Design, Synthesis, and Characterization of Three Kinds of π-Cross-Conjugated Hexacarbenes with High-Spin ($S = 6$) Ground States

Kenji Matsuda,[†] Nobuo Nakamura, Kazuyuki Takahashi, Katsuya Inoue, Noboru Koga, and Hiizu Iwamura*,[†]

Contribution from the Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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Abstract: Three kinds of nonlinearly π-conjugated hexadiazo compounds were obtained from the corresponding hexaketones for which cyclotrimerizaton of the ethynyl ketones to form 1,3,5-triaroylbenzenes and deoxygenation of a calix[6]arene were key steps. The diazo compounds were photolyzed in MTHF solid solutions at cryogenic temperatures to give the corresponding hexacarbenes **3**, **4**, and **5**. Their magnetization data obtained on a Faraday magnetic balance were analyzed in terms of the Brillouin function. On the basis of these analyses, all the hexacarbenes were concluded to have tridecet ($S = 6$) ground states. The temperature dependence of their ESR fine structures obeyed Curie law at 10–50 K. As **3**, **4**, and **5** have 1,3,5-benzenetriyl, partially dendritic, and macrocyclic structures, respectively, it has most dramatically been demonstrated that it is not the shape or geometrical symmetry of the molecules but the topological symmetry, i.e., connectivity of the carbenic centers on the π-cross-conjugated frameworks, which is most important in determining the spin multiplicity of the alternant hydrocarbon molecules. Some merits of these polycarbenes over the linear structures are discussed.

Introduction

Synthesis and characterization of organic molecules with very high-spin ground states are current topics of great interest.[1–3] In typical organic molecules, all the electrons are paired to form singlet ground states. Triplets with two parallel spins are often generated only as their lowest excited states. Not all diradicals have triplet ground states either. According to Hund's rule, triplet states can become energetically more favorable than the corresponding singlets when there are two electrons for two orthogonal orbitals that are mutually degenerate or lie within a small energy gap. The Coulombic repulsion between the two electrons would then be minimized as dictated by Pauli's exclusion principle. Two singly occupied orbitals in diradicals are most typically made orthogonal to each other when they are orthogonal in space or when non-Kekulé hydrocarbons in which two nonbonding molecular orbitals (NBMO) are effectively orthogonal by periodicity of the 2p atomic orbitals. Triplet diphenylcarbene and Schlenk hydrocarbon are typical examples of the two cases, respectively. By combining these two classes of molecules, Itoh and Wasserman prepared the m-phenylenedicarbene **1** ($n = 2$) and 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 ESR fine structures and/or magnetization data to have $S = 3, 4$, and 5 ground states, respectively.[5]

The polycarbenes are kinetically unstable but can be kept for days at cryogenic temperature. They enjoy the advantages of being produced efficiently by irradiation of the corresponding diazo compounds. Thus, the quantitative production and characterization of the polycarbenes can be readily achieved if the precursor polydiazo compounds are isolated in matrices or organic solid solutions, photolyzed at cryogenic temperature, and studied at that temperature *in situ*. By this method, the data both before and after photolysis can be measured, thus the paramagnetic impurities can be subtracted and the results are more accurate. Furthermore, the magnetic materials obtained by photochemical production would serve as prototypes of optomagnetic recording devices.

The linear structure can in principle be extended to poly(m-phenylenecarbene)s **1** ($n \rightarrow \infty$). In practice, however, there are a number of drawbacks in the linear structure. First, it becomes more and more difficult to produce all the carbene centers without fail and 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.[6] The linear polyketone, one of the precursors, becomes less and less soluble in typical organic solvents in which further chemical transformations have to be carried out. One-dimensional alignment of

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[†] Current address: Institute for Fundamental Research in Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-81, Japan.

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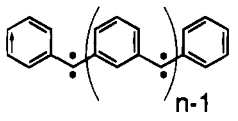
spins is said to be unstable from a thermodynamic point of view; inversion of all of the second half of the one-dimensionally aligned electron spins would require an additional enthalpy of only $2J$ which is defined by the Heisenberg Hamiltonian $\mathcal{H} = -2JS_a \cdot S_b$ for the energies of the interacting spins S_a and S_b of neighboring sites a and b. While the magnitude of the required enthalpy $2J$ is independent of the length of the units, such inversion of all of the second half of the spins near the center of the one-dimensional alignment of the electron spins would become more and more favorable in terms of entropy as the chain length increases. Thus, any magnetic linear chain including **1** is expected to exhibit no spontaneous magnetization at finite temperature. These difficulties inherent in the one-dimensional structures might be overcome by employing two-dimensional structures. Now, inversion of all of the second half of the one-dimensionally aligned electron spins would require an additional enthalpy of $4nJ$ (Figure 1). A calculation based on the Ising model by Tyutyulkov and his co-workers suggests that introduction of the interchain interaction two orders of magnitude as weak as the intrachain coupling ($-2J$) in **1** would raise the Curie temperature to 1000 K.[6b,d]



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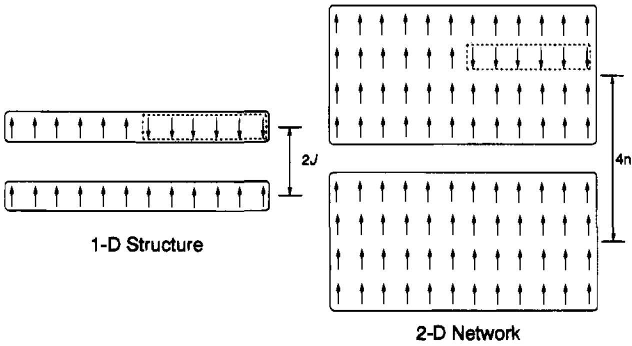
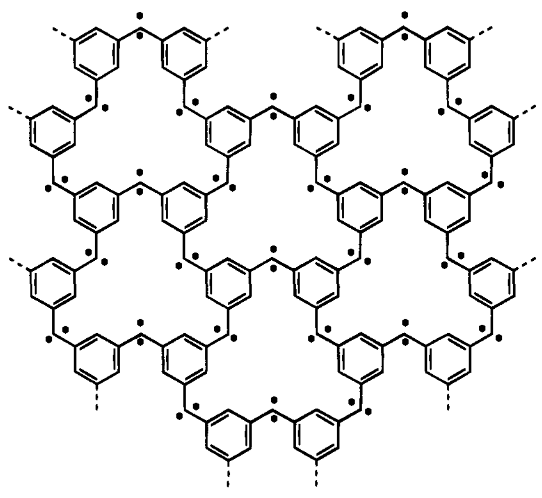


Figure 1. Spin alignment in a 1-D chain vs a 2-D network. n and J are the number and the exchange coupling parameter of the neighboring spins. Intra- and interchain J values are presumed to be the same for simplicity.

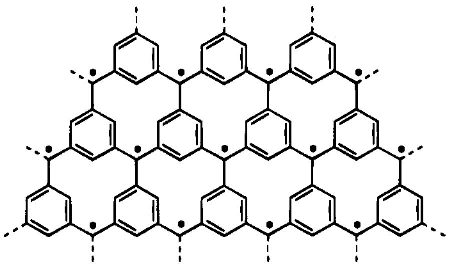
The foregoing analyses dictate the design and construction of polycarbenes in which a large number of the triplet carbene centers are joined ferromagnetically to form a two-dimensional network structure. A rigid structure would also help to reduce the high reactivity of triplet carbene centers as one-center diradicals toward recombination, etc. Thus we have arrived at network structure **2a** as a long-range goal of the strongly magnetic super-high-spin polycarbenes. This structure is obtained on paper by removing every third benzene ring from Mataga's network polyradical **2b**.[6c]

Results and Discussion

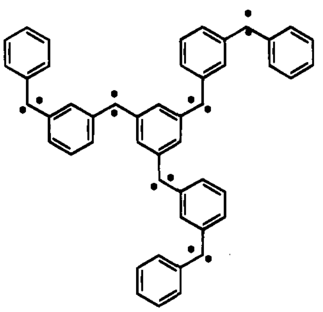
Molecular Design and Synthesis of the Precursors. As a step nearer to the ideal structure **2a**, we have employed in this study three unique structures present in **2a**: 1,3,5-trisubstituted and partially dendritic structures **3**[7] and **4** for branched pseudo-two-dimensional structures, and a macrocycle **5** for the two-dimensional cyclic structure. It was of most interest to explore the synthetic strategy and to see if all three hexacarbenes really have $S = 6$ ground states and offset the demerits of the linear structures described above. A 1,3,5-benzenetriyl unit can be deemed as good as and even better than a *m*-phenylene unit in



2a



2b



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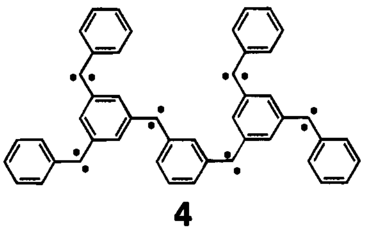

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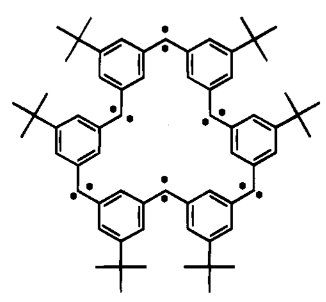
(7) (a) A preliminary account for **3**: Nakamura, N.; Inoue, K.; Iwamura, H.; Fujioka, T.; Sawaki, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1484. (b) Furukawa, K.; Matsumura, T.; Teki, Y.; Kinoshita, T.; Takui, T.; Itoh, K. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 251. (c) Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872.



