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Quintet Bis(carbene) from Triplet Diarylcarbenes Introduced at the 1,8-Position of Anthracene

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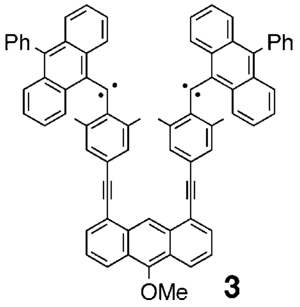
ABSTRACT



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[9-{10-Phenyl}anthryl](4-bromo-2,6-dimethylphenyl)diazomethane was found to be stable enough to survive Sonogashira coupling reaction conditions and was converted to [9-{10-phenyl}anthryl](4-trimethylsilylethynyl-2,6-dimethylphenyl)diazomethane, which was reacted with 1,8-diiodoanthracene to give bis(diazo) compound. Bis(carbene) generated by irradiation of the bis(diazo) compound generated a fairly persistent $S = 2$ quintet state.

Recently, there has been much interest in the synthesis of organic materials with magnetic properties for potential organo-magnetic materials.[1,2] In this regard, a great deal of work has been directed toward high-spin polycarbenes, in which the carbenic subunits are coupled in a ferromagnetic fashion.[3] The majority of the high-spin systems that have been investigated focused on *meta*-phenylene linkers, as in the prototypical *m*-phenylenebis(methylene).[4] It is potentially possible to use a polynuclear aromatic compound as a linker.

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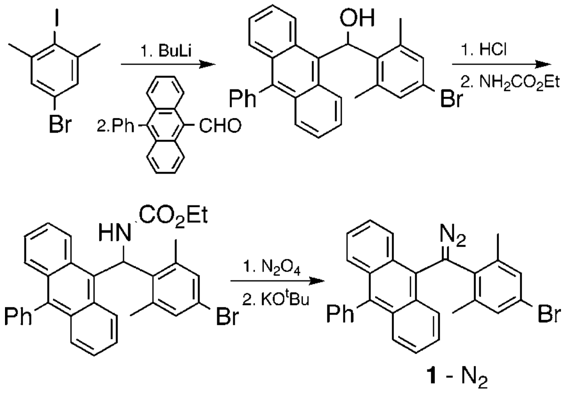
For instance, radical centers properly introduced on anthracene rings interact ferromagnetically to generate a high-spin state.[5,6] Those polynuclear aromatic compounds have an advantage over simple aromatic rings in that they have more positions to accept spin sources. The maximum number of available positions for ferromagnetic coupling in naphthalene and anthracene are four and five, respectively, while this number is three for benzene. Thus, a spin state with a spin-quantum number higher than three in one molecule can be generated by using polynuclear aromatic rings. However, almost no attempts have been made to introduce triplet carbene units on a polynuclear aromatic system. This is most probably because of the difficulty entailed in synthesizing a proper precursor. The diazo functional groups are sensitive not only to heat and light but also to acid, metal, and other reagents employed for further modification and, hence, are usually introduced at the last step of the synthesis.[7] This makes the versatility of the group less variable. In this paper, we report the experimental results for triplet carbene spin coupling through an anthracene unit.

