

Headline Articles

Toward Dendritic Two-Dimensional Polycarbenes: Syntheses of 'Starburst'-Type Nona- and Dodecadiazo Compounds and Magnetic Study of Their Photoproducts

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'Starburst'-type nona- and dodecadiazo compounds were designed and synthesized by using the cyclotrimerization of ethynyl ketones as a key step. Construction of the larger dodecadiazo compounds was facilitated by using a trimethylsilyl protecting group for an acetylenic moiety. The diazo compounds were photolyzed in MTHF solid solution at cryogenic temperatures and analyzed by means of Faraday magnetometry and ESR spectroscopy. From the field dependence of the magnetization, the nonacarbene, the photoproduct of nonadiazo compound, was evidenced to have a nonadecet ($S=9$) ground state. This spin multiplicity is the highest value ever reported for purely organic materials. On the other hand, the spin multiplicity was low and antiferromagnetic interaction operated in the photoproduct of the dodecadiazo compound. This result was interpreted not in terms of the intermolecular antiferromagnetic interaction but of the intramolecular cross-linking between the carbene centers. In the 'Starburst'-type polycarbenes with extended branching, the reactive carbene centers can become mutually too close to each other in space and so appear to recombine readily. This study showed one of the limitations of the extension of the carbene network by way of flexible 'Starburst'-type structures.

Great efforts have been made by many scientists to embody very high-spin molecules or superparamagnetic materials based on organic molecules which show spontaneous magnetization.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. Construction of a high-spin molecule is an antithesis of chemical bonding. The first example of this kind of molecule is the *m*-phenylenedicarbene **1** ($n=2$) prepared by Itoh and Wasserman. They demonstrated that it has a quintet ground state ($S=2$).⁴⁾ The dicarbene has been extended to linear tri-, tetra-, and pentacarbenes **1** ($n=3, 4, 5$, respectively). These were established from their EPR fine structures and/or magnetization data to have $S=3, 4$, and 5 ground states, respectively.⁵⁾

The linear structure can in principle be extended to poly(*m*-phenylenedicarbene)s **1** ($n \rightarrow \infty$). In practice, however, there are a number of drawbacks in the linear structure. Firstly, it becomes more and more difficult to produce all the carbene centers without fail and to keep them intact. Once such a chemical defect is formed in the middle of the cross-

conjugated main chain, the high spin multiplicity would be halved.^{3e)} The linear polyketones, key precursors, become less and less soluble in typical organic solvents in which further chemical transformations have to be carried out. One-dimensional alignment of spins is said to be unstable from a statistical mechanic point of view. No magnetic linear chain including **1** is expected to exhibit any spontaneous magnetization at finite temperature 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 and not much greater than kT .⁶⁾

To overcome these problems, construction of a high-dimensional network became one of the important objectives. A rigid structure would also help to reduce the high reactivity of triplet carbene centers as one-center diradicals toward recombination, etc. Thus we have arrived at network structure **2** as a long-range goal of the strongly magnetic super-high-spin polycarbenes (Chart 1). We have reported design, synthesis, and characterization of pseudo-two-dimensional hexacarbenes.⁷⁾ In these studies, it has been demonstrated that it is not the shape or geometrical symmetry of the

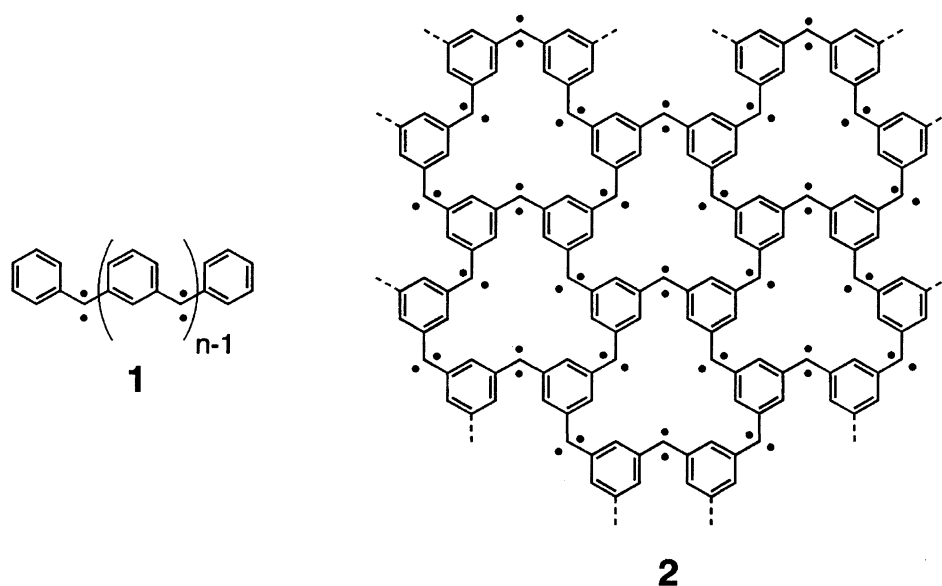


Chart 1.

molecules but the topological symmetry which is most important in determining the spin multiplicity of the alternant hydrocarbon molecules. To investigate how far this strategy can be adopted, we extended these systems to nonacarbenes **3**⁸⁾ and **5** (Charts 2 and 3).⁹⁾ From the study of the latter, the limitation of this strategy started to manifest itself. In this paper we report the extension of these polycarbenes toward dendritic 'Starburst'-type polycarbenes, featuring dodecacarbene **4** in reference to nonacarbene **3**.

Results and Discussion

Molecular Design and Synthesis of the Precursors.

The photochemical precursors for polycarbenes were the corresponding diazo compounds which were derived from polyketones. The way to construct the skeleton of the ketones is the focal point of the synthetic strategy. The nonaketone **13**, the precursor of the nonadiazocompound **15**, was syn-

thesized by the simple extension of hexaketone previously reported.⁷⁾ The dodecaketone **28**, the precursor of dodecadiazocompound **30**, which has a more dendritic structure, was synthesized in the way used to construct dendrimer. Among the several ways to construct a dendrimer, we chose Fréchet's convergent approach¹⁰⁾ (Fig. 1). To adopt the convergent approach, two units are required as building blocks and two kinds of aryl ethynyl ketones **21** and **22** were chosen (Chart 4). Secondary-amine-catalyzed trimerization of ethynyl ketone¹¹⁾ and deprotection of trimethylsilyl protecting group was used as key steps in the construction of the structure. The 'Starburst'-type structure is also popular in physics as a Bethe lattice.¹²⁾ Ising spins on a Bethe lattice are calculated to show a phase transition at finite temperature. The number of the spins which are connected to the system becomes drastically large as the system extends. Thus, also from a statistical mechanics point of view, the construction

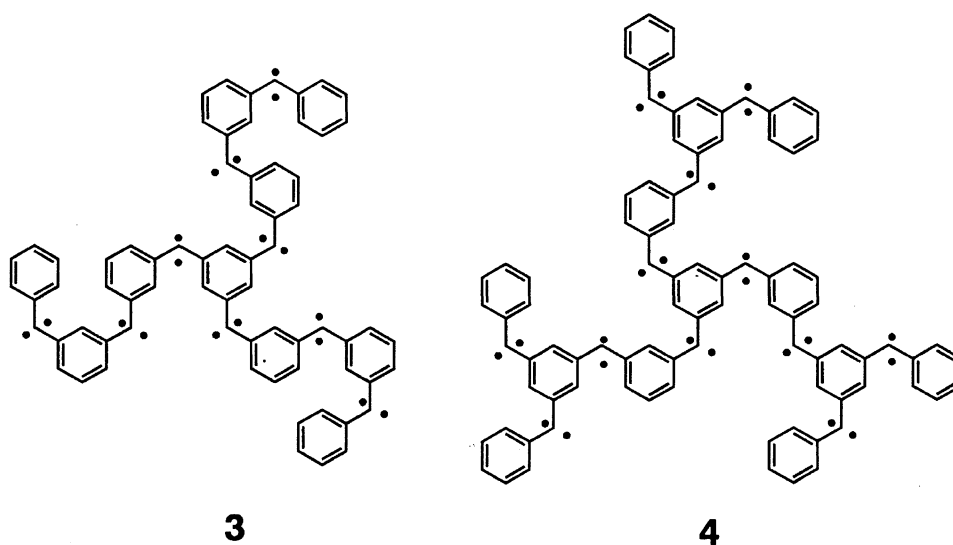


Chart 2.

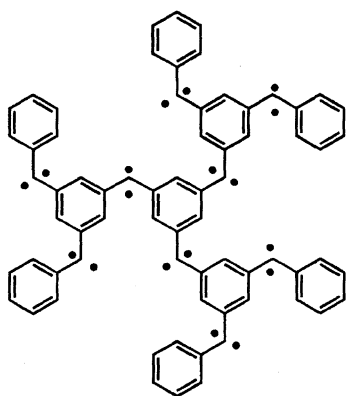
**5**

Chart 3.

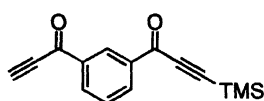
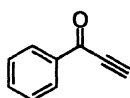
**21****22**

Chart 4.

of a dendritic spin system is intriguing.

The preparative route to the nonaketone **13** is shown in Scheme 1. Bromo compound **6** was lithiated, then reacted with *m*-bromobenzaldehyde to give alcohol **7**, which was reduced to bromo compound **8**. The bromo compound **8** were lithiated, then reacted with DMF to afford aldehyde **9**. Reaction of aldehyde **9** with lithium monoacetylide followed by Jones oxidation gave ethynyl ketone **11**. The ethynyl ketone **11** was cyclotrimerized, then oxidized to give nonaketone **13**.