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assembling organic free radical centers in higher concentrations within a molecule and aligning those spins in parallel.[2b,8]

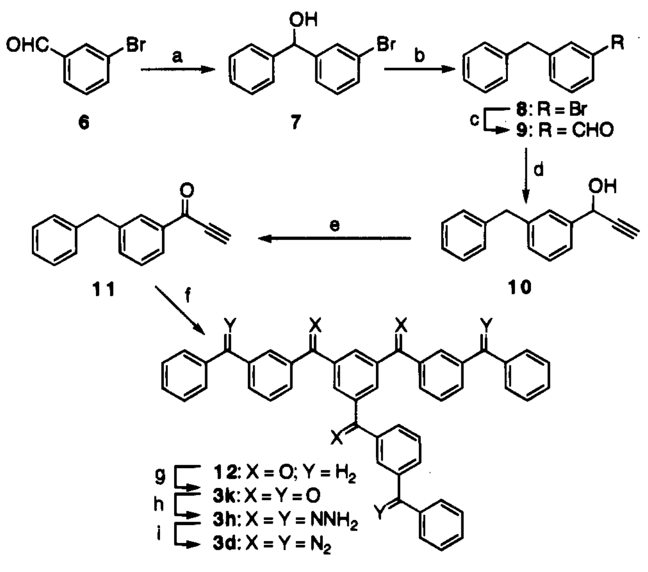
These polycarbenes were obtained by photolysis of the corresponding diazo precursors. The preparation of the diazo precursors was carried out in an usual way from the corresponding ketones. An exploratory study was made on the synthetic route to these ketones.

The first type of hexaketone **3k** was synthesized from *m*-bromobenzaldehyde as summarized in Scheme 1. Addition of phenylmagnesium bromide to *m*-bromobenzaldehyde **6** followed by reduction gave bromo compound **8**. The bromo substituent was converted to the formyl group and then to the propargyl moiety. After oxidation of alcohol **10** to ethynyl ketone **11**, a secondary-amine-catalyzed cyclotrimerization reaction[9] followed by oxidation gave hexaketone **3k**. This sequence of reactions making use of the cyclotrimerization reaction is also applicable to the higher analogs of **3**.[7c]

The second type of hexaketone **4k** was synthesized in good yields from tribromobenzene as shown in Scheme 2. This skeleton constitutes a partial structure of the dendritic "Starburst" polycarbenes in which some carbene centers appear to be situated in so close proximity that they are born dimerized; it is very difficult to keep them isolated.[10] Taking this point into account, we thought that less-branched partially-dendritic structure would be appropriate for isolating the carbene centers. Tribromobenzene **13** was lithiated and then allowed to react with *N,N*-dimethylformamide to give 3,5-diformylbromobenzene **14**. Phenyllithium was added to **14** and then reduced to give bromo compounds **16**. This bromo compound **16** was again lithiated and added to isophthalaldehyde and oxidized to afford hexaketone **4k**. This type of hexaketone has another advantage of giving good overall yields of the synthetic sequence.

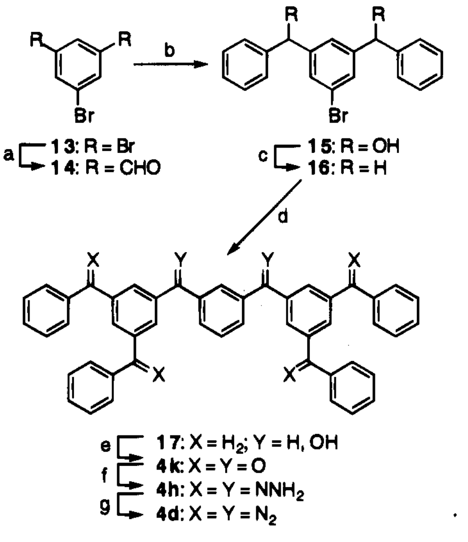
The third type of hexaketone **5k** was synthesized *via* a calix[6]arene derivative. The ring structure was constructed by using the established method of synthesis of calix[6]arene **19**. The hydroxyl groups were removed so that their facile insertion or the hydrogen migration reactions of the OH group might not occur with the carbene centers to be generated.[11] Hexa-*p*-*tert*-butyl[1^6]metacyclophane **20** was readily oxidized to hexaketone **5k** by a method used in the oxidation of **12** and **17**, while [1^4]metacyclophane was not.[12] The synthetic route is summarized in Scheme 3.

Scheme 1



[a] Reagents and Conditions: (a) PhMgBr, ether, 98%; (b) $LiAlH_4$-$AlCl_3$, ether, 85%; (c) Mg, ether, and then DMF, 94%; (d) HC≡CH-TMEDA, THF, 62%; (e) CrO_3-H_2SO_4, acetone, 98%; (f) EtNH, toluene, 84%; (g) $Na_2Cr_2O_7$, AcOH, 95%; (h) N_2H_4, N_2H_4·HCl, DMSO, quant.; (i) HgO, EtOK, Et_2O, benzene, 65%.

Scheme 2



[a] Reagents and Conditions: (a) 4 equiv. of *t*-BuLi, ether, and then DMF, 84%; (b) PhLi, THF; (c) $LiAlH_4$-$AlCl_3$, ether, 47%, 2 steps; (d) *n*-BuLi, THF, and then isophtalaldehyde; (e) $Na_2Cr_2O_7$, AcOH, 72%; (f) N_2H_4, N_2H_4·HCl, DMSO, 45%; (g) HgO, EtOK, CH_2Cl_2, Et_2O, benzene, 47%.

These ketones were fully characterized by ^1H, ^{13}C NMR, IR, and mass spectroscopy. HH-COSY NMR spectroscopy was firmly in support of their structures. For example the ^1H NMR spectrum of hexaketone **4k** gave singlets at δ 8.40, and 8.41, a meta-substitution pattern at δ 8.36 (t), 8.07 (dd), 7.67 (t), and a mono-substitution pattern at δ 7.83 (d), 7.59 (t), 7.48 (t). The ^{13}C NMR spectrum showed two signals of carbonyl carbons at δ 193.7, 194.5 and twelve signals for aromatic carbons at δ 128.6, 129.0, 130.0, 131.0, 133.2, 133.9, 134.1, 134.4, 136.2, 136.9, 137.3, and 138.3. The HH-COSY NMR spectra of hexaketone **4k** showed three sets of off-diagonal resonances,

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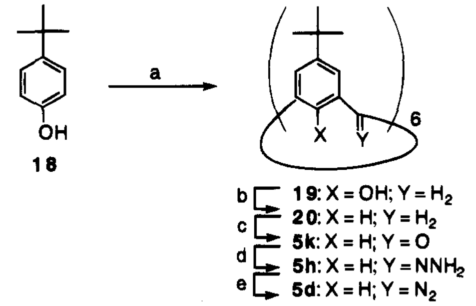
[12] Takahashi, K.; Matsuda, K.; Iwamura, H. to be published elsewhere.

Scheme 3



[a] Reagents and Conditions: (a) 37% HCHO, KOH, xylene, 74.3%; (b) $(EtO)_2POCl$, Bu_4NBr, 50% NaOH aq, and then K, NH_3; (c) $Na_2Cr_2O_7$, AcOH, 31%; (d) N_2H_4, $N_2H_4{\cdot}HCl$, DMSO, quant.; (e) HgO, EtOK, CH_2Cl_2, benzene, 9%.

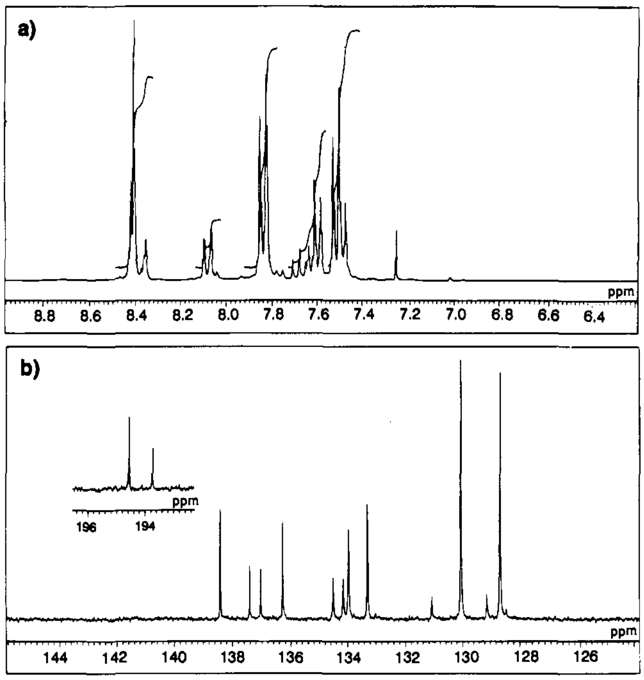


Figure 2. (a) ^{1}H NMR (270 MHz, $CDCl_3$) and (b) ^{13}C NMR (67.8 MHz, $CDCl_3$) spectra of hexaketone **4k**.

confirming the presence of three benzene units with patterns of mono-, *meta*-di-, and 1,3,5-trisubstitution (Figures 2 and 3).

