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Persistent High-Spin Polycarbene. Generation of Polybrominated 1,3,5-Tris-[2-[4-(Phenylcarbeno)-phenyl]ethynyl]benzene ($S = 3$) and Spin Identification by Two-Dimensional Electron Spin Transient Nutation Spectroscopy

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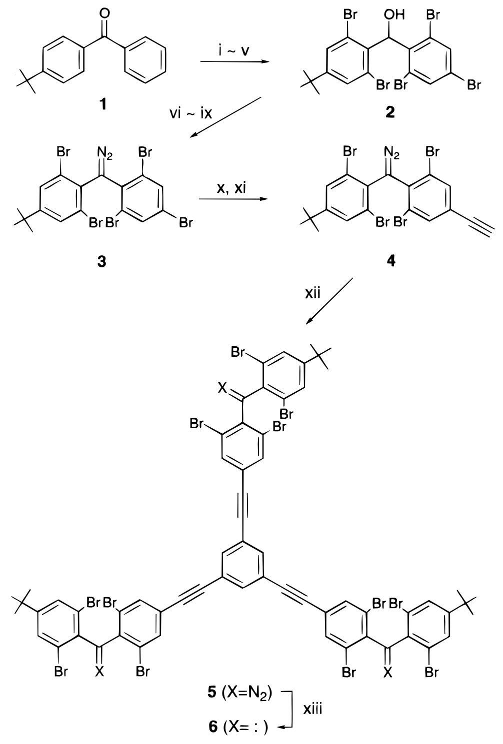
Since bis(*m*-phenylenecarbene) was established to have a quintet ground state in 1967,[1] triplet diphenylcarbene units have served as the source of electron spins in constructing high-spin molecules as models for purely organic ferromagnetics.[2] Thus, poly(*m*-phenylenecarbenes) have been most systematically studied inter alia and are accepted as the highest spin organic molecules.[3,4] The highly transient nature of the species,[5] however, is an inherent drawback for further extension to usable magnetic materials. In this light, it is highly desirable to synthesize persistent triplet carbenes and to connect them in a ferromagnetic fashion with an appropriate topological coupler. During the course of our efforts to stabilize a triplet carbene, we were able to generate fairly stable triplet diarylcarbenes; polybrominated diphenylcarbenes not only survived for minutes in solution and but also existed for years in the crystalline state at room temperature.[6] So, the next step should be to explore a way to connect them with robust π-spin polarization retained. We prepared polybrominated tris(diazodiarylmethane) **5** coupled by a topological linker, 1,3,5-triethynylbenzene, and demonstrated that the tris(carbene) **6** generated therefrom is persistent and spin-septet in its electronic ground state.

Scheme 1[a]



[a] (i) HNO_3/H_2SO_4; (ii) H_2/Pd−C; (iii) $NaBH_4$; (iv) Br_2; (v) $NaNO_2/H^+/H_3PO_2$; (vi) $SOCl_2$; (vii) $H_2NCO_2Et/AgBF_4$; (viii) $NaNO_2$; (ix) tBuOK; (x) $Me_3SiC{\equiv}CH/(Ph_3P)_2PdCl_2/CuI$; (xi) KOH/MeOH; (xii) 1,3,5-$I_3C_6H_3/(Ph_3P)_2PdCl_2/CuI$; (xiii) $h\nu$ ($\lambda > 300$ nm).

Diazo groups are generally labile, and hence, these groups are usually introduced at the last step of the synthesis when preparing not only mono(diazo)[7] but also poly(diazo) compounds.[4] Application of this strategy to these highly sterically congested diazo compounds, prepared mostly by base treatment of *N*-nitrosocarbamates,[7,8] is almost impossibly difficult. Fortunately, however, in this work, the polybromodiphenyldiazomethane **3** was found to be stable enough to survive in the presence of Pd(0) and CuI under Sonogashira coupling reaction conditions.[9] This is obviously due to the fact that the four bromine groups at the ortho positions which effectively protect the carbene center from the external reagents also are able to protect equally effectively the diazo carbon. Moreover, each of the four ortho carbons is also protected by these bromine groups from the approach of external reagents. This enabled us to introduce connecting groups at the para position of the monomer diazo compound (e.g., **3**) to give the functionalized monomer **4** and then to connect it to an appropriate linker satisfying the topological requirement for intramolecular ferromagnetic spin alignment. Thus, we were able to introduce an ethynyl functional group very selectively at the para position in a reasonable yield. Deprotection of the trimethylsilyl group proceeded almost quantitatively to give **4**. Subsequent coupling with 1,3,5-triiodobenzene took place smoothly to produce tris(diazo) compound **5**,[10] where three carbene precursor units are properly introduced so as to generate tris(carbene) connected in a ferromagnetic fashion.[2,3,11]

Photolysis ($\lambda > 300$ nm) of **5** in a 2-methyltetrahydrofuran (2-MTHF) glass at 5 K gave a fine-structure ESR spectrum[12] which was different from that observed by the photolysis of hexabromodiphenyldiazomethane.[6] Salient features[13,14] of organic high-spin species apparently failed to show up in the observed spectrum. Canonical peaks dominated in the $g \sim 2$ region, and

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(10) The tris(diazo) compound (**5**) was obtained as rather stable orange solid after purification by gel permeation chromatography on a Shodex GPC H-2001 column with $CHCl_3$ eluent and characterized by NMR spectroscopy. See Supporting Information for details.

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(12) ESR/ESTN measurements were made on Brucker ESR 300/380 FT-pulsed spectrometers. Sample temperatures were controlled by a Oxford ESR 910 helium gas flow system equipped on the ESP 300 spectrometer.