The preparative route to diketone **21** is summarized in Scheme 2. Trimethylsilylacetylene was lithiated, then reacted with isophthalaldehyde **16** to give alcohol **17**. Alcohol **17** was protected by a THP group, then reacted with lithium monoacetylide. After deprotection, Jones oxidation was performed to give diketone **21**.

Cross-trimerization of two kinds of ethynyl ketones **21** and **22** afforded a mixture of four kinds of trimers: trimer **23** from three moles of **21**, 2 : 1 trimer **24**, 1 : 2 trimer **25**, and trimer

26 from three moles of **22**. These trimers could be separated by gel permeation chromatography (GPC). The trimer **25** was the required molecule in the subsequent reactions. After deprotection of the trimethylsilyl group, the trimerization reaction of tetraketone **27** was carried out once again to afford dodecaketone **28** (Scheme 3).

Figure 2 shows the NMR spectra of tetraketone **27** and dodecaketone **28**. The signals in the low-field region, where the 1,3,5-triaroyl-substituted phenyl proton appeared, showed a clear difference between the spectra before and after trimerization. These ketones were characterized by ^1H , ^{13}C , and HH-COSY NMR, IR, and FAB mass spectroscopy. The ^1H NMR spectrum of **28** showed singlets at $\delta = 8.35$, 8.40, a mono-substituted benzene pattern at $\delta = 7.49$ (t), 7.61 (t), 7.83 (d), and a *meta*-substituted benzene pattern at $\delta = 7.69$ (t), 8.06–8.12 (d $\times$ 2), 8.35 (bs). The ^{13}C NMR showed sixteen signals of aromatic carbons at $\delta = 128.6$, 129.2, 130.0, 131.0, 133.2, 133.9, 134.12, 134.17, 134.25, 134.5, 136.2, 136.7, 137.1, 137.3, 137.9, 138.3, and three signals of carbonyl carbons at $\delta = 193.3$, 193.6, and 194.5. The HH-COSY NMR of dodecaketone **28** clearly showed four sets of phenyl rings (Fig. 3). FAB mass spectroscopy revealed $(m+1)/z = 1327.3689$, while the calculated value was 1327.3694.

These ketones were converted to the corresponding hydrazones **14** and **29**. The oxidation reaction with yellow mercury(II) oxide was carried out in the dark and monitored by thin-layer chromatography (TLC) on alumina. The diazo compounds **15** and **30** were purified by column chromatography on alumina (activity IV) in the dark.

The IR spectra of **15** and **30** showed absorptions at 2060 and 2040 cm^{-1} characteristic of the diazo groups, respectively. The UV-vis spectra of **15** and **30** had an absorption maximum at 520 nm attributable to the $n\text{--}\pi^*$ transition. The molar absorptivities (ϵ) were 950 and 1660 for **15** and **30**, respectively, values nearly nine and twelve times as large as that of diphenyldiazomethane, indicating that the molecules had nine and twelve cross-conjugated diazo groups (Fig. 4).

Magnetization of Photoproducts. The photolysis was carried out at 2 K in the sample compartment of a Faraday magnetic balance. The light (400 nm $< \lambda < 500$ nm) from a Xe lamp treated with a combination of a band-pass fil-

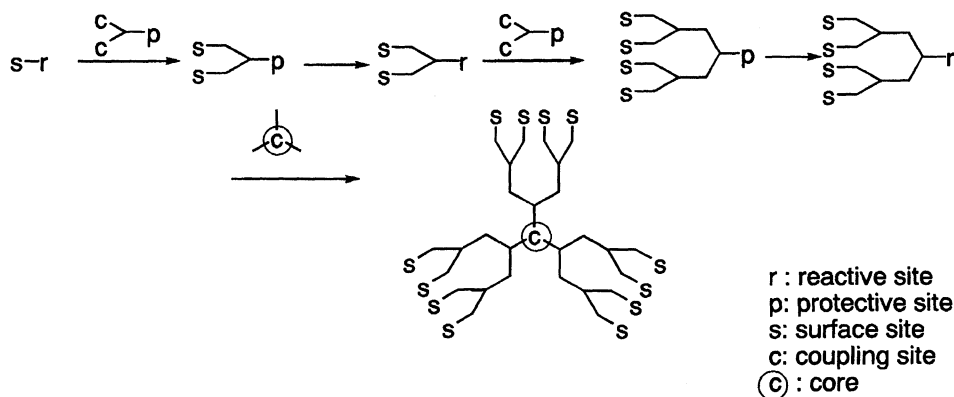
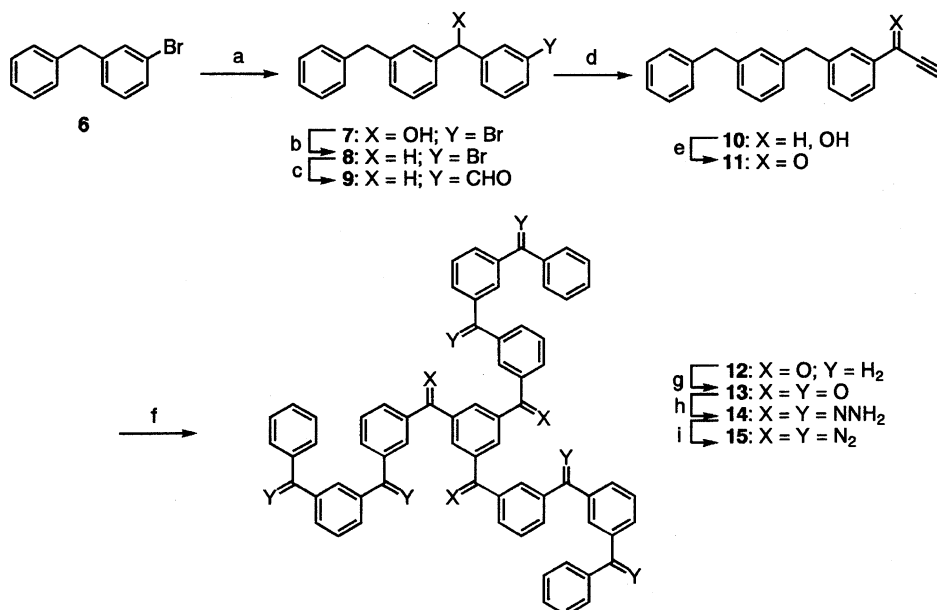
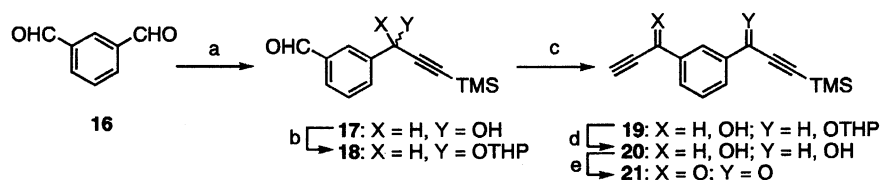


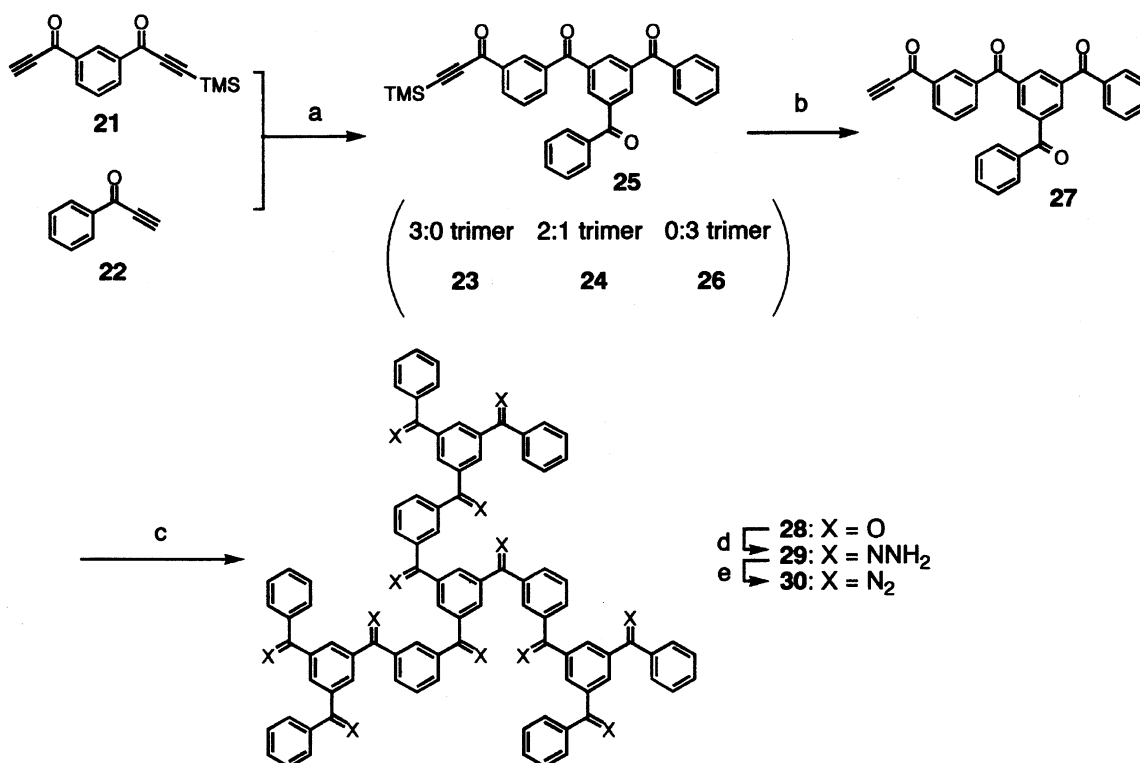
Fig. 1. Convergent approach to dendrimer.