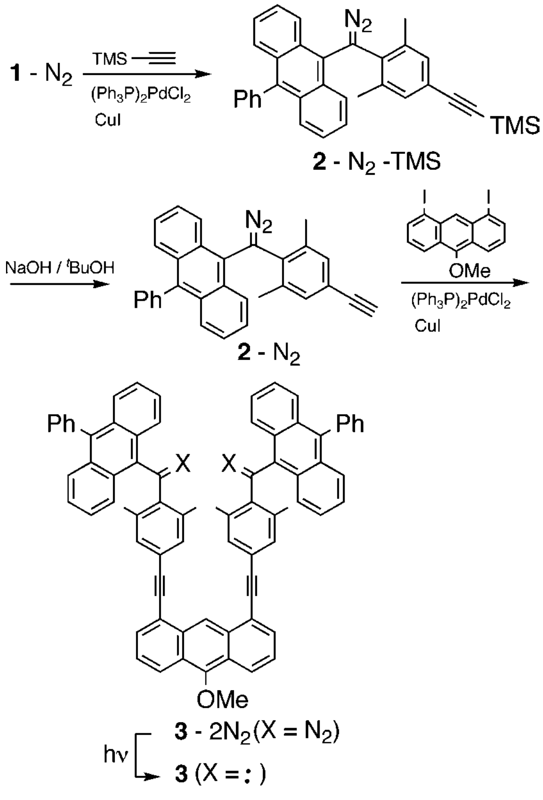
The preparation of a desired precursor for such a study is based on our finding that a diaryldiazomethane prepared to generate a persistent triplet carbene is also persistent for a diazo compound and, hence, can be further modified into a more complicated diazo compound while leaving the diazo group intact. For instance, bis(2,4,6-tribromophenyl)diazomethane survives under Sonogashira coupling reaction conditions,[8] leading to bis(2,6-dibromo-4-trimethylsilylethynylphenyl)diazomethane.[9] This means that diazo compounds can be used as a building block to construct a complicated polydiazo compound.

The starting diazo compound used in this study was [9-{10-phenyl}anthryl](4-bromo-2,6-dimethylphenyl)diazomethane (**1**-N_2), which was prepared according to the procedure outlined in Scheme 1; this compound can generate a fairly persistent triplet carbene.[10,11] Treatment of **1**-N_2 with trimethylsilylacetylene in the presence of $(Ph_3P)_2PdCl_2$ and CuI at 40 °C for 2 days gave [9-{10-phenyl}anthryl](4-trimethylsilylethynyl-2,6-dimethylphenyl)diazomethane (**2**-N_2-TMS). Deprotection[12] of the trimethylsilyl group with NaOH proceeded smoothly to give an ethynyl derivative (**2**-N_2). A desired bis(diazo) compound (**3**-2N_2) was relatively easily prepared in 45% yield by coupling 2 equiv of **2**-N_2 with 1,8-diiodoanthracene[13] under mild Sonogashira coupling reaction conditions (Scheme 2).[8]

Scheme 1



Scheme 2



Those reactions are realized because the diazo functional groups in the present system are well shielded by two

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dimethyls on the phenyl group as well as two peri-hydrogens on the anthryl ring and, hence, are relatively stable for a diazo group. The bis(diazo) compound thus obtained is also relatively stable and could be purified by repeated chromatography on a gel permeation column without any appreciable decomposition.

Photolysis of the bis(diazo) compound **3**-2N_2 in a 2-methyltetrahydrofuran (2-MTHF) solid solution was performed at 113 K in an ESR cavity with light from a high-pressure mercury lamp attached with a cut filter ($\lambda > 350$ nm). The ESR spectrum (Figure 1) after photolysis was completely different from that observed by the photolysis of the monodiazo compound **2**-N_2-TMS and showed a set of fine structure lines at 181, 260, 299, 345, 376, and 398 mT with rather small signal spacing. Weak signals at 140, 238, and 421 mT are similar to those observed in the photolysis of the monodiazo compound and, hence, are attributable to the triplet monocarbene ($D = 0.195$ cm^{-1}, $E = 0.00461$ cm^{-1})[10,14] presumably formed as a result of the incomplete photolysis of the bisdiazo compound. The smaller signal spacing observed for the major spectrum, in comparison to that for the triplet monocarbene, is consistent with the tendency that, as the spin multiplicity became higher, the D value became smaller.[15] Indeed, the major signals are well reproduced by computer simulation[16] employing a quintet Hamiltonian with $S = 2$, $g = 2.003$, $D = 0.047$ cm^{-1}, and $E = 0.000$ cm^{-1}. We, therefore, assigned the signals to the quintet biscarbene, ^{5}**3** (Figure 2). To estimate the thermal stability of the signals, the temperature at which the quintet signals disappear was measured. Thus, the 2-MTHF glass containing ^{5}**3** was warmed gradually in 10 K increments to a desired temperature, allowed to stand at this temperature for 5 min, and recooled to 113 K to measure the ESR again. The signals started to disappear when the 2-MTHF glass was warmed to around 130 K and disappeared completely at around 160 K. This is to be compared with that observed for septet state 1,3,5-tris(phenylmethylene)benzene, which has been shown to be persistent only up to 50 K in rigid glass.[17] Significant thermal stability was thus noted. Note that the ESR signals of triplet monocarbene from **2**-N_2-TMS also decayed at around 160 K. Thus, the thermal stability was not deteriorated by this modification.