These ketones were converted to the corresponding hydrazones **3h, 4h,** and **5h**. The oxidation reactions with yellow mercury oxide were carried out in the dark, monitored by thin layer chromatography (TLC) on alumina. The diazo compounds **3d**, **4d**, and **5d** were purified by column chromatography on alumina (activity IV) in the dark.

The ^{1}H, ^{13}C, and HH-COSY NMR spectra of the hexadiazo compound **4d** were fully assigned. The ^{1}H NMR spectrum of hexadiazo compound **4d** gave complex signals in the region δ 6.97–7.38. The ^{13}C NMR spectrum showed two signals of carbons possessing the diazo group at δ 62.95, 62.99 and twelve signals for aromatic carbon at δ 118.97, 119.00, 121.68, 123.02, 125.60, 126.28, 129.33, 129.54, 130.22, 130.89, 131.92, and 132.46 (Figure 4). The HH-COSY NMR spectrum of hexadiazo compound **4d** clearly resolved the complex ^{1}H NMR signals and it showed three sets of off-diagonal resonances, confirming the presence of three benzene units with patterns of mono-, *meta*-di-, and 1,3,5-trisubstitution (Figure 5). It is noted that the hydrogens ortho to the diazo group are upfield-shifted by 0.55 ppm relative to those of the corresponding carbonyl group. The ^{13}C signals of the diazo group are also upfield-shifted by 4.4 ppm. The UV–vis spectra of the three diazo compounds had the absorption maxima at 520 nm attributable to the n–π^* absorption. The molar absorptivities (ϵ) of these absorptions were in the range 510–608, values nearly six times as large as that of diphenyldiazomethane, indicating that these molecules had six cross-conjugated diazo groups.

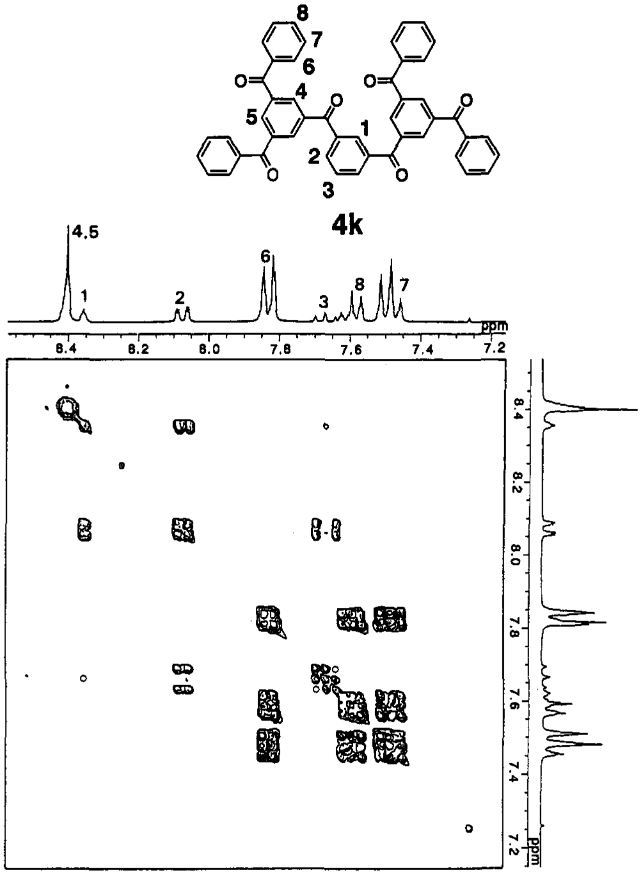


Figure 3. HH-COSY NMR spectrum of hexaketone **4k** (270 MHz, $CDCl_3$).

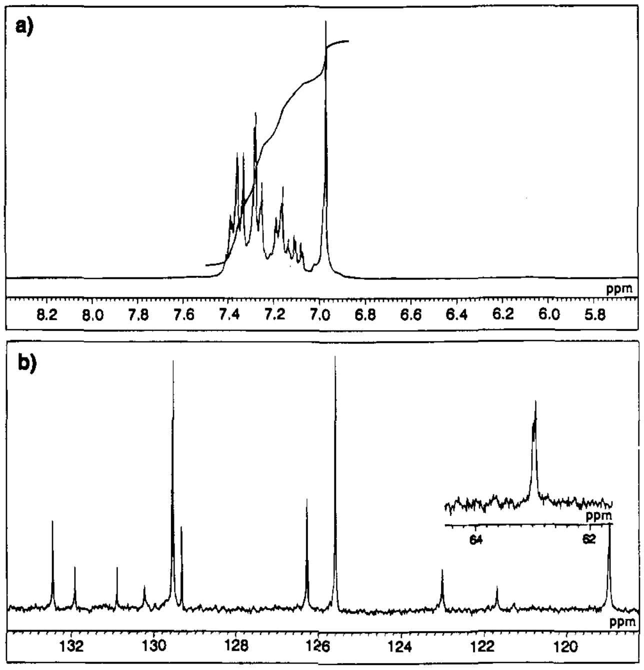


Figure 4. (a) ^{1}H NMR (270 MHz, CD_2Cl_2) and (b) ^{13}C NMR (67.8 MHz, CD_2Cl_2) spectra of hexadiazo compound **4d**.

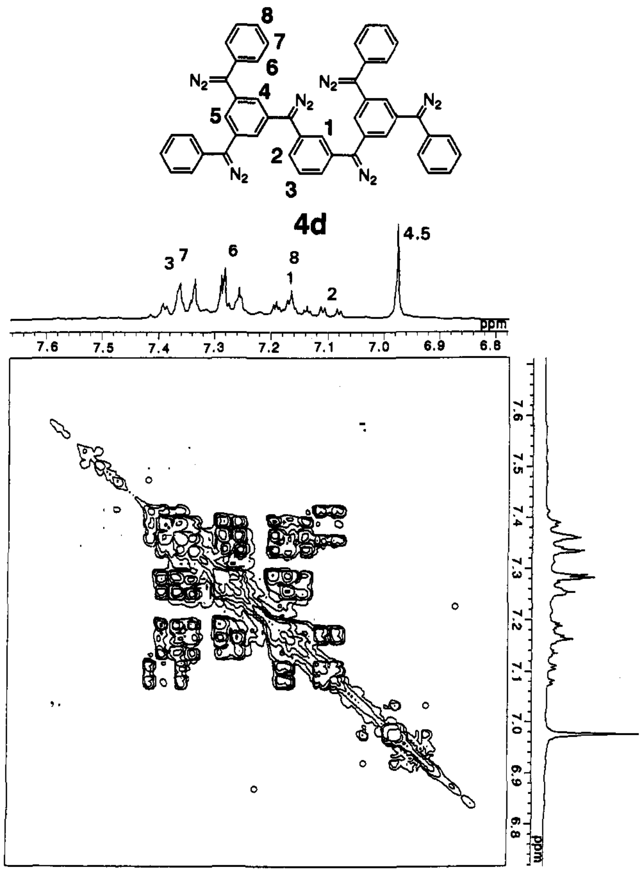


Figure 5. HH-COSY NMR spectrum of hexadiazo compound **4d** (270 MHz, CD_2Cl_2).

The Mechanism of the Cyclotrimerization Reaction. In view of the wide scope and versatility of the secondary amine-catalyzed cyclotrimerization reaction,[9] we have studied the mechanism of the reactions in some detail.[13] It is well-known that a monosubstituted acetylene RC≡CH is heated with nickel or cobalt carbonyls to give mainly the 1,2,4-trisubstituted benzene, with a lesser amount of the 1,3,5-benzene also generally obtained and little, if any, of the 1,2,3-isomer.[14] The secondary amine-catalyzed reactions have their advantage in high 1,3,5-regioselectivity. It was found that ethynyl phenyl ketone gave a diethylamine adduct upon reaction with an equivalent amount of diethylamine. This Michael adduct is considered to be produced at the initial stage of the trimerization reactions and serves as an important intermediate. A plausible mechanism is shown by mechanism A in Scheme 4, according to which two more molecules of the ethynyl ketone are added to give a six-membered ring. Then the diethylamino group is trapped by another ethynyl ketone molecule to form the aromatized ring and regenerate the ketoenamine. Basically there are two more mechanisms B and C conceivable (Scheme 4); in mechanism B, the ketoenamine plays the role of a catalyst, and in mechanism C, the ketoenamine is in preequilibrium with the ethynyl ketone.

