photolysate was determined in situ in the dark. The plots of the magnetization vs. the temperature-normalized magnetic field (H/T) (Fig. 3) were analyzed in terms of the Brillouin function [Eq. (1)].

$$M = NgS\mu_B B_S(x) \qquad (1)$$

where

$$B_S(x) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{x}{2S}\right) \qquad (2)$$

and

$$x = \frac{Sg\mu_B H}{k_B T} \qquad (3)$$

(N is the number of molecules, S the spin quantum number, μ_B the Bohr magneton, g the Landé g factor, and k_B the Boltzmann constant). Since these carbenes are hydrocarbons and contain only light elements, the orbital angular momentum should be negligible and S can be used for total angular momentum in Equations (1–3). The observed data were fitted best with the Brillouin function with $S = 7$. The data were collected at two different temperatures, but no temperature dependence was observed. This confirms that the pentadecet is the ground state. The reason why $S = 7$ was observed instead of the theoretically expected $S = 9$ will be discussed below.

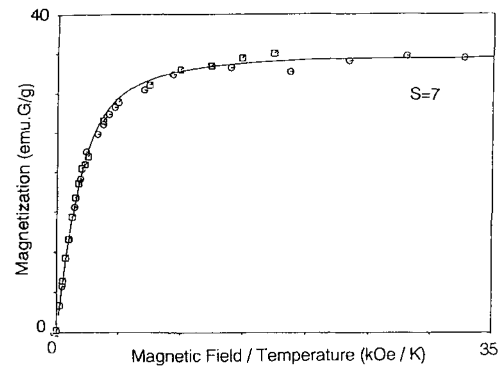


Fig. 3. Field dependence of the magnetization of the photoproduct of nonadiazo compound **19** in an MTHF matrix (0.04 mM), measured at 2.1 (○) and 4.0 K (□). The ordinates are normalized by the amount of the starting diazo compounds and uncorrected for the degree of photolysis.

The magnetization curves of hexacarbene **7** were also recorded at different stages of the photolysis (Fig. 4). The spin quantum numbers of these curves are nearly constant (in the range $S = 6.5$–7). These values were larger than would be expected for a random generation of the carbenes. This suggests that the diazo groups attached to the same molecule are probably eliminated preferentially. After 200 min of photolysis, the observed S value became somewhat smaller (5.67). This may be due to the recombination of the carbene centers on prolonged irradiation. This recombination is also considered to explain why $S = 7$ is observed instead of $S = 9$ (vide infra). The irradiation time shoud therefore be kept below 100 min.

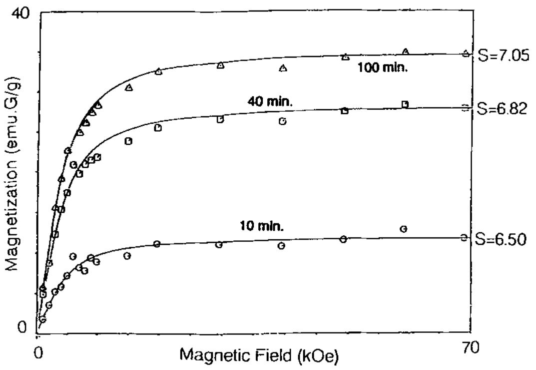


Fig. 4. Magnetization curves for the photoproduct of nonadiazo compound **19** after photolyses at 2.1 K for 10, 40, and 100 min.

The carbene generated from the "starburst"-type diazo compound **19** was concluded to be a pentadecet ($S = 7$) species from the analysis based on the Brillouin function. To confirm this observation and to obtain further information, we measured the UV/Vis spectra before and after the magnetic measurements, that is, before and after irradiation. The rate of the photolysis could be determined by comparing the n–π* absorptions. From the comparison of the UV/Vis data, the degree of the photolysis was concluded to be 90% complete (Fig. 5).

From these data, two theoretical curves were obtained. The $S = 9$ curve in Figure 6 is for the ideal case, that is, all the carbene centers are generated and remain intact. The $S = 7$ curve corresponds to the case where only seven carbene centers are intact and ferromagnetically coupled to each other.

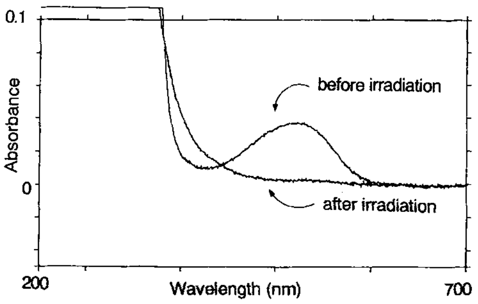


Fig. 5. UV/Vis spectra measured before and after photolysis of nonadiazo compound **19**.