Scheme 1. Reagents and Conditions: (a) Mg, THF, then 3-Br-C₆H₄-CHO, 86%; (b) LiAlH₄-AlCl₃, Et₂O, 62%; (c) Mg, THF, then DMF, 94%; (d) HC≡C-Li, TMEDA, THF, -78 °C, 62%; (e) 2/3 mol amt. of CrO₃-H₂SO₄, acetone; (f) Et₂NH, toluene; (g) Na₂Cr₂O₇·2H₂O, AcOH, 78%, 3 steps; (h) N₂H₄, N₂H₄·HCl, DMSO, 90 °C, 94%; (i) HgO, EtOK, benzene, 65%.



Scheme 2. Reagents and Conditions: (a) 1 mol amt. of TMS-C≡C-Li, TMEDA, THF, -78 °C, 26%; (b) DHP, PPTS, CH₂Cl₂; (c) HC≡C-Li, TMEDA, THF, -78 °C; (d) EtOH, PPTS; (e) 4/3 mol amt. of CrO₃-H₂SO₄, acetone, 79%, 4 steps.



Scheme 3. Reagents and Conditions: (a) Et₂NH, toluene, then GPC, 31%; (b) KF, MeOH, -20 °C, 96%; (c) Et₂NH, toluene, 35%; (d) N₂H₄, N₂H₄·HCl, DMSO, 90 °C, 63%; (e) HgO, EtOK, Et₂O, CH₂Cl₂, 24%.

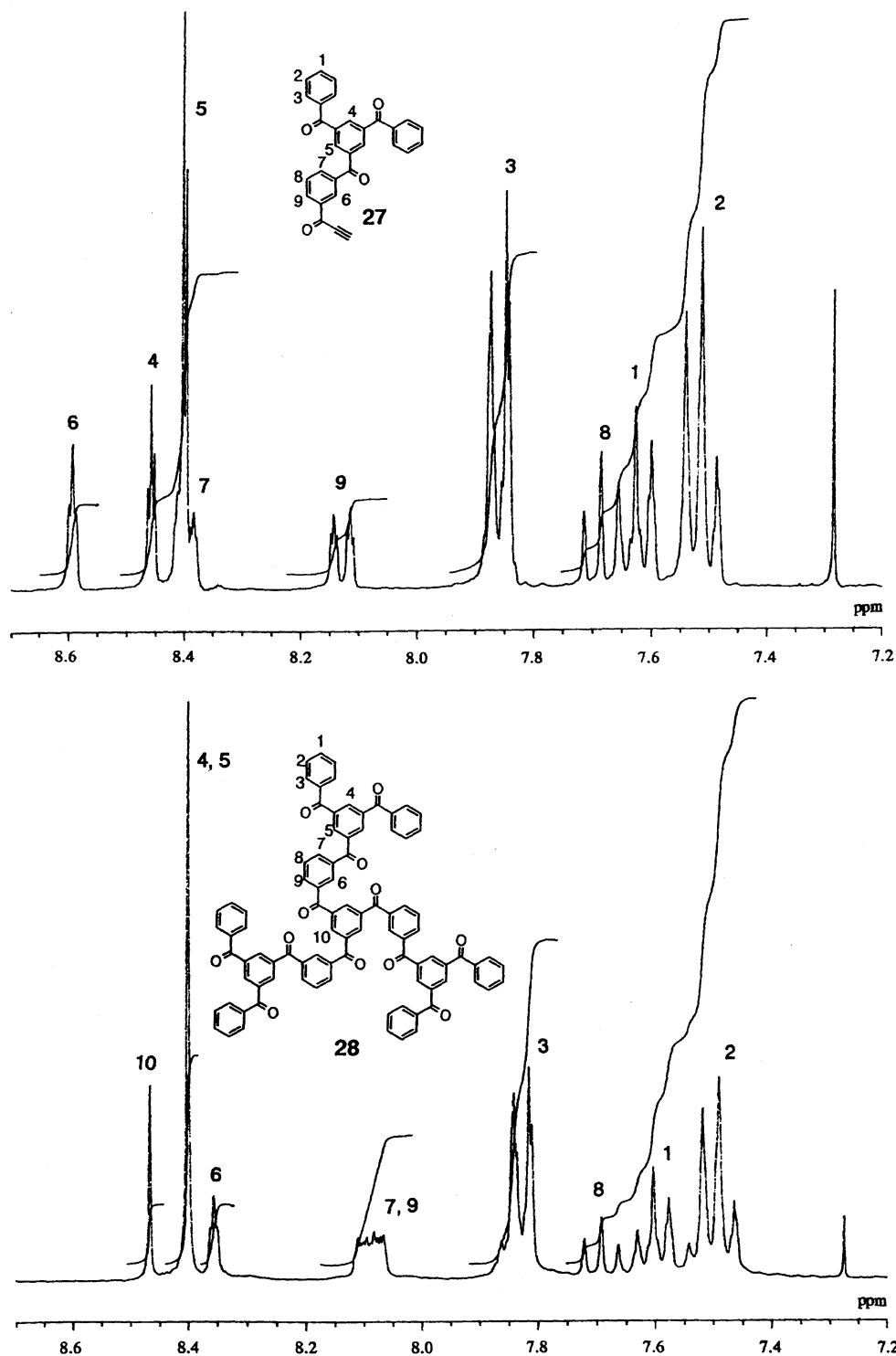
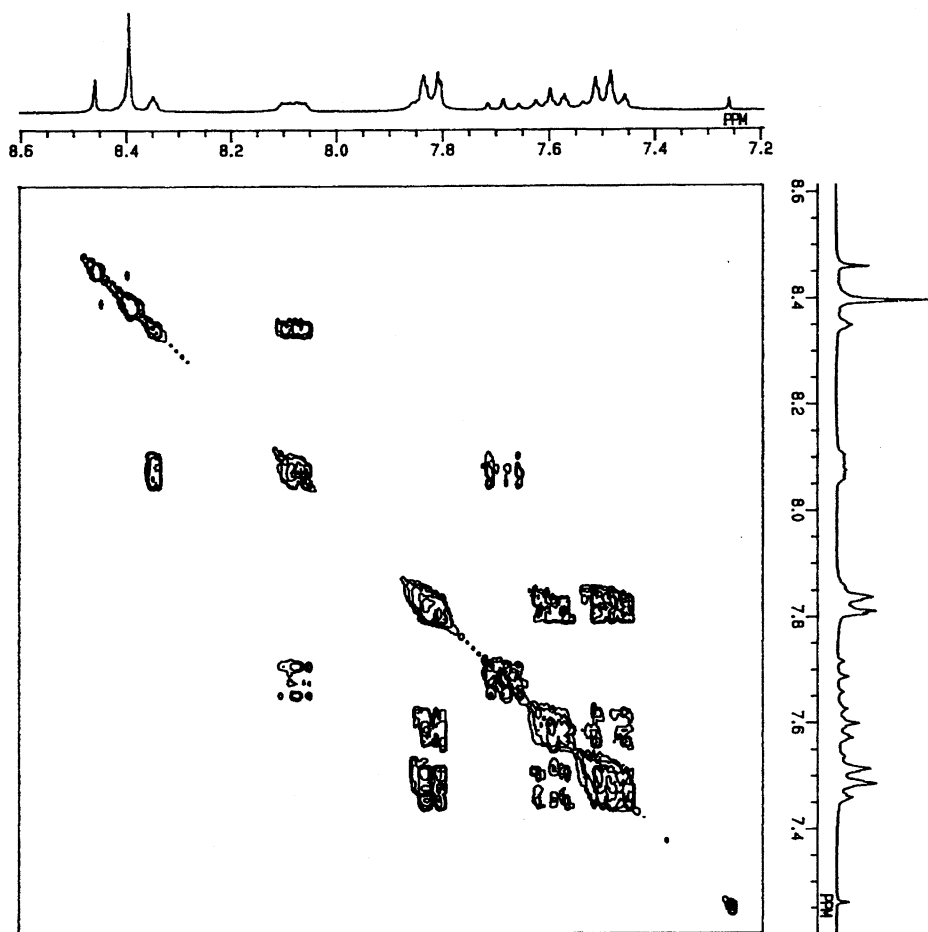
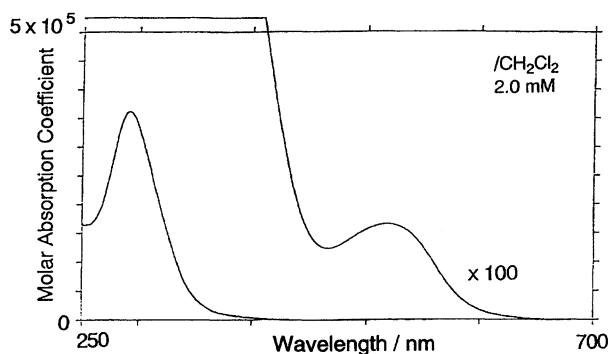


Fig. 2. ¹H NMR spectra (270 MHz, CDCl₃) of a) tetraketone **27** (before trimerization) and b) dodecaketone **28** (after trimerization).

ter and a cold mirror was introduced through a quartz light guide installed for irradiation of the precursor.^{1d)} After the photolysis, the field dependence of the magnetization of the photoproduct was measured in situ in the dark. The plots of the magnetization vs. the temperature-normalized magnetic field (H/T) due to the polycarbenes were analyzed in terms of Eq. 1 (Figs. 5 and 6):

$$M = Ng\mu_B S B_S(x) \quad (1)$$

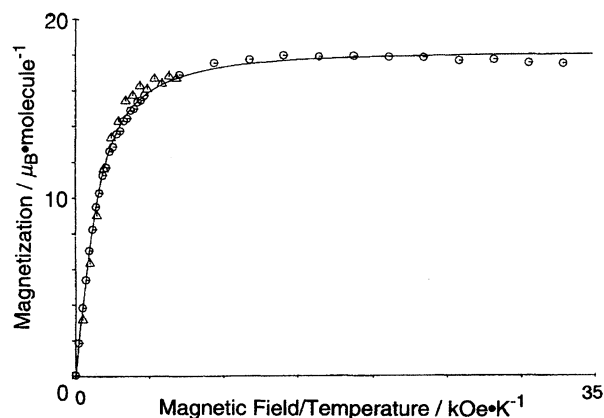
where N is the number of the molecule, S is the spin quantum number, μ_B is the Bohr magneton, g is the Landé g -factor, and $B_S(x)$ is the Brillouin function. Since these carbenes are hydrocarbons and have only light elements, the orbital angular momentum should be negligible and S can be used

Fig. 3. ${}^1\text{H}$ -COSY NMR spectra (270 MHz, CDCl_3) of dodecaketone **28**.Fig. 4. UV-vis spectra of dodecadiazo compound **30** (2.0 mM, CH_2Cl_2).

for total angular momentum in Eq. 1.