In order to differentiate among the three mechanisms, we performed mixed cyclotrimerization experiments. γ-(Diethylamino)propenoylbenzene (**21**, 90 mg, 0.44 mmol) and 4-*tert*-butylbenzoylacetylene (**22**, 170 mg, 0.90 mmol) were refluxed in 1 mL of toluene for 12 h. Four different products **21**, **23**, **24**, and **25** were obtained (Scheme 5). The ketoenamine and triketone fractions were obtained from the reaction mixture by column chromatography on silica gel with hexane/dichloromethane (2:1, v/v) eluent. The combined yields were 89% for ketoenamines **21** and **23** and 88% for triketones **24** and **25**. The proportions of ketoenamine **23** to **21** and triketone **25** to **24** were determined by NMR spectra of these fractions to be 1.2 and 2.5, respectively. The triketone fraction could indeed be separated by gel permeation chromatography (GPC) to two triketones **24** and **25** (obtained from 50 mg of the mixture), and their structures were confirmed by NMR spectroscopy. It was found that the trimers contained no more than one phenyl group originating from ketoenamine **21**. Only triketone **24**, a trimer of ethynyl ketone **22**, would have been formed in mechanism B, and the products would have been a mixture of four different trimers of all combination of benzoylacetylene and *p*-*tert*-butylbenzoylacetylene in mechanism C. From these qualitative considerations alone, mechanism A should be acceptable.

Assuming that trapping of diethylamino group by ethynyl ketone was sufficiently faster than the trimerization step, the number of the molecules was sufficiently large, and the reaction rates of **21** and **23** to **22** are similar, we were able to calculate the proportion of the products. In mechanism A, two molecules of **22** react with one molecule of **21** or **23** according to the proportion of products **21** to **23**, which changes as the catalytic cycle proceeds. The proportions of ketoenamine **23** to **21** and triketone **25** to **24** are computed to be 0.95 and 2.7, respectively. These theoretical values are consistent with the proportions determined by NMR spectroscopy and GPC, further supporting mechanism A semiquantitatively.

Magnetization of Photoproducts. The photolyses of the hexadiazo compounds **3d**−**5d** in MTHF solid solutions were carried out at 2 K in the sample room of a Faraday magnetic balance. The light (400 nm < λ < 500 nm) from a Xe lamp with a combination of band-pass filter and cold mirror was introduced through a quartz light guide installed for irradiation of the precursor. After the photolysis, the field dependence of magnetization of the photoproducts was determined *in situ* in the dark. The plots of the magnetization vs the temperature-normalized magnetic field (*H/T*) (Figure 6) were analyzed in terms of the Brillouin function (eq 1):[1]

$$M = NgJ\mu_B B_J(x) \qquad (1)$$

where

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

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

N is the number of the molecule, J is the quantum number of the total angular momentum, μ_B is the Bohr magneton, g is the Landé g factor, and k_B is the Boltzmann constant. Since these carbenes are hydrocarbons and have only light elements, the orbital angular momentum should be negligible and J can be replaced with spin quantum number S in eqs 1−3.

The observed data were fitted best with the Brillouin function with $J = S = 6.0$ for **3** as expected for a paramagnet with a tridecet state. The data for **4** and **5** in reference with the theoretical $S = 6$ curve are given in Figures 6b and 6c, respectively. The data were collected at three different temperatures, but no unusual temperature dependence was observed, confirming that the tridecet is a ground state.

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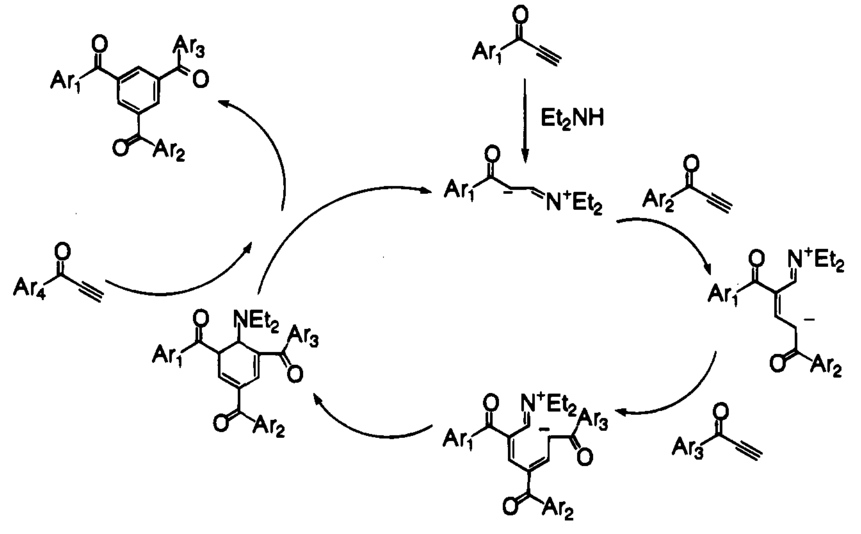
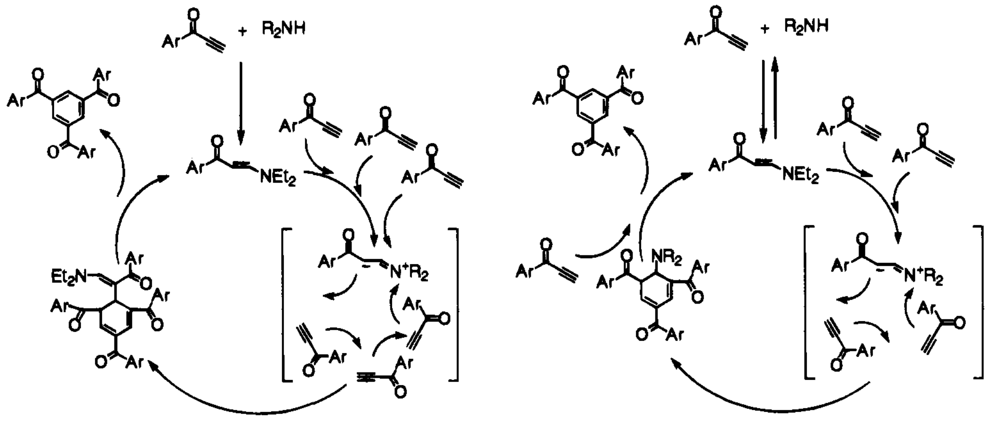
[13] A preliminary account is given in: Matsuda, K.; Nakamura, N.; Iwamura, H. *Chem. Lett.* **1994**, 1765.

[14] Reppe, W.; von Kutepow, N.; Magin, A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 727.

Scheme 4

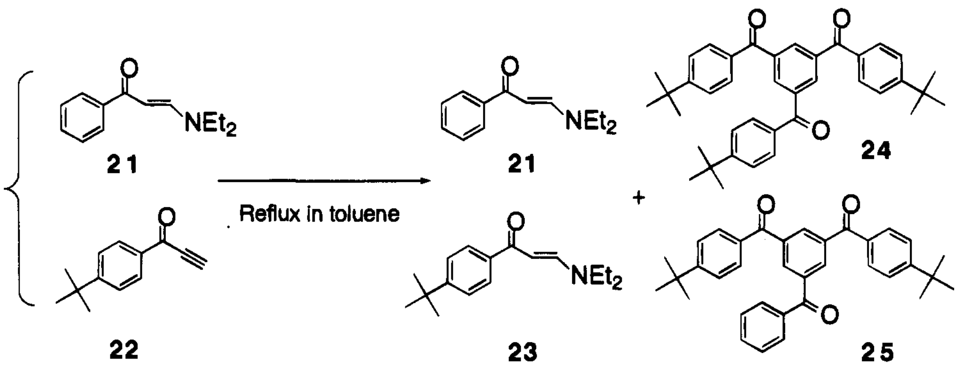


Mechanism A



Mechanism B Mechanism C

Scheme 5



The magnetization curves of hexacarbene **4** were recorded at different stages of photolysis (Figure 7). The spin quantum number of these curves is nearly constant at $S = 5-6$. These values were larger than those expected for random generation of the carbenes. If the elimination of nitrogen occurred randomly with similar probability at all the diazo groups, the expected value would be derived from a binomial distribution and would be rather small. From this consideration, it was confirmed that the six diazo groups of the same molecule are likely to be eliminated simultaneously. A one-photon multicleavage reaction may be evoked.[5] However, the possibility of the photolytic reaction occurring from the irradiated surface and progressing inward of the sample solid solutions may not be excluded.