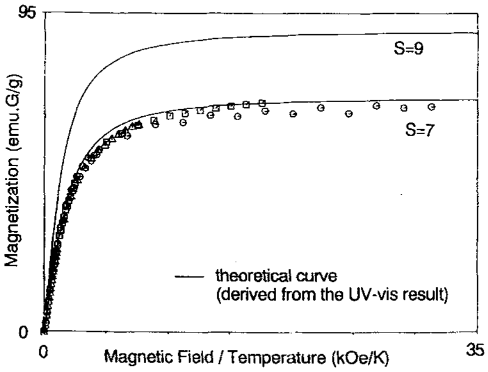


Fig. 6. Magnetization curves (measured at 2.2 (○), 3.9 (□), and 9.0 K (△)) compared to the theoretical curve derived from the results of UV/Vis spectra.

ESR Spectra of the Photoproduct: Photolyses were carried out in an ESR cavity with light ($400 < \lambda < 500$ nm) obtained from a Xe lamp with a combination of band-pass filter and cold mirror. The ESR signals observed in situ were centered at $g = 2$ (Fig. 7).

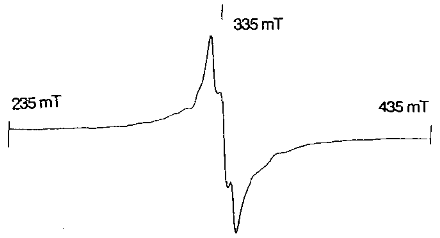


Fig. 7. ESR spectrum (9.40 GHz) of the photoproduct of nonadiazo compound **19** in an MTHF matrix (0.1 mM) at 9.5 K.

The signal shapes did not change from the initial stages of the irradiation. It was difficult to simulate the observed spectra because the line width was broader than the simulated line spacing. But the smaller signal spacing than for $S = 6$ hexacarbene[8] suggested that the D value of this carbene was smaller than that of the hexacarbene. This observation is consistent with the trend towards smaller D values with higher spin multiplicities.[5e] For further study, the ESR fine structure of the oriented species should be analyzed.

Temperature dependence of this spectrum obeyed a Curie law in the temperature range 10–40 K ($I = C(1 \pm 0.12)/T$, where I is the ESR signal intensity). At temperatures above 40 K, the carbene started to decompose with no change of the signal shape due to thermally populated lower spin states. These results suggests that the observed carbenes are the ground state (Fig. 8).

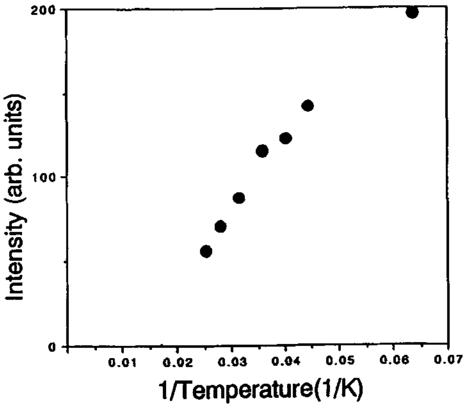
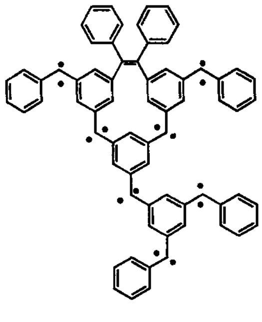


Fig. 8. Temperature dependence of the ESR signal intensities (Curie plot) of the photoproduct of nonadiazo compound.