The data of the nonacarbene **3**, a photoproduct of nonadiazocompound **15**, showed saturation of the magnetization at a field less than 1 T, demonstrating that an unconventionally high spin species was generated. The formation of a nonadecet ground state species was supported by best-fitting the observed data to the theoretical curve with $S=9$. This material did not show any spontaneous magnetization and hysteresis and therefore was concluded to be a paramagnetic species with exceptionally large Landé magnetic moment.

In Fig. 6 the field dependence of magnetization of the photoproduct of dodecadiazo compound **30** is displayed. The data obtained at three different temperatures did not agree with one another (Fig. 6a), suggesting that an antiferromagnetic interaction is operative in this photoproduct. When the sample concentration as low as 0.1 mM is taken into account,

Fig. 5. Field dependence of the magnetization of the photoproduct of nonadiazocompound **15** in 0.10 mM MTHF matrix, measured at 2.1 ($\circ$) and 10.0 (Δ) K. The ordinates are normalized at $18\mu_{\text{B}}$. Solid line shows theoretical curve with $S=9$.

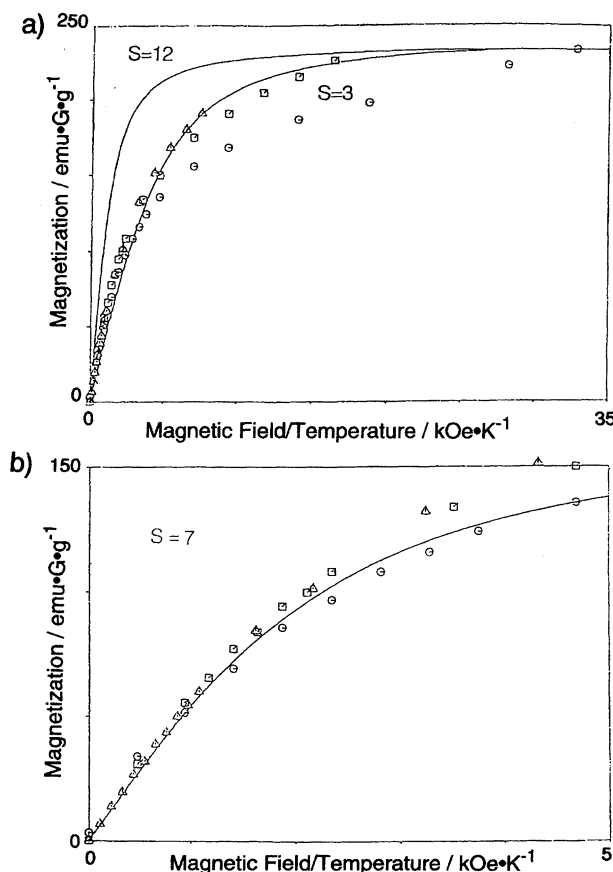


Fig. 6. Field dependence of the magnetization of the photoproduct of dodecadiazo compound **30** in 0.10 mM MTHF matrix, measured at 2.1 (○), 4.2 (□), and 9.1 (△) K. The ordinates are normalized by the amount of the starting diazo compounds and uncorrected for the degree of photolysis. a) full region; b) expansion of a) in the region shown in the axis.

the observed antiferromagnetic interaction is assigned to an interbranch interaction within a molecule rather than between molecules. Furthermore, the observed data did not obey the theoretical curve either with $S=12$ or that with any other spin quantum number. As H/T was increased, the magnetization rose rapidly but leveled off rather slowly. The formation of several spin species of different spin multiplicities was also suggested in this photoproduct. Interpretation of these magnetic data will be made later.

In Fig. 6b, the expansion of Fig. 5a, is given the fitting of the observed data with the $S=7$ theoretical curve. Thus, whereas the observed spin multiplicity appeared to be much lower than the expected $S=12$, it was also found that high-spin species like $S=7$ species were also generated. Compared to the Rajca's dendritic polyarylmethyl radicals,^{3e)} this spin quantum number is still very high for purely organic material. This showed one of the merits of the strategy of using carbenes as spin sources. In the case of Rajca's polyarylmethyl radicals, the last step of a sequence of reactions is oxidation in fluid solution with exclusion of air. The polycarbene enjoyed the advantages of being produced efficiently

by irradiation of the diazo precursors. Though the carbenes are very reactive, the structural defects during the generation could mostly be avoided.

ESR Spectra of the Photoproducts. Photolyses of **15** and **30** were carried out in an ESR cavity with the light ($400 < \lambda < 500$ nm) generated from a Xe lamp and treated with a combination of a band-pass filter and a cold mirror. The ESR signal of the photoproduct of **30** observed in situ was single line centered at $g=2$ (Fig. 7a), while the signal of the photoproduct of **15** consisted of many lines gathered at $g=2$. It was difficult to simulate these observed spectra because the linewidths were broader than the simulated line spacings. The signal spacing was so small that no fine structures were observed. This is consistent with a tendency that the higher the spin multiplicity, the smaller the D values.^{5e)} ESR fine structure analysis of the oriented species remains to be made.

To investigate the origin of the low spin state observed in the case of dodecacarbene **4**, we performed the photolysis of dodecadiazo compound **30** by using the weak light (1/10 intensity) and measured the ESR spectrum at the initial stage (Fig. 7b). It was naively postulated that the triplet and quintet species might be found at the initial stage. But the amounts of these low-spin species were small and negligible when the photoreaction had sufficiently proceeded. We have reported that the diazo groups of the hexacarbenes^{7d)} are likely to be eliminated simultaneously and that a one-photon-multicleavage reaction may be operative.^{5e)} We have concluded that the low spin species observed at the very initial stage of the photolysis did not affect the result of the magnetic measurement.

The temperature dependence of this spectrum obeyed a

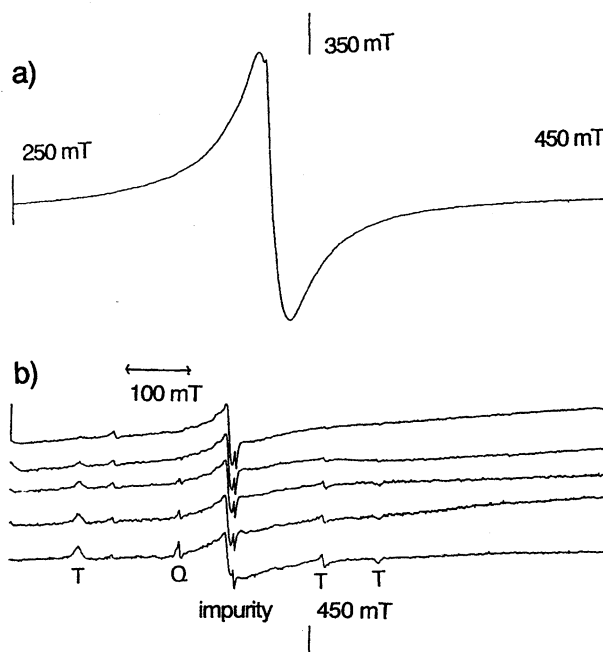


Fig. 7. a) ESR Spectrum of the photoproduct of dodecadiazo compound **30** in 0.1 mM MTHF matrix at 9.5 K (9.43 GHz); b) ESR Spectrum of the photoproduct of dodecadiazo compound **30** at the initial stage by using the light of 1/10 intensity.

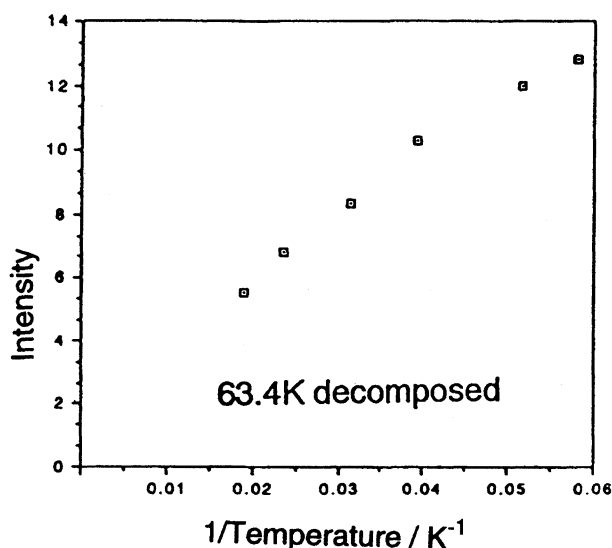


Fig. 8. Temperature dependence of the ESR signal intensities (Curie Plot) of the photoproduct of dodecadiazo compound **30**.