ESR Spectra of Photoproduct. Photolyses were carried out in an ESR cavity by 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* centered at $g = 2$

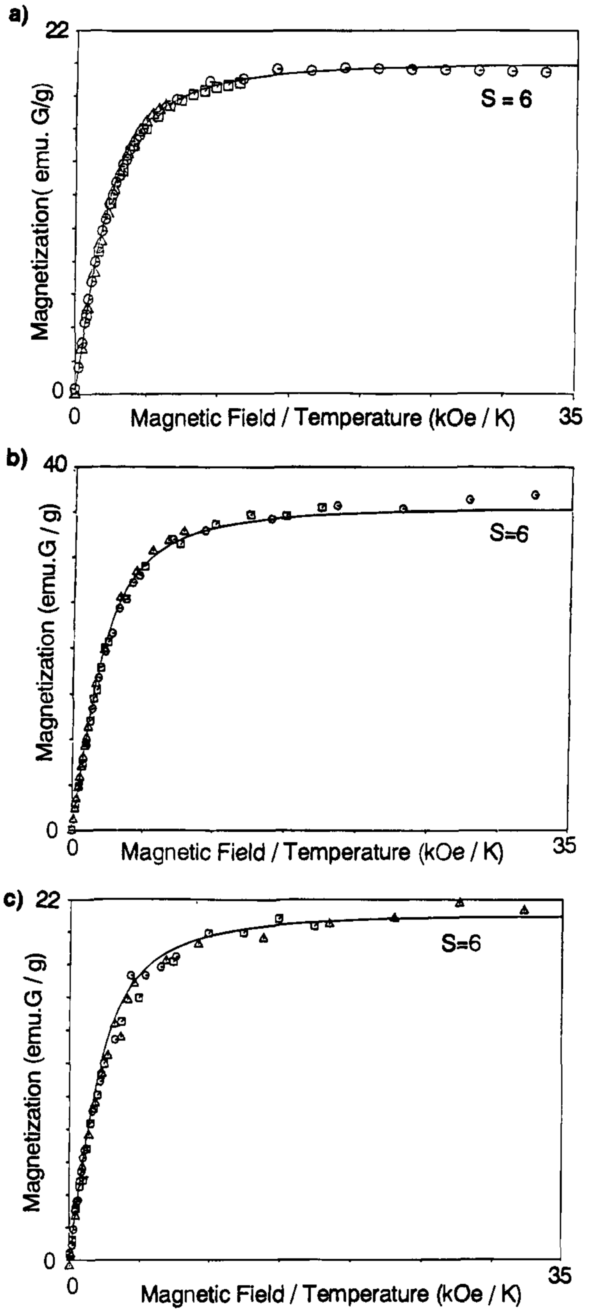


Figure 6. Field dependence of the magnetization of the hexacarbenes: (a) **3** in 5 mM MTHF matrix, measured at 2.1 (○), 4.8 (□), and 10.0 (△) K; (b) **4** in 0.09 mM MTHF matrix, measured at 2.1 (○), 4.0 (□), and 8.9 (△) K; (c) **5** in 0.1 mM MTHF matrix, measured at 2.1 (△), 4.2 (□), and 9.0 (○) K. The ordinates are normalized by the amount of starting diazo compounds and uncorrected for the degree of photolysis.

showed characteristics of fine structures of high-spin states (Figure 8). These signal shapes did not change from the initial stage of the irradiation. The three spectra were very similar in line shape, but differed in line width. The difference in the line width may arise from the difference in conformation, symmetry, and so on. Signals of cyclic-type hexacarbene **5** were sharper than those of partially-dendritic-type **4**, which indicates the number of conformations of **5** in the MTHF matrices were less than those of **4**. It was difficult to simulate these observed spectra because the line width was broader than the simulated line spacing. For further analysis, ESR fine structure analysis of the oriented species has to be made.[7b]

Temperature dependence of these spectra obeyed the Curie–Weiss laws in the temperature range 10–50 K, with no change of signal shape due to thermally populated lower spin states. The observed carbenes are consistent with the ground-state tridecet.

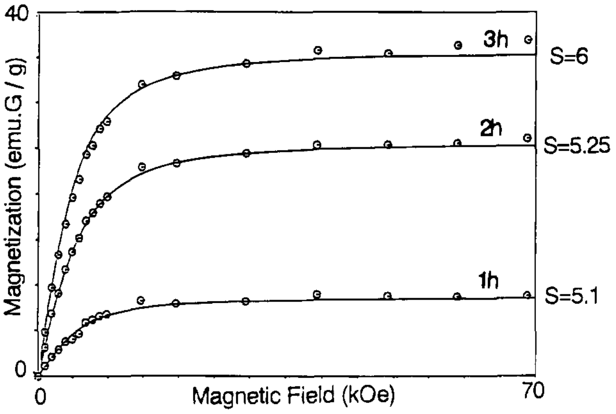


Figure 7. Magnetization curves for hexacarbene **4** after 1, 2, and 3 h of photolyses at 2.1 K.

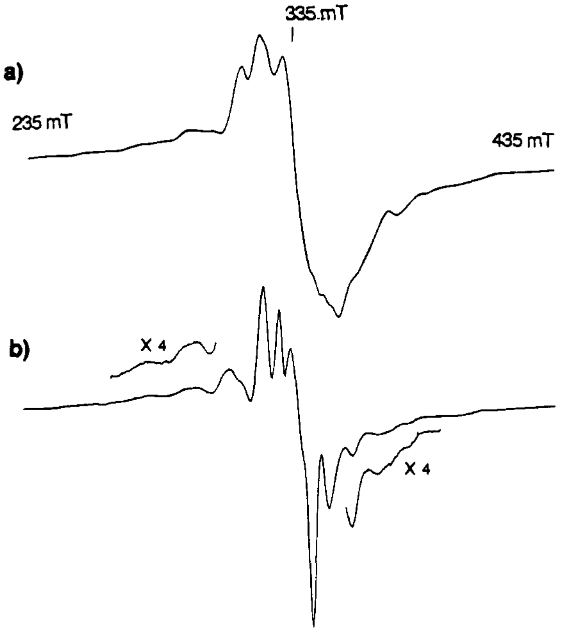


Figure 8. ESR spectra of hexacarbenes: (a) **4** in 0.9 mM MTHF matrix at 13.1 K, 9.39 GHz, and (b) **5** in 0.1mM MTHF matrix at 9.1 K, 9.40 GHz.

Conclusion

Three different *m*-phenylene-connected hexacarbenes were prepared by the photolyses of corresponding diazo compounds in the MTHF solid solutions at cryogenic temperature. The temperature dependence of their ESR fine structures obeyed Curie law at 10–50 K. The magnetic field dependence of magnetization measured by the Faraday method was in good agreement with the expected value formulated by Brillouin function with $J = S = 6$. Photolysis of the diazo compounds proceeded effectively without generation of low spin species. The amount of spin estimated from the degree of photolysis was in good agreement with the observed value (see Experimental Section C). On the basis of these observations it was demonstrated that all the carbenes possess the tridecet ($S = 6$) ground state regardless of the molecular shapes. It has most dramatically been demonstrated that it is not molecular shape or geometrical symmetry of the molecules but the topological symmetry which is most important in determining the spin multiplicity of the alternant hydrocarbon molecules. The molecular shapes affect the ESR spectra because the zero-field splitting parameters depend on the molecular shapes and conformations. Otherwise the difference in the chemical and magnetic properties among the three hexacarbenes **3**, **4**, and **5** was found to be quite small. This is due to the merit of our experimental conditions: photolytic production in solid solutions at cryogenic temperature under helium and *in situ* magnetic measurements. Under these conditions, most of the undesirable bimolecular side reactions were avoided. In the case of poly(triaryl radical)s similar in skeletal structure to **3** from Rajca,[3] the last step of a sequence of reactions is oxidation in fluid solution with exclusion of air. Generation of chemical defects seems to be difficult to avoid. Under these conditions, it becomes important to have more-than-one coupling route among the spin centers in the molecules for extended spin alignment. Therefore the merit of the cyclic structure similar to **5** over the branched linear structure similar to **3** and **4** manifests itself in the synthesis of the octaradical.[3] Such an effect was not applicable in our hexacarbenes **3**–**5**. Still macrocyclic polycarbene **5** has a rigid structure in which the carbene centers appear to be fixed in mutually non-reactive positions, and it is the most promising candidate for a building block for constructing higher-spin polycarbenes. Once such super-high-spin polycarbenes acquire remnant magnetization due to either magnetocrystalline anisotropy or weak ferromagnetic intermolecular interaction, the systems will have the potential of serving as magnetic recording devices in which magnetic memory will be generated by photochemistry as in the production of photoresists in the printing of circuit elements.

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 270–30 and a Hitachi I-5040 spectrometer. UV–vis spectra were recorded on a JASCO UVDEC-610C and a Hitachi U-3300 spectrophotometer. Mass spectra were obtained by a JEOL JMX-SX102L instrument. Melting points are not corrected.

Diethyl ether and tetrahydrofuran (THF) used in the reactions were distilled, under a dry nitrogen atmosphere, from lithium aluminium hydride just before use. 2-Methyltetrahydrofuran (MTHF) used in magnetic measurements was purified by successive distillation from lithium aluminium hydride under a nitrogen atmosphere and from sodium–benzophenone ketyl under an argon or nitrogen atmosphere. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled under reduced pressure from lithium aluminium 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) 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-Bromophenyl)phenylmethanol (7). To a stirred solution of phenylmagnesium bromide prepared from 4.80 g (0.45 mol) of magnesium turnings, 70.0 g (0.45 mol) of bromobenzene, and 180 mL of ether was added a solution of 76.2 g (0.41 mol) of 3-bromobenzaldehyde **6** in 210 mL of ether. 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 with ether, washed with water, dried, and concentrated. Distillation *in vacuo* gave 105 g (98%) of (3-bromophenyl)phenylmethanol (**7**): ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.49 (d, J = 3.8 Hz, 1 H, O*H*), 5.73 (d, J = 3.8 Hz, 1 H, C*H*(OH)), 7.16 (t, J = 8.0 Hz, 1 H, H-5), 7.22–7.40 (m, 7 H, Ar), 7.53 (t, J = 2.0 Hz, 1 H, H-2); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 75.5, 122.5, 125.0, 126.5, 127.8, 128.6, 129.4, 129.9, 130.5, 143.1, 145.9. HRMS Calcd for $C_{13}H_{11}OBr$: 263.9974 and 261.9993. Found: 264.0016 (9.9) and 261.9914 (18.3).