Feasible Structures for the Oligocarbene Responsible for the Observed $S = 7$: Our analyses showed that, while the nine diazo groups were photolyzed from nonadiazo compound **19**, only seven carbene centers appeared to be aligned parallel in the photoproduct. It is not likely that the nonacarbene **8** has a pentadecet ground state ($S = 7$). Two terminal carbene centers must have strong antiferromagnetic interaction with each other. A feasible and extreme case of such an interaction would be the formation of a chemical bond, as shown in heptacarbene **20**. When diphenyldiazomethane is photolyzed at high concentrations, azine, anthracene, and phenanthrene as well as tetraphenylethylene are obtained.[14] Recombination of two triplet carbene centers to form a singlet ethylene is considered to be a chemical version of triplet–triplet annihilation and is spin-allowed. The structures with azine or phenanthrene instead of the stilbene unit in **20** cannot be excluded. Unfortunately, the amount of the photoproduct from our experiments did not allow us to obtain independent structural proof for **20**. The nonacarbene **8** has a highly branched starburst structure. After the release of the nitrogen molecules, two carbene centers might therefore be generated in close proximity and undergo facile recombination. After bonding, the molecule would not be flexible enough to undergo further recombination. The spin quantum number was constant at 7 regardless of the extent of the photolysis. An energetic one-photon cascade reaction with multiple diazo group cleavage and/or surface effects of the solid photolysis might explain this phenomenon; the preferential release of only seven diazo groups from nonadiazo compound **19** seems unlikely.



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Conclusion

In this paper, we have described the synthesis and magnetic characterization of a "starburst"-type polycarbene. The photolysis of the diazo precursor proceeded smoothly and the degree of the photolysis was determined by UV/Vis absorptions. The magnetization curves obtained were consistent with $S = 7$, regardless of the degree of photolysis. The nonacarbene **8** has a highly branched starburst structure, and, after release of the

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nitrogen molecules from the diazo groups, two carbene centers might therefore be generated in close proximity and undergo facile recombination. The side chains of the less highly branched nonacarbene **7** are thought to be more stretched out and may contain solvent molecules intertwined with the chains, which provide greater protection against the cross-linking of the carbene centers. In fact, analysis of the zero-field tensor of **1** ($n = 4$) revealed that the linear chain is reasonably stretched out and surrounded by host molecules.[5e] It is concluded that, while the polycarbenes based on the *m*-phenylene and 1,3,5-benzenetriyl coupling units are promising candidates for extending the two-dimensional structures, too much branching of the flexible polycarbene chains might generate problems. Efforts to extend the polycarbene strategy should therefore focus on the higher analogues of less branched **7** and more rigid **6**.

Experimental Section

A. Materials: ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-270 instrument. IR spectra were obtained on a Hitachi I-5040 spectrometer. UV/Vis spectra were recorded on a Hitachi U-3300 spectrophotometer. Mass spectra were obtained by JEOL JMX-SX102L instruments. Melting points are not corrected. Diethyl ether and tetrahydrofuran (THF) used in the reactions were distilled, under a dry nitrogen atmosphere, from lithium aluminum hydride just before use. 2-Methyltetrahydrofuran (MTHF) used in the magnetic measurements was purified by successive distillation from lithium aluminum hydride under a nitrogen atmosphere and from sodium-benzophenone ketyl under a dry nitrogen atmosphere. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled under reduced pressure from lithium aluminum hydride. *N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were distilled under reduced pressure from calcium hydride. All reactions were performed under an atmosphere of dry nitrogen unless otherwise specified. Anhydrous magnesium sulfate was used as the drying agent. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light as a detector. Column chromatography was performed on silica gel (Wakogel C-200, 200 mesh) or neutral alumina (ICN, activity grade IV).

3,5-Dibenzylbenzaldehyde (13): To a stirred solution of 3,5-dibenzylbromobenzene **12** [8a] (2.0 g, 6.0 mmol) in dry THF (50 mL) was added 1.6 M *n*-butyllithium in hexane (5.5 mL, 7.2 mmol) under argon atmosphere at −78 °C. After the mixture had been stirred for 1 h at −78 °C, DMF (0.56 mL) was added. The solution was allowed to warm to 10 °C with stirring. The reaction mixture was treated with aqueous ammonium chloride and extracted with diethyl ether. The organic layer was washed with water, dried, filtered, concentrated, to give **13** (1.79 g) as a pale yellow oil. The product was sufficiently pure for the next step. IR (NaCl): $\tilde{\nu} = 1694\ \mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 4.01$ (s, 4H, CH_2), 7.15–7.32 (m, 11 H, Ar), 7.53 (d, $J = 1.1$ Hz, 2H, Ar), 9.91 (s, 1H, CHO). FAB HRMS $\{(m+1)/z\}$ calcd for $C_{21}H_{19}O$: 287.1436; found: 287.1436 (100).