Curie law in the temperature range 10–50 K. The signal shape did not change in this temperature range; no population of the lower spin states were observed. This result suggests that the observed carbenes are in the ground-state (Fig. 8). At the temperatures higher than 50 K, the carbene started to decompose, and at 63 K the signal changed to a sharp single line which may be attributed to doublet species.

Possible Interpretation of the Magnetic Data Due to the Photoproduct from **30.** Here we will discuss the origin of the low spin species and the antiferromagnetic interaction observed in the magnetic measurement of the photoproduct of dodecadiazo compound **30**. We will consider the magnetization curve when antiferromagnetic interaction is in operation between high spin molecules by using mean-field approximation.^{2b)} The magnetic susceptibility is given by Eq. 2 in this approximation.

$$\chi = \frac{Ng^2\mu_B^2S(S+1)}{3k(T-\theta)} \quad (2)$$

where $\theta = C\lambda$, λ describes the magnitude of the internal field. The field dependence of the magnetization can be described as

$$M = Ng\mu_B SB_S(x) \quad (3)$$

$$x = \frac{g\mu_B S(H_{\text{ext}} + \lambda M)}{kT} \quad (4)$$

Let us introduce the sublattices A and B. For sublattice A, magnetization M_A is described as below:

$$M_A = \frac{1}{2}Ng\mu_B SB_S(x_A) \quad (5)$$

$$\text{where } x_A = \frac{g\mu_B SH_{\text{ext}}}{kT} + \frac{2 \cdot 3\theta}{g(S+1)TN\mu_B} M_B \quad (6)$$

For sublattice B:

$$M_B = \frac{1}{2}Ng\mu_B SB_S(x_B) \quad (7)$$

$$\text{where } x_B = \frac{g\mu_B SH_{\text{ext}}}{kT} + \frac{2 \cdot 3\theta}{g(S+1)TN\mu_B} M_A \quad (8)$$

Net magnetization M can be expressed as

$$M = M_A + M_B \quad (9)$$

$$\text{and therefore } M = Ng\mu_B SB_S(x) \quad (10)$$

$$\text{where } x = \frac{g\mu_B SH_{\text{ext}}}{kT} + \frac{3\theta}{g(S+1)TN\mu_B} M \quad (11)$$

When $S=12$, the magnetization M can be obtained as the crossing point of the two curves,

$$\begin{cases} y = M \\ y = 12Ng\mu_B B_{12} \left(\frac{12g\mu_B H}{kT} + \frac{3\theta}{13gT} \cdot \frac{M}{\mu_B} \right) \end{cases}$$

The computational results are shown in Fig. 9. When the antiferromagnetic interaction is operative the magnetization curve rises slowly and becomes saturated. The observed phenomena are not consistent with this. Thus, the antiferromagnetic interaction alone cannot explain the result even semi-quantitatively.

From the reason given above, the observed data in Fig. 5a should in principle be simulated by a sum of several theoretical curves with different spin quantum numbers. Some of the photoproduct should be with lower spin state than $S=3$ because the theoretical curve for $S=3$ lay higher than the observed data in the high field region. We have demonstrated that, while ‘Starburst’-type nonacarbene **5** was predicted to be with a nonadecet ($S=9$) ground state, the observed magnetic data of the photoproduct was more consistent with a pentadecet ($S=7$) species.⁹⁾ 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. When diphenyldiazomethane is photolyzed in high concentration, azine, anthracene, and phenanthrene as well as tetraphenylethylene are obtained.¹³⁾ Recombination of two triplet carbene centers to form a singlet ethylene is considered to be a chemical version of triplet–triplet annihilation and spin-allowed. In our case, the crowdedness of the branches in the ‘Starburst’-type structures is responsible for high local concentrations. In reference to this nonadiazo compound, we think the most reasonable explanation is the cross-linking of the carbene chains which would cleave the π -cross-conjugated network into small spin segments and induce an antiferromagnetic interaction between them.

Conclusion

In this paper we have described the synthesis of dendritic ‘Starburst’-type dodecadiazo compounds which are the precursors of dendritic polycarbenes. The construction of the network was facilitated by using cross-cyclotrimerization of two kinds of ethynyl ketones and trimethylsilyl group as a protecting group. The magnetic data on the photoproducts should be explained by the undesired cross-linking of the highly-branched carbene chains. Like the result from polyarylmethyl radical,^{3e)} the highly branched structure was not

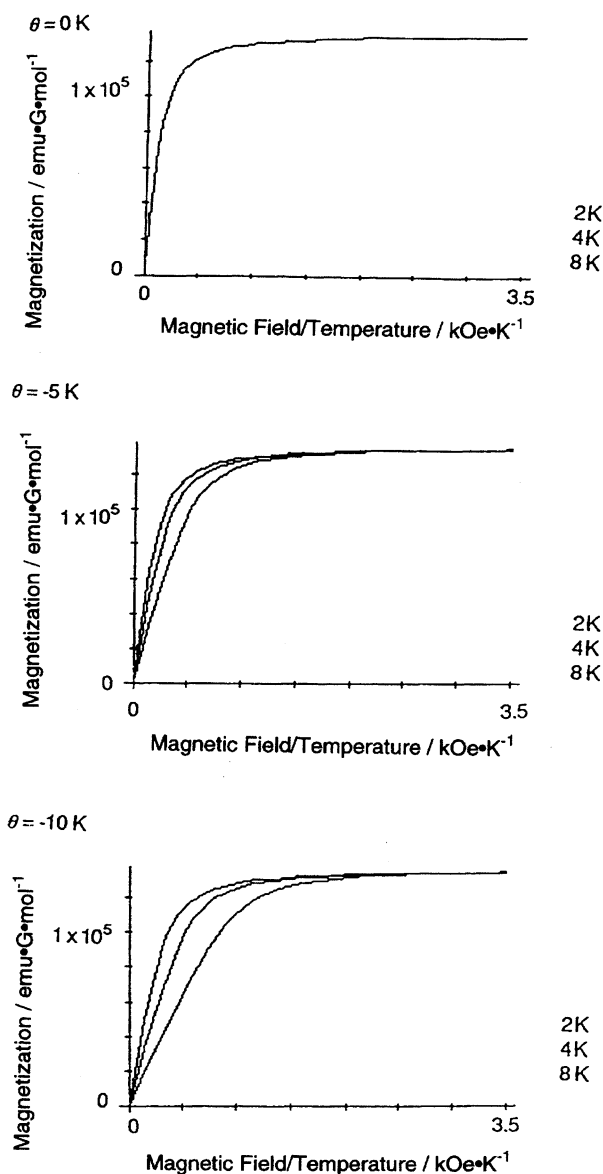


Fig. 9. Calculated field dependence of magnetization by using mean-field approximation.

difficult to construct, but from a point of view of chemical stabilization of high-spin states, the star-branched structure exhibited some limitations. More rigid structures such as the carbene network **2** or those utilizing of the molecular assembling with transition metal ions¹⁴⁾ will solve these problems by preventing the carbene centers from recombination. When the spins were aligned in the mesoscopic region, very small magnetic particles would be generated. Such material should obey both quantum mechanics and classical mechanics.¹⁵⁾ To make such spin cluster is one of our goals in the synthesis of organic magnetic materials.

Experimental

A. Materials. ¹H and ¹³C NMR spectra were recorded on a JEOL GX-270 and JEOL EX-270 instruments. 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 JMS-SX102L and JEOL JMS-SX/SX102A 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 argon 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) using 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-Benzyl-3'-bromodiphenylmethanol 7. To a stirred solution of phenylmagnesium bromide in THF prepared from magnesium turnings (5.54 g, 228 mmol), 3-bromodiphenylmethane **6**^{7d)} (53.2 g, 215 mmol), and THF (100 mL) was added a solution of 3-bromobenzaldehyde (40.0 g, 216 mmol) in THF (110 mL). After the addition was complete, the reaction mixture was refluxed for 1.5 h, and then quenched at 0 °C by cautious addition of saturated aqueous ammonium chloride. The mixture was extracted by ether, then the organic layer was washed with water, dried, filtrated concentrated, then purified by short-path distillation in vacuo, giving 3-benzyl-3'-bromodiphenylmethanol **7** (65.0 g, 86%) as a colorless oil. ¹H NMR (270 MHz, CDCl₃) δ=2.58 (bs, 1 H, OH), 3.92 (s, 2 H, CH₂), 5.62 (s, 1 H, CH(OH)), 7.0–7.6 (m, 13 H, Ar-H); ¹³C NMR (67.8 MHz, CDCl₃) δ=41.7 (CH₂), 75.3 (CHOH), 122.4 (Ar), 124.2 (Ar), 125.0 (Ar), 126.0 (Ar), 127.0 (Ar), 128.3 (Ar), 128.4 (Ar), 128.7 (Ar), 128.8 (Ar), 129.4 (Ar), 129.8 (Ar), 130.3 (Ar), 140.7 (Ar), 141.4 (Ar), 143.3 (Ar), 145.9 (Ar). HRMS Calcd for C₂₀H₁₇BrO: M, 352.0441 and 354.0422. Found: *m/z* 352.0365 and 354.0434.