(3-Bromophenyl)phenylmethane (8). To a stirred suspension of a mixed hydride, prepared from 9.80 g (0.260 mol) of lithium aluminum hydride, 250 mL of ether, and 70.0 g (0.266 mol) of finely powdered aluminum chloride at −10 °C, was added a solution of 35.5 g (0.135 mol) of (3-bromophenyl)phenylmethanol (**7**) in 300 mL of ether 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 70 mL of ethyl acetate, followed by addition of 400 mL of 20% sulfuric acid. The mixture was extracted with ether, washed with water, dried, and concentrated to afford 31.0 g of an oil, which was purified by distillation *in vacuo*, bp 110–113 °C/0.4 mmHg (lit. bp 129–130 °C/1.0 mmHg), giving 27.5 g (83%) of (3-bromophenyl)phenylmethane (**8**): ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.92 (s, 2 H, C*H*$_2$), 7.34 (m, 9 H, Ar); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 41.5, 122.5, 126.3, 127.5, 128.5, 128.8, 129.2, 129.9, 131.8, 140.1, 143.4. HRMS Calcd for $C_{13}H_{11}Br$: 248.0025 and 246.0044. Found: 248.0001 (29.3) and 246.0022 (26.9).

3-(Phenylmethyl)benzaldehyde (9). To a stirred mixture of 1.55 g (63.8 mmol) of magnesium turnings and 10 mL of THF was added dropwise a solution of 12.9 g (52.2 mmol) of 3-(phenylmethyl)bromobenzene (**8**) and 2.18 g (11.6 mmol) of 1,2-dibromoethane in 70 mL of THF. The mixture was heated, with stirring, under gentle reflux for 2.5 h, followed by addition of a solution of 3.90 g (53.4 mmol) of DMF in 25 mL of THF. The reaction mixture was allowed to stand at room temperature overnight and then quenched by saturated aqueous ammonium chloride. The mixture was extracted with ether, washed with water, dried, and concentrated to give an oil, which was purified by distillation *in vacuo*, bp 120–125 °C/0.2 mmHg, producing 9.10 g (89%) of 3-(phenylmethyl)benzaldehyde (**9**): ^{1}H NMR (270 MHz, CDCl$_3$) δ 4.03 (s, 2 H, C*H*$_2$), 7.14–7.33 (m, 5 H, Ar), 7.41–7.46 (m, 2 H, Ar), 7.67–7.73 (m, 2 H, Ar), 9.95 (s, 1 H, C*H*O); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 41.5, 126.3, 127.7, 128.6, 128.8, 129.0, 129.8, 134.9, 136.5, 140.0, 142.2, 192.3. HRMS Calcd for $C_{14}H_{12}O$: 196.0888. Found: 196.0887 (47.0).

1-[3-(Phenylmethyl)phenyl]-2-propyn-1-ol (10). To a stirred mixture of 50 mL of a hexane solution (1.08 mol/L) of butyllithium and 10 mL of TMEDA was added 40 mL of THF 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 10.0 g (0.051 mol) of 3-(phenylmethyl)benzaldehyde (**9**) in 40 mL of THF 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 200 mL of 15% aqueous ammonium chloride. The mixture was extracted with ether, washed with water, dried, and concentrated, to afford a colorless oil, which was then chromatographed on silica gel eluted with a mixed solvent of hexane and dichloromethane to give 8.0 g (71%) of 1-[3-(phenylmethyl)phenyl]-2-propyn-1-ol (**10**) as a colorless oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.36 (bd, J = 4 Hz, 1 H, O*H*), 2.66 (d, J = 2.5 Hz, 1 H, -C≡C*H*), 4.02 (s, 2 H, C*H*$_2$), 5.43 (bs, 1 H, C*H*(OH)), 7.15–7.44 (m, 9 H, Ar); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 41.8, 64.3, 74.7, 83.4, 124.3, 126.1, 127.5, 128.4, 128.7, 128.9, 129.1, 140.1, 140.7, 141.6. HRMS Calcd for $C_{16}H_{14}O$: 222.1045. Found: 222.1064 (100).

1-[3-(Phenylmethyl)phenyl]-2-propyn-1-one (11). To a stirred solution of 5.50 g (25.0 mmol) of 1-[3-(phenylmethyl)phenyl]-2-propyn-1-ol (**10**) in 75 mL of acetone was added dropwise at 0 °C a 9.79 g (1.12 equiv) aliquot of aqueous Jones reagent, prepared from 11.0 g (110 mmol) of chromium trioxide, 27.5 mL of water, and 20.0 g of sulfuric acid at 0 °C. The reaction mixture was stirred overnight while the temperature was allowed to warm up to ambient temperature. The excess reagent was decomposed with 2-propanol, and the organic layer was poured into 300 mL of water. The mixture was extracted with ether, washed with water, dried, and concentrated to afford a colorless oil, which was then chromatographed on silica gel eluted with a mixed solvent of hexane and dichloromethane to give 5.34 g (98%) of the desired ketone **11**: ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.42 (s, 1 H, -C≡C*H*), 4.07 (s, 2 H, C*H*$_2$), 7.17–7.50 (m, 7 H, Ar), 8.02 (m, 2 H, *H*-2 and *H*-4); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 41.6, 80.2, 80.6, 126.3, 127.9, 128.6, 128.8, 129.7, 135.1, 136.3, 140.0, 141.9, 177.3. HRMS Calcd for $C_{16}H_{12}O$: 220.0888. Found: 220.0866 (100).

1,3,5-Tris[[3′-(phenylmethyl)phenyl]methanoyl]benzene (12). To a stirred solution of 5.00 g (22.7 mmol) of 1-[3-(phenylmethyl)phenyl]-2-propyn-1-one (**11**) in 22 mL of toluene was added 0.34 mL of diethylamine, and the resulting yellow solution was refluxed for 6 h, with stirring, under an argon atomsphere. 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 4.20 g (84%) of 1,3,5-tris[[3-(phenylmethyl)phenyl]methanoyl]benzene (**12**) as a viscous oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.04 (s, 2 H, C*H*$_2$), 7.12–7.30 (m, 5 H, Ar), 7.37–7.47 (m, 2 H, Ar), 7.64 (dt, J = 6.3 Hz, J = 1.8 Hz, 1 H, *H*-4), 7.69 (bs, 1 H, *H*-2), 8.33 (s, 3 H, central Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 41.6, 126.3, 128.0, 128.6, 128.7, 128.8, 130.3, 133.7, 133.9, 136.5, 138.1, 140.0, 141.9, 194.7. HRMS Calcd for $C_{48}H_{36}O_3$: 660.2664. Found: 660.2672 (100).

1,3,5-Tris[[3′-(phenylmethanoyl)phenyl]methanoyl]benzene (3k). To a stirred hot solution of 5.00 g (7.58 mmol) of 1,3,5-tris[3′-(phenylmethyl)phenylmethanoyl]benzene (**12**) in 110 mL of acetic acid was added 11.4 g (37.9 mmol) of sodium dichromate dihydrate in small portions, and the mixture was heated at 130 °C for 25 h. The warm reaction mixture was then treated with 300 mL of water to give precipitates, which were collected on a Buchner funnel, washed thoroughly 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 5.10 g (95%) of 1,3,5-tris[[3′-(phenylmethanoyl)phenyl]methanoyl]benzene (**3k**) as a glassy solid: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (tt, J = 7.6 Hz, J = 1.6 Hz, 6 H, *H*-3″,5″), 7.52 (tt, J = 7.6 Hz, J = 1.6 Hz, 3 H, *H*-4″), 7.62 (t, J = 7.6 Hz, 3 H, *H*-5′), 7.76 (dt, J = 7.6 Hz, J = 1.6 Hz, 6 H, *H*-2″,6″), 7.98–8.05 (m, 5 H, *H*-4′,6′), 8.17 (t, J = 1.6 Hz, 3 H, *H*-2′), 8.41 (s, 3 H, central Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 128.5, 129.0, 130.0, 131.2, 132.9, 133.4, 134.3, 134.4, 136.5, 136.7, 137.9, 138.1, 193.7, 195.4. FAB HRMS $\{(m + 1)/z\}$ Calcd for $C_{48}H_{31}O_6$: 703.2121. Found: 703.2148 (9.2).

1,3,5-Tris[[3′-[phenyl(1,1-diazanediyl)methyl]phenyl](1,1-diazanediyl)methyl]benzene (3h). To a solution of 600 mg (0.854 mmol) of 1,3,5-tris[[3′-(phenylmethanoyl)phenyl]methanoyl]benzene (**3k**) and 10.5 mL of anhydrous hydrazine in 10.5 mL of DMSO was added 1050 mg of hydrazine hydrochloride in one portion, and the mixture was heated, under an argon atmosphere, at 90 °C for 21 h. The reaction mixture was then diluted with 150 mL of cold water to give precipitates, 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 660 mg (98%) of 1,3,5-tris[[3′-[phenyl(1,1-diazanediyl)methyl]phenyl](1,1-diazanediyl)methyl]benzene (**3h**) as a glassy solid: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.25–5.65 (m, 12 H, N*H*$_2$), 7.0–7.7 (m, 30 H, Ar).