3,5-Dibenzyl-1-(1-hydroxy-2-propynyl)benzene (14): To dry THF (50 mL) was added with stirring a hexane solution of *n*-butyllithium (1.6 M, 5.5 mL) and TMEDA (1.2 mL) under argon atmosphere at −78 °C. Acetylene was then bubbled through the solution with vigorous stirring at −78 °C. After the acetylene absorption was complete, as judged by appearance of a slurry, the gas flow was stopped and the solution was stirred for 0.5 h. Crude **13** (1.79 g) was added to the mixture at −78 °C to give a clear solution, which was then allowed to warm up to 10 °C. The reaction mixture was quenched with aqueous ammonium chloride, extracted with diethyl ether. The organic layer was washed with water, dried, filtered, and concentrated to give **14** (1.87 g) as a pale yellow oil. The product was sufficiently pure for the next step. IR (NaCl): $\tilde{\nu} = 3544, 3287, 2118\ \mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 2.09$ (d, $J = 6.2$ Hz, 1H, OH), 2.62 (d, $J = 1.5$ Hz, 1H, C≡CH), 3.96 (s, 4H, CH_2), 5.38 (dd, $J = 6.2$ Hz, 2.0 Hz, 1H, CH(OH)), 7.16–7.31 (m, 12H, Ar). FAB HRMS $\{(m-1)/z\}$ calcd for $C_{23}H_{19}O$: 311.1436; found: 311.1448 (100).

3,5-Dibenzyl-1-(2-propynoyl)benzene (15): To a stirred solution of crude **14** (1.87 g) in acetone (100 mL) was added dropwise at 0 °C aqueous Jones reagent (2 g) prepared from chromium trioxide (400 mg), water (0.8 mL), and sulfuric acid (0.4 mL) at 0 °C. The reaction mixture was stirred for 1 h while the temperature was allowed to warm up to ambient temperature. After evaporation of acetone, water and diethyl ether were added. The mixture was extracted with diethyl ether, washed with water, dried, and concentrated, and purified by column chromatography on silica gel eluted with hexane/dichloromethane (2:1 v/v) to give **15** (1.28 g, 70% from **13**). M.p. 57.0–58.7 °C; IR (KBr): $\tilde{\nu} = 3270, 2095, 1651\ \mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 3.36$ (s, 1H, C≡CH), 4.01 (s, 4H, CH_2), 7.14–7.33 (m, 11 H, Ar), 7.85 (d, $J = 1.1$ Hz, 2H, Ar). FAB HRMS $\{(m+1)/z\}$ calcd for $C_{23}H_{19}O$: 311.1436; found: 311.1437 (84.3).

1,3,5-Tris(3,5-dibenzylbenzoyl)benzene (16): To a stirred solution of **15** (1.28 g, 4.12 mmol) in toluene (13 mL) was added diethylamine (40 mg). The resulting yellow solution was refluxed for 40 h, with stirring under argon atmosphere. The solvent was then removed in vacuo, and the residual brown oil was chromatographed on silica gel and eluted with hexane/dichloromethane (1:1 v/v) to give **16** (1.10 g, 86%) as a brown viscous oil. IR (NaCl): $\tilde{\nu} = 3085, 3061, 3027, 2915, 1663\ \mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 4.01$ (s, 12H, CH_2), 7.10-7.31 (m, 33 H Ar), 7.46 (d, $J = 1.1$ Hz, 6H Ar), 8.21 (s, 3H, Ar). FAB HRMS $\{(m+1)/z\}$ calcd for $C_{69}H_{55}O_3$: 931.4151; found: 931.4147 (100).

1,3,5-Tris(3,5-dibenzoylbenzoyl)benzene (17): To a stirred solution of **16** (1.10 g, 1.37 mmol) in acetic acid (10 mL) at 100 °C was added sodium dichromate dihydrate (8 g, 26.8 mmol), and the mixture was refluxed for 12h. The warm reaction mixture was poured into water, extracted with benzene, washed with water, dried, concentrated, and purified by column chromatography on silica gel. Elution with dichloromethane and concentration gave **17** (510 mg, 43%) as a white solid. M.p. 114–124 °C; IR (KBr): $\tilde{\nu} = 3061, 1663\ \mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 7.50$ (t, $J = 7.7$ Hz, 12H, Ar), 7.60 (t, $J = 7.3$ Hz, 6H, Ar), 7.84(d, $J = 7.3$ Hz, 12H, Ar), 8.42(s, 6H, Ar), 8.46(s, 3H, Ar), 8.55(s, 3H, Ar); ^{13}C NMR (67.8 MHz, CDCl$_3$): $\delta = 128.7$, 130.1, 133.4, 133.9, 134.6, 135.0, 136.2, 136.7, 133.7, 138.7, 192.8, 194.4. FAB MS (*m*-nitrophenyl octyl ether) $(m/z+1)$ calcd for $C_{69}H_{42}O_9$: 1015.3; found: 1015 (4).