3-Benzyl-3'-bromodiphenylmethane 8. To a stirred ethereal suspension of a mixed hydride, prepared from lithium aluminium hydride (10.00 g, 263 mmol), ether (250 mL), and finely powdered aluminium chloride (70.0 g, 524 mmol) at -10 °C, was added a solution of alcohol **7** (37.0 g, 105 mmol) in ether (300 mL) at -10 °C. After the addition was complete, the mixture was allowed to warm to room temperature and then refluxed for 1.5 h. After the reaction was complete, the reaction mixture was quenched by careful addition of ethyl acetate (70 mL), followed by addition of 20% sulfuric acid. The mixture was extracted by ether, then the organic layer was washed with water, dried, filtrated, concentrated, then purified by distillation in vacuo, giving 3-benzyl-3'-bromodiphenylmethane **8** (21.9 g, 62%) as a colorless oil. Bp 183–190 °C/0.5 mmHg (1 mmHg=133.322 Pa); ¹H NMR (270 MHz, CDCl₃) δ=3.86 (bs, 2 H, CH₂), 3.92 (s, 2 H, CH₂), 6.9–7.3 (m, 13 H, Ar-H); ¹³C NMR (67.8 MHz, CDCl₃) δ=41.4 (CH₂), 41.8 (CH₂), 122.5 (Ar), 126.0 (Ar), 126.6 (Ar), 126.9 (Ar), 127.5 (Ar), 128.4 (Ar), 128.7 (Ar), 128.8 (Ar), 129.1 (Ar), 129.5 (Ar), 129.9 (Ar), 131.8 (Ar), 140.2 (Ar), 140.9 (Ar), 141.3 (Ar), 143.4 (Ar). HRMS Calcd for C₂₀H₁₇Br: M, 336.0514 and 338.0493. Found: *m/z* 336.0508 and 338.0501.

3-Benzyl-3'-formyldiphenylmethane 9. To a stirred mixture of magnesium turnings (1.15 g, 47.3 mmol) and THF (10 mL) was added dropwise a solution of bromo compound **8** (13.0 g,

38.6 mmol) and 1,2-dibromoethane (1.63 g, 8.7 mmol) in THF (70 mL). The mixture was heated, with stirring, under gentle reflux for 2.5 h, followed by addition of a solution of DMF (3.10 g, 42.5 mmol) in THF (25 mL). The mixture was allowed to stand at room temperature overnight and then quenched by saturated aqueous ammonium chloride. The mixture was extracted by ether, then the organic layer was washed with water, dried, filtrated, concentrated, then purified by distillation in vacuo, giving 3-benzyl-3'-formyl-diphenylmethane **9** (10.4 g, 94%) as a colorless oil. Bp 175–185 °C/0.15 mmHg; ^1H NMR (270 MHz, CDCl_3) δ =3.94 (s, 2 H, CH_2), 4.00 (s, 2 H, CH_2), 6.96–7.13 (m, 4 H, Ar-H), 7.13–7.32 (m, 7 H, Ar-H), 7.37–7.45 (m, 1 H, Ar-H), 7.66–7.73 (m, 1 H, Ar-H), 9.94 (s, 1 H, CHO); ^{13}C NMR (67.8 MHz, CDCl_3) δ =41.4 (CH_2), 41.7 (CH_2), 125.9 (Ar), 126.0 (Ar), 126.6 (Ar), 127.0 (Ar), 127.6 (Ar), 128.4 (Ar), 128.7 (Ar), 128.8 (Ar), 129.0 (Ar), 129.5 (Ar), 129.9 (Ar), 135.0 (Ar), 140.2 (Ar), 140.9 (Ar), 141.4 (Ar), 142.4 (Ar), 192.3 (CHO). HRMS Calcd for $\text{C}_{20}\text{H}_{18}\text{O}$: M, 286.1358. Found: m/z 286.1355.

3-Benzyl-3'-(1-hydroxy-2-propynyl)diphenylmethane 10. To dry THF (90 mL) was added with stirring a 1.08 M solution of *n*-butyllithium in hexane (112 mL) and TMEDA (22.4 mL) at –60 °C. Acetylene was then bubbled through the solution with vigorous stirring, while keeping the temperature between –60 and –70 °C. After the acetylene absorption was complete, as was judged by appearance of a slurry, the gas flow was stopped. A solution of aldehyde **9** (10.95 g, 38.2 mmol) in THF (35 mL) was added to the mixture at –50 °C to give a clear solution, which was then allowed to warm up to 0 °C. The reaction mixture was quenched with aqueous ammonium chloride. The mixture was extracted by ether, then the organic layer was washed with water, dried, filtrated, concentrated, then purified by chromatography on silica gel eluted with a mixed solvent of hexane and dichloromethane to give 3-benzyl-3'-(1-hydroxy-2-propynyl)diphenylmethane **10** (7.40 g, 62%) as a colorless oil. ^1H NMR (270 MHz, CDCl_3) δ =2.3 (d, J =6.5 Hz, 1 H, OH), 2.61 (d, J =2.2 Hz, 1 H, $\text{C}\equiv\text{CH}$), 3.91 (s, 2 H, CH_2), 3.93 (s, 2 H, CH_2), 5.43 (dd, J =6.5 Hz and 2.2 Hz, 1H), 7.00–7.10 (m, 4 H, Ar), 7.12–7.45 (m, 9 H, Ar); ^{13}C NMR (67.8 MHz, CDCl_3) δ =41.7 (CH_2), 41.8 (CH), 64.3 (CHOH), 74.7 ($\text{C}\equiv\text{CH}$), 83.4 ($\text{C}\equiv$), 124.3 (Ar), 125.9 (Ar), 126.6 (Ar), 126.7 (Ar), 127.1 (Ar), 128.3 (Ar), 128.5 (Ar), 128.7 (Ar), 128.8 (Ar), 129.1 (Ar), 129.5 (Ar), 140.0 (Ar), 140.8 (Ar), 141.0 (Ar), 141.2 (Ar), 141.6 (Ar). HRMS Calcd for $\text{C}_{23}\text{H}_{20}\text{O}$: M, 312.1514. Found: m/z 312.1544.

1,3,5-Tris[3-(3-benzoylbenzoyl)benzoyl]benzene 13. To a stirred solution of alcohol **10** (6.65 g, 21.5 mmol) in acetone (75 mL) was added at 0 °C dropwise aqueous Jones reagent (1.12 equiv), prepared from chromium(IV) oxide (11.0 g, 110 mmol), water (27.5 mL), and sulfuric acid (20.0 g) at 0 °C. The reaction mixture was stirred overnight, while the temperature being allowed to warm up to an ambient temperature. The excess reagent was decomposed with 2-propanol, and the organic layer was poured into water. The organic layer was washed with water, dried, filtrated, concentrated, then chromatographed on silica gel eluted with a mixed solvent of hexane and dichloromethane to give 3-benzyl-3'-propioloyldiphenylmethane **11** (6.50 g).

To a stirred solution of ethynyl ketone **11** (9.30 g) in toluene (25 mL) was added diethylamine (0.3 mL), and the resulting yellow solution was refluxed for 6 h, with stirring, under an argon atmosphere. The solvent was then removed in vacuo, and the residual brown oil was chromatographed on silica gel eluted with a mixture of hexane and dichloromethane to give 1,3,5-tris[3-(3-benzylbenzoyl)benzoyl]benzene **12** (7.80 g) as a viscous oil.

To a stirred hot solution of triketone **12** (6.10 g) in acetic acid

(110 mL) was added solution dichromate dihydrate (19.6 g, 65.6 mmol) in small portions, and then the mixture was heated at 150 °C for 25 h. The warm reaction mixture was then treated with cold water to give precipitates, which were collected on a Buchner funnel, washed well with water, and air-dried. The crude product was purified by chromatography on silica gel eluted with a mixed solvent of hexane and dichloromethane, yielding nonaketone **13** (6.32 g, 78%, 3steps). Mp 118–119 °C; IR (Nujol) 1690 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ =7.41 (t, J =8.1 Hz, 6 H, 3''',5'''-H), 7.52 (t, J =8.1 Hz, 3 H, 4'''-H), 7.57 (t, J =8.1 Hz, 3 H, 5'''-H), 7.62 (t, J =8.1 Hz, 3 H, 5'-H), 7.74 (d, J =8.1 Hz, 6 H, 2''',6'''-H), 7.97 (d, J =8.1 Hz, 6 H, 4'',6''-H), 8.00 (d, J =8.1 Hz, 3 H, 4'-H), 8.03 (d, J =8.1 Hz, 3 H, 6'-H), 8.14 (t, J =1.7 Hz, 3 H, 2''-H), 8.23 (t, J =1.7 Hz, 3 H, 2'-H), 8.41 (s, 3 H, 2,4,6-H); ^{13}C NMR (67.8 MHz, CDCl_3) δ =128.5 (Ar), 128.7 (Ar), 129.1 (Ar), 130.0 (Ar), 131.1 (Ar), 132.0 (Ar), 133.4 (Ar), 133.8 (Ar), 133.9 (Ar), 134.3 (Ar), 134.4 (Ar), 136.6 (Ar), 136.8 (Ar), 136.9 (Ar), 137.6 (Ar), 137.9 (Ar), 138.0 (Ar), 193.5 (CO), 194.5 (CO), 195.5 (CO). FAB HRMS Calcd for $\text{C}_{69}\text{H}_{43}\text{O}_9$: M, 1015.3. Found: m/z 1015.4.

Nonahydrazone 14. To a solution of nonaketone **13** (504.3 mg, 0.497 mmol) and anhydrous hydrazine (7.5 mL) in DMSO (7.5 mL) was added hydrazine monohydrochloride (625 mg) in one portion, and the mixture was heated under an argon atmosphere at 90 °C for 21 h. The reaction mixture was treated with cold water to give precipitated, which were collected on a Buchner funnel, washed with ice water, and air-dried. The crude product was recrystallized from dichloromethane and hexane to give nonahydrazone **14** (535.5 mg, 94%) as a colorless powder. ^1H NMR (270 MHz, CDCl_3) δ =5.1–5.8 (bs, 18 H, NH_2), 7.0–7.7 (m, 48 H, Ar-H).