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key peaks appearing in the wings away from the $g \sim 2$ region were only vague. Nevertheless, considering a highly symmetric (C_3) molecular structure of the tris(carbene) **6** and the projection factor of spin quantum number S on fine structure constants, we expected a vanishing E value as well as a smaller negative D value and high spectral density in the $g \sim 2$ region, but robust π-spin polarization was anticipated for a symmetric septet ($S = 3$) tris(carbene) such as **6**.[2c] It is obvious, however, that well-established conventional continuous-wave (CW) ESR spectroscopy for randomly oriented organic high-spin species fails to give evidence of the unequivocal spin identification of the tris(carbene) under study.

To identify the spin multiplicity of the tris(carbene) **6** unequivocally, field-swept two-dimensional electron spin transient resonance (2D-ESTN) spectroscopy for nonoriented high-spin systems[15,16] was invoked. This technique is based a on pulsed FT ESR spectroscopic method[15−18] and is capable of elaborating straightforward information on electronic and environmental structures of high-spin species even in amorphous materials, which conventional CW ESR cannot provide.[15,16] According to a quantum mechanical treatment for the nutational motion of the spin magnetization in the presence of both the static magnetic and microwave fields, the nutation frequency ω_n observed for the allowed $|S,M_S\rangle \leftrightarrow |S,M_S{\pm}1\rangle$ ESR transition in the extreme weak limit ($H_1 \ll H_D$) for the microwave irradiation, H_1, is simply expressed as

$$\omega_n = [S(S+1) - M_S(M_S \pm 1)]^{1/2}\omega_1, \quad (S \geq 1) \qquad (1)$$

where M_S denotes the electron spin sublevel involved in the transition[13−16] and H_D stands for fine-structure terms. Thus, the nutation frequency spectrum depends on S, M_S, and ω_1. ω_1 is in proportion to the strength of the microwave field $\mathbf{B}_1$ ($\omega_1 = -\gamma_e \mathbf{B}_1$) and corresponds to the reference frequency for $S = {}^1/_2$. γ_e stands for the gyromagnetic ratio of electron. The magnetic field swept 2D-ESTN spectroscopy has been developed and can be appreciated for nonoriented high-spin mixtures[15,16] as well as fine-structure spectra in which high spectral density around the $g \sim 2$ region dominates, as shown in this work.

Figure 1 shows the corresponding contour plot (bottom) of field-swept 2D-ESTN spectra obtained in the photolysis of **5** under the same conditions as for the CW ESR spectrum. On the right of the contour plot, an electron spin−echo detected ESR fine-structure spectrum is given which corresponds to the conventional fine-structure ESR spectrum in an integrated mode. Figure 2 shows six typical slices of the nutation spectra in the range 200−350 mT. Three dominant peaks are discriminated at 22.0, 27.5, and 29.5 MHz which are denoted by a, b, and c, respectively. According to eq 1, the observed ratio of 22.0:27.5:29.5 uniquely agrees well with the theoretical value $\sqrt{6}\omega_1{:}\sqrt{10}\omega_1{:}2\sqrt{3}\omega_1$. These theoretical frequency values straightforwardly correspond to the allowed ESR transitions for septet states, unequivocally identifying that the observed fine-structure spectrum is due to a spin-septet state. Up to 90 K from 2.6 K, no other nutation peaks attributable to lower spin states ($S \geq 1$) were observed, showing the septet state to be the ground state with the excited low-spin states located above 300 cm^{-1}. We notice that these experiments alone cannot completely rule out the possible location of spin-singlet states nearby the septet state within a few cm^{-1} although it is unlikely.

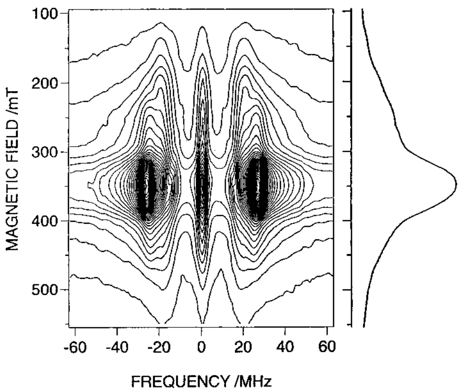

Figure 1. Contour plot of field-swept 2D nutation spectra of **6** observed at 5 K in a 2-MTHF glass. On the right, an electron spin−echo detected fine-structure ESR spectrum is given.

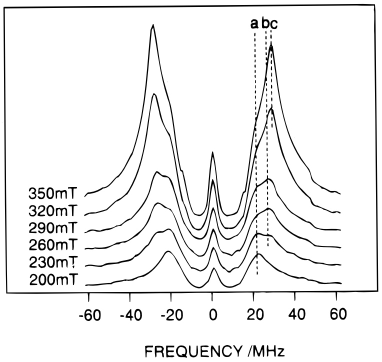

Figure 2. Six typical slices of the 2D nutation spectra in the range 200−350 mT of Figure 1.

A nutation peak arising from any doublet species of byproducts was not detected, showing a remarkable chemical stability of the tris(carbene) **6**. Also, a marked thermal stability of **6** manifested itself during an annealing process. A significant change in the ESR signal shape was observed when the matrix temperature was raised above 140 K and kept for 15 min. New fine-structure signals were irreversible with temperature, and they were characteristic of the small fine-structure constants. They were also identified to originate in a septet ground state by 2D-ESTN spectroscopy. This is in a sharp contrast with that observed for septet-state 1,3,5-tris(phenylmethylene)benzene, which has been shown to be persistent only up to 85[2c] and 50 K[19] in rigid glasses.

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Supporting Information Available: Experimental details and spectroscopic data for **5** and more detailed analysis of molecular and electronic spin structures for tris(carbene) **6** (8 pages). See any current masthead page for ordering and Web access instructions.

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