1,3,5-Tris[[3′,5′-bis[phenyl(1,1-diazanediyl)methyl]phenyl](1,1-diazanediyl)methyl]-benzene (18): To a solution of nonaketone **17** (100 mg, 0.10 mmol) in anhydrous hydrazine (1.5 mL) and dry DMSO (3.0 mL) was added hydrazine monohydrochloride (240 mg, 3.50 mmol). After being stirred at 110 °C under argon atmosphere for 6 h, the reaction mixture was poured into water. The precipitate was collected and washed with water to give nonahydrazone **18** (105 mg, 93%) as a white solid. IR (KBr): $\tilde{\nu} = 3393, 3285, 3204, 3056, 1561\ \mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 5.35$–5.57 (m, 18H, NH_2), 7.02–7.56 (m, 42H, Ar).

1,3,5-Tris[[3′,5′-bis[phenyl(diazo)methyl]phenyl](diazo)methyl]benzene (19): Yellow mercury oxide (600 mg) was added in the dark to a solution of nonahydrazone **18** (20 mg, 18 mmol) in dichloromethane (4 mL), diethyl ether (2 mL), benzene (4 mL), and saturated ethanolic potassium hydroxide (30 drops). The mixture was stirred for 4 d in the dark at ambient temperature and was monitored by TLC (alumina). Filtration, concentration, and purification by chromatography on alumina (act. IV, elution with benzene/hexane, 1:1, v/v) gave nonadiazo compound **19** (2.1 mg, 11%) as a deep red viscous oil. IR (KBr): $\tilde{\nu} = 2037, 1578\ \mathrm{cm^{-1}}$; UV/Vis (MTHF): $\lambda_{\max}$ (ε) = 289 (187000), 516 (954) nm; ^{1}H NMR (270 MHz, CD$_2$Cl$_2$): $\delta = 6.86$–7.38 (m, 42H, Ar).

B. Magnetic Measurements: Magnetic measurements of the polycarbenes were performed by using a Faraday-type magnetic balance system of Oxford Instruments in the temperature range 2.1–10 K. The diazo precursors were dissolved in a MTHF matrices in a quartz sample basket, which was suspended by means of a quartz filament in the cryostat, in the magnetic field and field gradient. Photochemical generation of the carbenes was accomplished by introducing, through a quartz light guide, the light ($400 < \lambda < 500$ nm) tapered through the band-pass filters. The temperature setting during the photolysis was under 2 K, but the temperature rose to 4 K during irradiation. The field dependence of magnetization was measured before irradiation at the same temperature and magnetic field. These data before irradiation were used as background data, and the net magnetization data for the carbenes were obtained by subtracting these data from those after photolysis.

Photolyses of solutions of diazo compound **19** in MTHF (100 µL) were carried out as follows: By using a field gradient of 5 Tm^{-1}, the main field was scanned from 0 to 7 T at temperatures of 2 and 8 K. The decrease in the magnetic force between 0 and 7 T due to diamagnetism of the precursors including the solvent and basket material was about 6.0 mg at 4 K. Relative to this background, the increase in the magnetic force due to the paramagnetism of the carbenes generated after the irradiation was ca. 0.2 mg and read to ±1 µg between 0 and 7 T at 4 K.

The degree of photolysis was determined by comparing the absorbance of the $n-\pi^*$ transitions. The UV/Vis spectra of a sample before and after photolysis were determined. UV/Vis spectra of the sample after photolysis were recorded after leaving the sample in the dark at 100 K for some time to exclude reactions between molecules. The ordinate of the magnetization curve was calibrated from these data.

C. ESR Spectra: Photolysis of diazo compounds **19** were carried out in MTHF matrices at 9 K in an ESR cavity. The light ($400 < \lambda < 500$ nm) was obtained from a Xe lamp with combination of a Kenko B-390 band-path filter and an OCLI B cold mirror. A Bruker ESP300 spectrometer was used to obtain X-band ESR Spectra. Temperatures were controlled by an Air Products LTD-3-110 cryogenic temperature controller. The cryostat was maintained at high vacuum by a diffusion/rotary pump set. The ESR intensities for Curie plots in the temperature range 4–50 K were measured at appropriate power attenuation calibrated to exclude saturation effect. The temperatures were stepped up from 9 to 70 K with intervals of ca. 5 K.

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