1,3,5-Tris[[3′-[phenyl(diazo)methyl]phenyl](diazo)methyl]benzene (3d). The following operations were thoroughly conducted in the dark or under a red light to avoid decomposition of the reaction product. To a stirred mixture of 1500 mg of mercury(II) oxide (yellow), 20 mL of benzene, and 2.0 mL of 17% (by weight) ethanolic potassium hydroxide was added a solution of 110 mg (0.140 mmol) of 1,3,5-tris[[3-[pheny(1,1-diazanediyl)methyl]phenyl](1,1-diazanediyl)methyl]benzene (**3h**) in 14 mL of benzene and 2 mL of dichloromethane. The mixture was stirred for 7 days 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 67 mg (62%) of 1,3,5-tris[[3′-[phenyl(diazo)methyl]phenyl](diazo)methyl]benzene (**3d**) as a deep red oil; IR (Nujol) 2036 cm^{-1}; UV-vis (MTHF) $\lambda_{max}(\epsilon)$ 520 (510) nm; ^{1}H NMR ($CDCl_3$) δ 6.8–7.6 (bm, Ar).

3,5-Diformylbromobenzene (14). To a suspension of 6.0 g (19.1 mmol) of tribromobenzene **13** in 200 mL of dry ether was added 50 mL of 1.7 M *tert* -butyllithium in pentane (85 mmol) under argon atmosphere at −78 °C. After the mixture was stirred for 1 h at −78 °C, 4.4 mL (57 mmol) of DMF was added. The solution was then allowed to warm to 10 °C with stirring. The reaction mixture was treated with aqueous ammonium chloride and extracted with ether. The organic layer was washed with brine, dried, filtrated, concentrated, and purified by chromatography on silica gel eluted with hexane/dichloromethane (1:1, v/v) to give 3.21 g (79.1%) of dialdehyde **14** as a white solid: mp 118–120 °C; IR (KBr) 3063, 1698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.26 (d, J = 1.1 Hz, 2 H, *H*-2, 6), 8.30 (t, J = 1.1 Hz, 1 H, *H*-4), 10.06 (s, 2 H, C*H*O). HRMS Calcd for $C_8H_5O_2Br$: 211.9473, 213.9452. Found: 211.9470 (100), 213.9442 (100).

3,5-Bis(hydroxyphenylmethyl)bromobenzene (15). To a solution of 6.48 g (4.4 mL, 41.3 mmol) of bromobenzene in 200 mL of dry THF was added 27 mL of 1.6 M *n*-butyllithium in hexane (43 mmol) under argon atmosphere at −78 °C. After the mixture was stirred for 1 h at −78 °C, a solution of 4.0 g (18.8 mmol) of dialdehyde **14** in 100 mL of THF 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 ether. The organic layer was washed with brine, dried, filtrated, and concentrated to give diol **15** as white solid. The product was sufficiently pure for the next step: m.p. 135–138 °C; IR (KBr) 3333 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.42 (bs, 2 H, O*H*), 5.72 (s, 2 H, C*H*(OH)), 7.27–7.41 (m, 13 H, Ar). HRMS Calcd for $C_{20}H_{17}O_2Br$: 368.0412, 370.0391. Found: 368.0382 (94.4), 370.0374 (92.2).

3,5-Dibenzylbromobenzene (16). To a stirred suspension of 1.42 g (37.4 mmol) of lithium aluminium hydride and 14.96 g (112.2 mmol) of anhydrous aluminium chloride in 60 mL of ether was added the solution of crude diol **15** in 150 mL of ether at 0 °C under argon atmosphere. After 1 h of refluxing, the reaction mixture was treated with ethyl acetate and 10% aqueous sulfuric acid and extracted with ether. The organic layer was washed with water, dried, filtrated, concentrated, and purified by chromatography on silica gel eluted with hexane/dichloromethane (2:1, v/v) to give 2.97 g (47%, 2 steps) of 3,5-dibenzylbromobenzene (**16**) as white crystals: mp 36.0–37.0 °C; IR (NaCl) 3085, 3063, 3029, 2913 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.90 (s, 4 H, C*H*$_2$), 6.97 (s, 1 H, Ar), 7.14–7.33 (m, 12 H, Ar); ^{13}C and ^{13}C DEPT NMR (67.8 MHz, $CDCl_3$) δ 41.5 (d), 122.6 (q), 126.3, 128.3, 128.6, 128.9, 129.7, 140.2 (q), 143.3 (q). HRMS Calcd for $C_{20}H_{17}Br$: 336.0514, 338.0493. Found: 336.0488 (100), 338.0478 (100).

1,3-Bis[3′,5′-(dibenzylphenyl)hydroxymethyl]benzene (17). To a solution of 2.0 g (6.0 mmol) of 3,5-dibenzylbromobenzene (**16**) in 50 mL of dry THF was added 4.1 mL of 1.6 M *n*-butyllithium in hexane (6.6 mmol) under argon atmosphere at −78 °C. After the mixture was stirred for 1 h at −78 °C, a solution of 400 mg (3.0 mmol) of isophthalaldehyde in 5 mL of THF was added. The mixture was stirred until the temperature was raised up to ambient temperature. The reaction mixture was treated with aqueous ammonium chloride and extracted with ether. Ether extracts were washed with water and dried. The filtrate was concentrated *in vacuo*. Purification by chromatography eluted with hexane/THF (4:1, v/v) gave 1.51 g (78%) of diol **17** as a white solid: mp 132–144 °C; IR (KBr) 3393 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.20 (d, J = 2.9 Hz, 2 H, O*H*), 3.91 (s, 8 H, C*H*$_2$), 5.69 (d, J = 2.9 Hz, 2 H, C*H*(OH)), 6.95 (s, 2 H, Ar), 7.05 (s, 4 H, Ar), 7.13–7.30 (m, 23 H, Ar), 7.38 (s, 1 H, Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 41.78, 76.08, 125.00, 125.03, 125.66, 125.74, 126.0, 128.4, 128.8, 128.9, 140.9, 141.4, 143.9, 144.0. HRMS Calcd for $C_{20}H_{42}O_2$: 650.3185. Found: 650.3182 (43.3).

1,3-Bis[[3′,5′-(phenylmethanoyl)phenyl]methanoyl]benzene (4k). To a solution of 320 mg (0.49 mmol) of diol **17** in 5 mL of acetic acid was added 1.91 g (6.4 mmol) of sodium dichromate dihydrate. After refluxing for 12 h, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried. Evaporation of the solvent followed by chromatography on silica gel eluted with dichloromethane gave 250 mg (72%) of hexaketone **4k** as a white solid: mp 91–93 °C; IR (KBr) 3061, 1663 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.48 (t, J = 8 Hz, 8 H, *H*-3″, 5″), 7.59 (t, J = 7 Hz, 4 H, *H*-4″), 7.67 (t, J = 8 Hz, 1 H, *H*-5), 7.83 (d, J = 7 Hz, 8 H, *H*-2″, 6″), 8.07 (dd, J = 8 Hz, 1.5 Hz, 2 H, *H*-4,6), 8.36 (t, J = 1.5 Hz, 1 H, *H*-2), 8.403 (s, 4 H, *H*-2′,4′), 8.409 (s, 2 H, *H*-6′); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 128.6, 129.0, 130.0, 131.0, 133.2, 133.9, 134.1, 134.4, 136.2, 136.9, 137.3, 138.3, 193.7, 194.5. FAB HRMS $\{(m + 1)/z\}$ Calcd for $C_{48}H_{31}O_6$: 703.2121. Found: 703.2148 (46.9).

1,3-Bis[[3′,5′-bis[phenyl(1,1-diazanediyl)methyl]phenyl](1,1-diazanediyl)methyl]benzene (4h). To a solution of 100 mg (0.14 mmol) of hexaketone **4k** in 1.5 mL of anhydrous hydrazine and 3.0 mL of dry DMSO was added 230 mg (3.36 mmol) of hydrazine monochloride. After being stirred at 100 °C under argon atmosphere for 6 h, the reaction mixture was poured into water. The precipitation was collected and washed with water to give 50 mg (45%) of hexahydrazone **4h** as a white solid: IR (KBr) 3391, 3287, 1560 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.29–5.57 (m, 12 H, N*H*$_2$), 7.02–7.64 (m, 30 H, Ar).

1,3-Bis[[3′,5′-bis[phenyl(diazo)methyl]phenyl](diazo)methyl]-benzene (4d). To a solution of 10 mg (13 mmol) of hexahydrazone **4h** in 2 mL of dichloromethane, 1 mL of ether, 1 mL of benzene, and 15 drops of saturated ethanolic potassium hydroxide was added 300 mg of yellow mercury oxide in the dark. The mixture was stirred for 2 days in the dark at ambient temperature with monitoring of the reaction by thin layer chromatography (alumina). Filtration, concentration, and purification by chromatography on alumina (activity IV) eluted with benzene/hexane (1:1, v/v) gave 4.6 mg (47%) of hexadiazo compound **4d** as a deep red solid: IR (KBr) 2035 cm^{-1}; UV–vis (MTHF) $\lambda_{max}(\epsilon)$ 520 (550) nm; ^{1}H NMR (270 MHz, CD_2Cl_2) δ 6.97 (s, 6 H, Ar), 7.06–7.38 (m, 24 H, Ar); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 62.95, 62.99, 118.97, 119.00, 121.68, 123.02, 125.60, 126.28, 129.33, 129.54, 130.22, 130.89, 131.92, 132.46.