Nonadiazole Compound 15. The following operations were thoroughly conducted in a dark or under a red light to avoid decomposition of the reaction product. To a stirred mixture of yellow mercury(II) oxide (1.80 g), saturated ethanolic potassium hydroxide (20 mL), was added a solution of nonahydrazone **14** (140 mg, 0.123 mmol) in benzene (14 mL) and dichloromethane (2 mL). The mixture was stirred for 7 d at room temperature, and then filtered through tight cotton plugs. The wine red colored filtrate was concentrated in vacuo to leave an oil, which was immediately purified by chromatography on alumina at 0 °C eluted with a mixed solvent of hexane and benzene, giving nonadiazole compound **15** (88 mg, 65%) as a deep red oil. IR (Nujol) 2060 cm^{-1} ; UV-vis (MTHF) $\lambda_{\text{max}}(\epsilon)$ 520 (950) nm; ^1H NMR (270 MHz, CDCl_3) δ =6.9–7.4 (m, 48 H, Ar-H).

3-(1-Hydroxy-3-trimethylsilyl-2-propynyl)benzaldehyde 17. To dry THF (200 mL) was added with stirring a 1.6 M solution of *n*-butyllithium in hexane (69 mL, 0.11 mol) and TMEDA (16.6 mL, 0.11 mol) at –78 °C. Trimethylsilylacetylene (14.1 mL, 0.1 mol) was added to the solution at –78 °C and stirred for 0.5 h. After lowering the temperature down to –100 °C, isophthalaldehyde **16** (13.4 g, 0.1 mol) in THF (100 mL) was added. The solution was allowed to warm up to room temperature and stirred for 5 h. The reaction mixture was quenched with aqueous ammonium chloride and extracted with diethyl ether. The organic layer was washed with water, dried, filtered, and concentrated. Chromatography on silica gel eluted with hexane/dichloromethane (1 : 1, v/v) gave 3-(1-hydroxy-3-trimethylsilyl-2-propynyl)benzaldehyde **17** (6.04 g, 26%) as a pale yellow oil. IR (NaCl), 3410, 2960, 2170, 1700 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ =0.23 (s, 9 H, Si-Me), 2.32 (d, J =6 Hz, 1 H, OH), 5.54 (d, J =6 Hz, 1 H, $\text{CH}(\text{OH})$), 7.56 (t, J =7.7 Hz, 1 H, Ar-H), 7.84 (dd, J =7.3 Hz, 1.8 Hz, 1 H, Ar-H), 7.85 (dd, J =7.3 Hz, 1.8 Hz, 1 H, Ar-H), 8.07 (t, J =1.8 Hz, 1 H, Ar-H), 10.04 (s, 1 H, CO-H); ^{13}C NMR (67.8 MHz, CDCl_3) δ =–0.3

(Si-Me), 64.2 (C-OH), 92.4 (C≡C), 104.3 (C≡C), 128.1 (Ar), 129.3 (Ar), 129.4 (Ar), 132.7 (Ar), 136.6 (Ar), 141.5 (Ar), 192.1 (CO). HRMS Calcd for $C_{13}H_{16}O_2Si$: M, 232.0920. Found: m/z 232.0919.

1-(2-Propynoyl)-3-(3-trimethylsilyl-2-propynoyl)benzene 21.

To a stirred solution of aldehyde **17** (8.65 g, 37.4 mmol) in dichloromethane (100 mL) was added 3,4-dihydro-2H-pyran (4.72 g, 56.2 mmol) and pyridinium *p*-toluenesulfonate (0.47 g, 1.9 mmol). The solution was stirred for 6 h. To the reaction mixture was added diethyl ether then washed with brine. The organic layer was dried, filtrated, and concentrated to give a 1:1 mixture of two diastereomer of 3-(1-tetrahydropyranyloxy-3-trimethylsilyl-2-propynoyl)benzaldehyde **18** (11.54 g) as a pale yellow oil. This product was sufficiently pure for the next step.

To dry THF (120 mL) was added with stirring 1.6 M solution of *n*-butyllithium in hexane (34.4 mL, 54.9 mmol) and TMEDA (9.12 mL, 60.4 mmol) at -78°C . Acetylene was 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 aldehyde **18** (11.54 g) was added to the mixture at -78°C to give a clear solution, which was then allowed to warm up to room temperature. The reaction mixture was quenched with aqueous ammonium chloride and extracted with diethyl ether. The organic layer was washed with water, dried, filtrated, and concentrated, to give 1:1:1 mixture of four diastereomer of 1-(1-hydroxy-2-propynyl)-3-(1-tetrahydropyranyloxy-3-trimethylsilyl-2-propynyl)benzene **19** (12.35 g) as a pale yellow oil. The product was sufficiently pure for the next step.

To a solution of crude tetrahydropyranyl ether **19** (12.35 g) in dry ethanol (50 mL), pyridinium *p*-toluenesulfonate (0.90 g, 3.6 mmol) was added, and the mixture was stirred at 55°C for 1 h. After evaporation of solvent, diethyl ether and water were added. The mixture was extracted with diethyl ether, washed with water, dried and concentrated to give 1:1 mixture of two diastereomer of 1-(1-hydroxy-2-propynyl)-3-(1-hydroxy-3-trimethylsilyl-2-propynyl)benzene **20** (10.24 g) as a yellow viscous oil. The product was sufficiently pure for the next step.

To a stirred solution of crude diol **20** (10.24 g) in acetone (250 mL) was added dropwise at 0°C aqueous Jones reagent prepared from chromium(IV) oxide (5.29 g, 52.93 mmol), water (10.58 mL), and sulfuric acid (5.29 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 (7:3 v/v) to give 1-(2-propynoyl)-3-(3-trimethylsilyl-2-propynoyl)benzene **21** (7.49 g, 79% from **17**). Mp $96.0-96.7^\circ\text{C}$; IR (KBr) 3200, 2200, 2100, 1630 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) $\delta=0.34$ (s, 9 H, Si-Me), 3.51 (s, 1 H, C≡CH), 7.65 (t, $J=8$ Hz, 1 H, Ar-H), 8.38 (dt, $J=8$ Hz, 1.8 Hz, 2 H, Ar-H), 8.94 (t, $J=1.8$ Hz, 1 H, Ar-H); ^{13}C NMR (67.8 MHz, CDCl_3) $\delta=-0.8$ (Si-Me), 79.9 (C≡C), 81.7 (C≡C), 100.2 (C≡C), 102.3 (C≡C), 129.2 (Ar), 131.4 (Ar), 134.1 (Ar), 134.6 (Ar), 136.5 (Ar), 136.9 (Ar), 176.2 (CO), 176.3 (CO). Anal. Found: C, 70.71; H, 5.48%. Calcd for $C_{15}H_{14}O_2Si$: C, 70.83; H, 5.55%.

1,3-Dibenzoyl-5-[3-(3-trimethylsilyl-2-propynoyl)benzoyl]benzene 25. To a stirred solution of diketone **21** (590 mg, 2.3 mmol) and ethynyl phenyl ketone **22** (600 mg, 4.6 mmol) in toluene (5 mL) was added one drop of diethylamine and heated at 120°C for 24 h. Evaporation of solvent followed by chromatography on silica gel eluted with hexane/dichloromethane (4:1, v/v)

afforded the mixture of four kinds of trimerized ketones. The third fraction out of four peaks shown in recycling GPC (eluent: chloroform) was collected and evaporated to give tetraketone **25** (370 mg, 31%) as a yellow oil. IR (KBr) 2150, 1670 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) $\delta=0.29$ (s, 9 H, Si-Me), 7.52 (t, $J=8$ Hz, 4 H, Ar-H), 7.64 (t, $J=7$ Hz, 2 H, Ar-H), 7.69 (t, $J=8$ Hz, 1 H, Ar-H) 7.86 (d, $J=8$ Hz, 4 H, Ar-H), 8.12 (dt, $J=8$ Hz, 1.8 Hz, 1 H, Ar-H), 8.39 (d, $J=1.8$ Hz, 2 H, Ar-H), 8.41 (t, $J=1.8$ Hz, 1 H, Ar-H), 8.47 (t, $J=1.8$ Hz, 1 H, Ar-H), 8.58 (t, $J=1.8$ Hz, 1 H, Ar-H). FAB HRMS Calcd for $C_{33}H_{27}O_4Si$: M, 515.1679. Found: m/z 515.1680.

1,3-Dibenzoyl-5-[3-(2-propynoyl)benzoyl]benzene 27. To a solution of tetraketone **25** (630 mg, 1.2 mmol) in methanol (120 mL) was added potassium fluoride (350 mg, 6 mmol) at -20°C and then stirred for 10 min. The reaction mixture was poured into ice-cold water. Extraction with benzene, washing with brine, drying with magnesium sulfate, and evaporation afforded deprotected tetraketone **27** (520 mg, 96%) as a yellow oil. IR (KBr) 2090, 1660 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) $\delta=3.55$ (s, 1 H, C≡CH), 7.51 (t, $J=7$ Hz, 4 H, Ar-H), 7.62 (t, $J=7$ Hz, 2 H, Ar-H), 7.68 (t, $J=8$ Hz, 1 H, Ar-H), 7.85 (dt, $J=7$ Hz, 1.5 Hz, 2 H, Ar-H), 8.12 (dt, $J=8$ Hz, 1.8 Hz, 1 H, Ar-H), 8.38 (d, $J=1.8$ Hz, 2 H, Ar-H), 8.41 (t, $J=1.8$ Hz, 1 H, Ar-H), 8.45 (t, $J=1.8$ Hz, 1 H, Ar-H), 8.58 (t, $J=1.8$ Hz, 1 H, Ar-H); ^{13}C NMR (67.8 MHz, CDCl_3) $\delta=79.7$ (C≡C), 82.1 (C≡C), 128.6 (Ar), 129.3 (Ar), 130.0 (Ar), 130.6 (Ar), 133.2 (Ar), 133.7 (Ar), 133.9 (Ar), 134.5 (Ar), 135.2 (Ar), 136.15 (Ar), 136.21 (Ar), 136.9 (Ar), 137.2 (Ar), 138.3 (Ar), 176.1 (Ar), 193.5 (CO), 194.5 (CO). FAB HRMS Calcd for $C_{30}H_{19}O_4$: M, 443.1283. Found: m/z 443.1287.