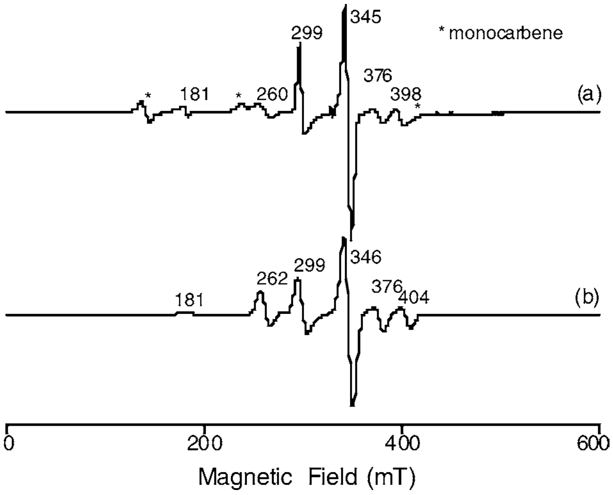

Figure 1. (a) ESR spectra obtained by irradiation of bis(diazo) compound **3**-2N_2 in 2-methyltetrahydrofuran at 77 K. (b) Simulated spectra of bis(carbene) ^{5}**3** with $S = 2$, $g = 2.003$, $D = 0.047$ cm^{-1}, and $E = 0.000$ cm^{-1}.

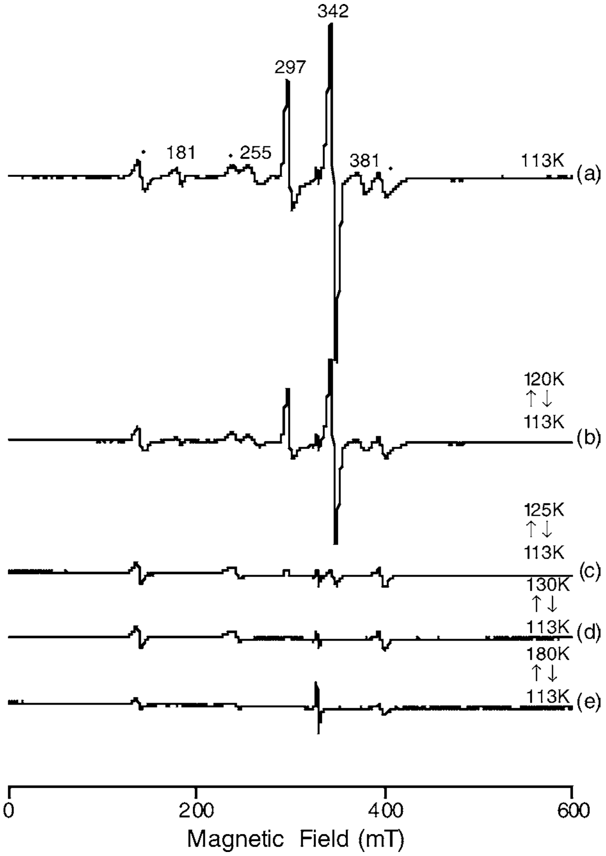

Figure 2. (a) ESR spectra of ^{5}**3** observed at 113 K and (b−e) the same sample observed at 113 K after warming to (b) 120, (c) 125, (d) 130, and (e) 180 K.

The present study shows another example in which a precursor for persistent triplet carbene can be used as a

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building block to construct a more complicated polydiazo compound that eventually generated a high-spin polycarbene with remarkably high thermal stability. It is potentially possible to introduce five diazo units at maximum on an anthracene ring so as to generate persistent pentakis(carbene) in the high-spin ground state. A study along this line is under progress.

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Supporting Information Available: Preparation of bis(diazo) compound **3**-N_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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