Hexa-*p*-*tert*-butyl[1^6]metacyclophane (20). To a suspension of 2.01 g (2.06 mmol) of calix[6]arene **19** in 35 mL of chloroform were added 0.40 g (1.24 mmol) of tetrabutylammonium bromide, 3.74 mL (25.8 mmol) of diethyl chlorophosphate, and 6.50 mL of 50% aqueous sodium hydroxide under nitrogen atmosphere. The mixture was vigorously stirred for 3 h at ambient temperature. The clear solution was extracted with chloroform. The organic layer was washed with brine and dried. The filtrate was concentrated to give 5.62 g of phosphate as a dark brown oil. To a stirred liquid ammonia solution was dissolved 4.33g (110 mmol) of potassium in portions under nitrogen atmosphere at −78 °C. After a solution of 5.48 g (3.06 mmol) of phosphate in 36 mL of dry THF was added dropwise to the reaction mixture, a cooling bath was removed, and the solution was refluxed for 15 min. The solution was cooled down to −78 °C again and 6.3 g of ammonium chloride was added to the blue solution to give a brown solution and white precipitation. The solution was diluted with 90 mL of ether and left at ambient temperature. After ammonia was evaporated, 90 mL of hot ether was added to the solution and concentrated. Purification by chromatography on silica gel eluted with hexane/dichloromethane (4:1, v/v) gave 0.79 g (45%) of metacyclophane **20** as a white solid: mp 163–164 °C; IR (KBr) 2959, 2924, 2855 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29 (s, 54 H, C*H*$_3$), 3.93 (s, 12 H, C*H*$_2$), 6.79 (t, *J* = 1.5 Hz, 6 H, H-1), 7.09 (d, *J* =1.5 Hz, 12 H, *H*-3,5); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 31.3, 34.5, 42.1, 123.6, 126.7, 140.5, 151.0; Anal. Calcd for $C_{66}H_{84}$: C, 90.35; H, 9.65. Found: C, 90.08; H, 9.39.

Cyclic Hexaketone (5k). To a solution of 237 mg (0.27 mmol) of metacyclophane **20** in 48 mL of acetic acid was added 2.00 g (6.7 mmol) of sodium dichromate dihydrate. After 24 h of refluxing, 1.00 g of sodium dichromate dihydrate was added to the solution, then the solution was refluxed again. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was dried. Evaporation of the solvent followed by chromatography on silica gel eluted with hexane/ether (9:1, v/v) gave 81.4 mg (31%) of hexaketone **5k** as a white solid: IR (KBr) 1669 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.35 (s, 54 H, C*H*$_3$), 8.03 (t, *J* = 1.5 Hz, 6 H, H-1), 8.05 (d, *J* = 1.5 Hz, 12 H, H-3,5); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 31.14, 35.11, 128.57, 130.67, 137.15, 152.66, 195.20. Anal. Calcd for $C_{66}H_{72}O_6$: C, 82.46; H, 7.55. Found: C, 82.18; H, 7.57.

Cyclic Hexahydrazone (5h). To a solution of 101 mg (0.104 mmol) of hexaketone **5k** in 2.0 mL of anhydrous hydrazine and 2.0 mL of dry DMSO was added 172 mg (2.54 mmol) of hydrazine monochloride. After being stirred at 110 °C under argon atmosphere for 8 h the reaction mixture was poured into water. The precipitation was collected and filtrate was extracted with ether. The precipitate was dissolved into the organic layer and the organic extract was dried and concentrated to give 110 mg (quant.) of hexahydrazone **5h** as a pale yellow solid: IR (KBr) 1593 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.0–1.5 (m, 54 H, C*H*$_3$), 5.1–5.8 (m, 12 H, N*H*$_2$), 6.6–8.2 (m, 18 H, Ar).

Cyclic Hexadiazo Compound (5d). To a solution of 55 mg (0.053 mmol) of hexahydrazone **5h** in 10 mL of dichloromethane, 10 mL of benzene, and 75 drops of saturated ethanolic potassium hydroxide was added 1.50 g of yellow mercury oxide in the dark. The mixture was stirred for 2 days in the dark at ambient temperature with monitoring the reaction by thin layer chromatography (alumina). Filtration, concentration, and purification by chromatography on alumina (activity IV) eluted with benzene/hexane (1:10, v/v) gave 5 mg (9%) of hexadiazo compound **5d** as a red oil: IR (NaCl) 2040.9 cm^{-1}; UV–vis (MTHF) λ_{max} (ϵ) 522 (608) nm.

3-(Diethylamino)-1-phenyl-3-propenone (21). To a solution of 500 mg (3.8 mmol) of ethynyl phenyl ketone in 5 mL of toluene was added 400 μL (280 mg, 3.8 mmol) of diethylamine. The mixture was refluxed for 11 h under nitrogen atmosphere and then the solvent was evaporated. The crude was purified by chromatography on silica gel eluted with ether to give 330 mg (42.3%) of diethylamine adduct as a pale yellow oil; IR (KBr) 3474, 3058, 3023, 2974, 2934, 2872, 1638 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.3 Hz, 6 H), 3.33 (q, *J* = 6.9 Hz, 4 H), 5.77 (d, *J* = 12.5 Hz, 1 H), 7.37–7.45 (m, 3 H), 7.82 (d, *J* = 12.5 Hz, 1 H), 7.86–7.90 (m, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 11.3 (br), 14.5 (br), 42.5 (br), 50.3 (br), 91.4, 127.2, 127.8, 130.5, 140.5, 152.2, 188.5. HRMS Calcd for $C_{13}H_{17}ON$: 230.1310. Found: 203.1324 (100).

Tri-*tert*-butylbenzoylbenzene (24) and Bis(*tert*-butylbenzoyl)-benzoylbenzene (25). 3-(Diethylamino)-1-phenyl-3-propenone (**21**, 90 mg, 0.44 mmol) and 4-*tert*-butylbenzoylacetylene (**22**, 170 mg, 0.90 mmol) were refluxed in 1 mL of toluene for 12 h. The ketoenamine and triketone fractions were obtained from the reaction mixture by column chromatography on silica gel with hexane/dichloromethane (2:1, v/v) elution. The combined yields were 89% for **21** and **23** and 88% for **24** and **25**. The triketone fraction could be separated by gel permeation chromatography (GPC) to two triketones (8 mg of **24** and 28 mg of **25** were obtained from 50 mg of the mixture).

24: IR (KBr) ν 2961,1653 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.36 (s, 27 H), 7.52 (d, *J* = 8.4 Hz, 6 H), 7.80 (d, *J* = 8.4 Hz, 6 H), 8.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, 67.8MHz) δ 31.07, 35.21, 125.62, 130.20, 133.83, 133.85, 138.40, 157.11, 194.78. HRMS Calcd for $C_{39}H_{42}O_3$: 558.3134. Found: 558.3157 (8.8).

25: IR (KBr) ν 2960, 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.36 (s, 18 H), 7.49–7.54 (m, 6 H), 7.63 (t, *J* = 7.3 Hz, 1 H), 7.85 (d, *J* = 7.0 Hz, 2 H), 7.80 (d, *J* = 8.4 Hz, 4 H), 8.39 (s, 3 H); ^{13}C NMR ($CDCl_3$, 67.8MHz) δ 31.06, 35.19, 125.62, 128.62, 130.12, 130.18, 133.19, 133.75, 133.82, 134.01, 136.53, 138.08, 138.45, 157.14, 194.68, 195.08. HRMS Calcd for $C_{35}H_{34}O_3$: 502.2508. Found: 502.2485 (59.6).

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 < λ < 500 nm) tapered through the band-pass filters onto the diazo precursors dissolved in 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.[1c] 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 strength. 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 100 μL MTHF solutions of diazo compounds **3d**–**5d** were carried out as follows. By using a field gradient of 5 T/m, the main field was scanned from 0 to 7 T at three temperatures of 2, 4, and 9 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 these background data, 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 the photolysis was determined by comparing the absorbances of the n– π* absorptions at 520 nm before and after the photolysis and the magnetic measurement at room temperature. In an attempt to minimize the loss of the unreacted diazo groups, the sample solutions after the magnetic measurement were kept at 100 K for 1 h in the dark. Under these conditions, MTHF, fp 136 K, is still rigid but reactive with the carbene centers preferentially as judged by the decay of the ESR signals. In the case of the photolysis of **4d**, for example, 4.9×10^{-9} mol of hexacarbene **4** was estimated to be formed.

C. ESR Spectra. Photolyses of diazo compounds **3d**, **4d**, and **5d** were carried out in MTHF matrices at 9 K in an ESR cavity. The light (400 nm $< \lambda <$ 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 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 were measured at appropriate power attenuation which was calibrated to exclude the saturation effect. The temperatures were stepped up from 9 to 70 K with intervals of ca. 5 K.

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