1,3,5-Tris[3-(3,5-dibenzoylbenzoyl)benzoyl]benzene 28. To a solution of deprotected tetraketone **27** (400 mg, 0.9 mmol) in toluene (2 mL) was added one drop of diethylamine and heated at 120°C for 26 h. Evaporation of solvent followed by chromatography on silica gel eluted with hexane/dichloromethane (1:1, v/v), and then purified by means of GPC afforded dodecaketone **28** (140 mg 35%) as a yellow oil. IR (KBr) 3060, 1660 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) $\delta=7.49$ (t, $J=8$ Hz, 12 H, Ar-H), 7.61 (t, $J=8$ Hz, 6 H, Ar-H), 7.69 (t, $J=8$ Hz, 3 H, Ar-H), 7.83 (d, $J=7$ Hz, 12 H, Ar-H), 8.06-8.12 (m, 6 H, Ar-H), 8.35 (bs, 3 H, Ar-H), 8.40 (s, 9 H, Ar-H), 8.47 (s, 3 H, Ar-H); ^{13}C NMR (67.8 MHz, CDCl_3) $\delta=128.6$ (Ar), 129.2 (Ar), 130.0 (Ar), 131.0 (Ar), 133.2 (Ar), 133.9 (Ar), 134.12 (Ar), 134.17 (Ar), 134.25 (Ar), 134.5 (Ar), 136.2 (Ar), 136.7 (Ar), 137.1 (Ar), 137.3 (Ar), 137.9 (Ar), 138.3 (Ar), 193.3 (CO), 193.6 (CO), 194.5 (CO). FAB HRMS Calcd for $C_{90}H_{55}O_{12}$: M, 1327.3694. Found: m/z 1327.3689.

Dodecahydrazone 29. To a solution of dodecaketone **28** (70 mg, 53 μmol) in anhydrous hydrazine (1.3 mL) and dry DMSO (1.3 mL) was added hydrazine monohydrochloride (125 mg, 1.8 mmol). After stirring at 90°C under argon atmosphere for 22.5 h, the reaction mixture was poured into water. The precipitation was collected and washed with water to give dodecahydrazone **29** (50 mg, 63%) as white solid. IR (KBr) 3400, 1560, 1580 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) $\delta=5.2-5.6$ (m, 24 H, NH_2), 7.0-7.5 (m, 54 H, Ar).

Dodecadiazo Compound 30. To a solution of dodecahydrazone **29** (10 mg, 6.7 μmol) in dichloromethane (5 mL), diethyl ether (3 mL), and saturated ethanolic potassium hydroxide (20 drops), yellow mercury(II) oxide (300 mg) was added in the dark. The mixture was stirred for 4 d in the dark at ambient temperature with monitoring the reaction by the thin layer chromatography (alumina). Filtration, concentration, and purification by chromatography on alumina (act. IV) eluted with benzene/hexane (1:1, v/v) gave dodecadiazo compound **30** (2.4 mg, 24%) as a deep red viscous oil. IR (KBr)

2040, 1580 cm^{-1} ; UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\epsilon)$ 292 (362000), 520 (1660) nm; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ = 6.9–7.6 (m, 54 H, 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. 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 onto the diazo precursors 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. The temperature setting during the photolysis was under 2 K, but the temperature rose up to 4 K during irradiation. Field dependence of magnetization was measured before irradiation at the same temperature and magnetic field. These data before irradiation were used as a background data, and the net magnetization data for the carbenes were obtained by subtracting these data from those after photolysis.

Photolyses of 100 μL MTHF solutions of diazo compounds were carried out as follows. By using a field gradient of 5 T m^{-1} , the main field was scanned from 0 to 7 T at the temperature 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 mg between 0 and 7 T at 4 K.

C. ESR Spectra. Photolysis of diazo compounds were carried out in MTHF matrices at 9 K in an ESR cavity. The light ($400 \text{ nm} < \lambda < 500 \text{ nm}$) was obtained from a Xe lamp with combination of a Kenko B-390 band-path filter and an OCLI B cold mirror. A Bruker ESP 300 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 was 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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References

- For recent reviews see: a) H. Iwamura, *Adv. Phys. Org. Chem.*, **26**, 179 (1990); b) D. A. Dougherty, *Acc. Chem. Res.*, **24**, 88 (1991); c) O. Kahn, "Molecular Magnetism," VCH, New York (1993); d) H. Iwamura and N. Koga, *Acc. Chem. Res.*, **26**, 346 (1993); e) H. Kurreck, *Angew. Chem., Int. Ed. Engl.*, **32**, 1409 (1993); f) J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, **33**, 385 (1994); g) A. Rajca, *Chem. Rev.*, **94**, 871 (1994); h) J. S. Miller and A. J. Epstein, *C&EN*, **1995**, Oct. 2, 30; i) G. Allinson, R. J. Bishby, and J.-L. Paillaud, to be published.
- Perchloropolyarylmethyl: a) J. Veciana, C. Rovira, M. I. Crespo, O. Arnet, V. M. Domingo, and F. Palacio, *J. Am. Chem. Soc.*, **113**, 2552 (1991); b) J. Veciana, C. Rovira, N. Ventosa, M. I. Crespo, and F. Palacio, *J. Am. Chem. Soc.*, **115**, 57 (1993).
- Polyarylmethyl: a) A. Rajca, *J. Am. Chem. Soc.*, **112**, 5890 (1990); b) A. Rajca, S. Utamapanya, and J. Xu, *J. Am. Chem. Soc.*, **113**, 9235 (1991); c) A. Rajca, S. Utamapanya, and S. Thayumanavan, *J. Am. Chem. Soc.*, **114**, 1884 (1992); d) A. Rajca and S. Utamapanya, *J. Am. Chem. Soc.*, **115**, 2396 (1993); e) A. Rajca and S. Utamapanya, *J. Am. Chem. Soc.*, **115**, 10688 (1993); f) A. Rajca, S. Rajca, and R. Padmakumar, *Angew. Chem., Int. Ed. Engl.*, **33**, 2091 (1994); g) A. Rajca, S. Rajca, and S. R. Desai, *J. Am. Chem. Soc.*, **117**, 806 (1995).
- a) K. Itoh, *Chem. Phys. Lett.*, **1**, 235 (1967); b) E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinski, *J. Am. Chem. Soc.*, **89**, 5076 (1967).
- a) Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, *J. Am. Chem. Soc.*, **105**, 3722 (1983); b) T. Sugawara, S. Bandow, K. Kimura, H. Iwamura, and K. Itoh, *J. Am. Chem. Soc.*, **106**, 6449 (1984); c) Y. Teki, T. Takui, H. Yagi, K. Itoh, and H. Iwamura, *J. Chem. Phys.*, **83**, 539 (1985); d) T. Sugawara, S. Bandow, K. Kimura, and H. Iwamura, *J. Am. Chem. Soc.*, **108**, 368 (1986); e) Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, *J. Am. Chem. Soc.*, **108**, 2147 (1986); f) I. Fujita, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, F. Miko, Y. Sawaki, H. Iwamura, A. Izuoka, and T. Sugawara, *J. Am. Chem. Soc.*, **112**, 4074 (1990).
- R. L. Carlin, "Magnetochemistry," Springer-Verlag, Berlin (1986).
- a) N. Nakamura, K. Inoue, H. Iwamura, T. Fujioka, and Y. Sawaki, *J. Am. Chem. Soc.*, **114**, 1484 (1992); b) K. Furukawa, T. Matsumura, Y. Teki, T. Kinoshita, T. Takui, and K. Itoh, *Mol. Cryst. Liq. Cryst.*, **232**, 251 (1993); c) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, and H. Iwamura, *J. Am. Chem. Soc.*, **117**, 5550 (1995).
- N. Nakamura, K. Inoue, and H. Iwamura, *Angew. Chem., Int. Ed. Engl.*, **32**, 872 (1993).
- K. Matsuda, N. Nakamura, K. Inoue, N. Koga, and H. Iwamura, *Chem. Eur. J.*, **2**, 259 (1996).
- C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **112**, 7638 (1990).
- a) T. Sasaki and Y. Suzuki, *Tetrahedron Lett.*, **32**, 3137 (1967); b) K. Balasubramanian, P. S. Selvaraj, and P. S. Venkataramani, *Synthesis*, **1980**, 29; c) K. Matsuda, N. Nakamura, and H. Iwamura, *Chem. Lett.*, **1994**, 1765.
- D. Stauffer, *Phys. Rep.*, **54**, 1 (1979); J. Güémez and S. Velasco, *Physica A*, **171**, 486 (1991).
- N. J. Turro, M. Aikawa, and J. A. Butcher, Jr., *J. Am. Chem. Soc.*, **102**, 5127 (1980).
- a) K. Inoue and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, **1994**, 2273; b) K. Inoue and H. Iwamura, *J. Am. Chem. Soc.*, **116**, 3173 (1994); c) K. Inoue, T. Hayamizu, and H. Iwamura, *Chem. Lett.*, **1995**, 746; d) K. Matsuda and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, in press; e) K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizume, and Y. Ohashi, *J. Am. Chem. Soc.*, **118**, 1803 (1996); f) N. Koga, Y. Ishimaru, and H. Iwamura, *Angew. Chem., Int. Ed. Engl.*, in press.
- D. D. Awschalom, D. P. DiVincenzo, and J. F. Smyth, *Science*, **258**, 414 (1992).