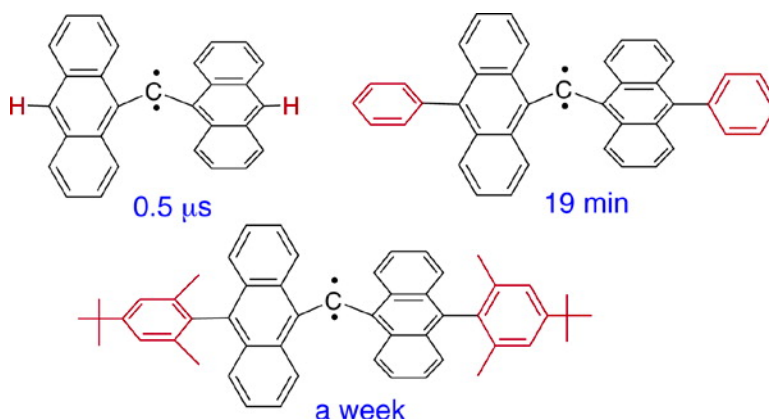Communication

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# A Triplet Carbene Surviving a Week in Solution at Room Temperature

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As a rule, carbenes are highly reactive intermediates that can be isolated only in a solid matrix at low temperature. This view has been upset by the recent synthesis of "bottleable" carbenes with a singlet ground state.[1] Stable carbenes with another electronic state, that is, triplet state, are more difficult to obtain,[2] and, yet, it is the triplet state that is attracting an ever-increasing interest as a potential building block for organic ferro-magnetics.[3] Thus, it is highly desirable to construct a stable triplet carbene to realize a usable organo-magnetic material consisting of this unit. A fairly stable triplet carbene with a half-life of ca. 20 min under normal conditions has been reported.[4,5] A triplet carbene with a half-life of 20 min is stable for a carbene, but it is still an ephemeral existence for a typical molecule. Here, we report the preparation of a triplet carbene that survives days in a solution at room temperature.

A stable triplet carbene was proposed by a simple modification of the previously most persistent example.[5] Di(9-anthrylcarbene) [3]**1** is shown to have a 180° angle at the carbene center, the aryl substituents being of orthogonal geometry with extensive delocalization of nonbonded electrons onto anthryl rings.[6] The extensive delocalization is expected to stabilize this carbene thermodynamically, while the perpendicular geometry of the anthryl groups stabilizes the carbene center kinetically through shielding with the four peri-hydrogens. However, it was found to be unusually short-lived; its lifetime in degassed benzene solution at room temperature is only 0.5 μs.[6b] A product analysis study indicates that [3]**1a** forms, as a main product, trimer (**2a**), suggesting that delocalization of the nonbonded electrons in [3]**1a** leads to their "leaking out" from the carbene center to position 10, where sufficient spin density builds up for the trimerization to take place. Once this reaction was quenched by introducing a substituent at position 10, the lifetime of the triplet carbene was dramatically increased. Thus, bis[9-(10-phenyl)anthryl]carbene ([3]**1b**) decayed very slowly with a half-life of 19 min.[5]

a: R = H, b: R = Ph
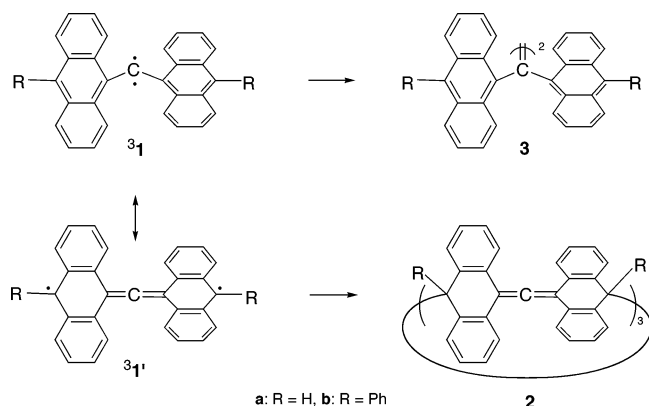
Product analysis in this case shows that the carbene [3]**1b** forms a product **3b** obviously generated as a result of dimerization at the carbene center, indicating that the reaction from leaked electrons is substantially quenched. However, the product was always

6: X= O₂ 7: X = O
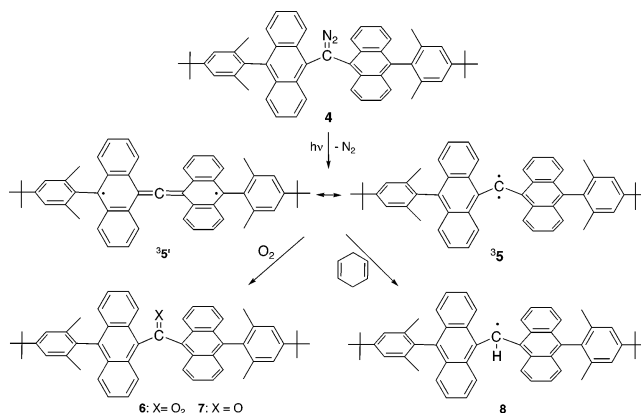
accompanied by a significant amount of an unidentifiable tarry component. This suggests that not all of the carbene decayed by undergoing dimerization at the carbenic center. It is possible that some of the triplet state still finds a route to react at position 10 because it is obvious that sufficient spin density is localized at this position and moreover the dimerization reaction forming **3** must suffer from severe steric hindrance in the light of the four peri-hydrogens.

Inspired by this interpretation of the data, we attempted to prepare a precursor di(9-anthryl)diazomethane in which the C₁₀ position is effectively blocked with a more bulky group. We were able to prepare a diazo compound **4**, in which 2,6-dimethyl-4-*tert*-butyl-phenyl groups were introduced at each of the two C₁₀ positions; hence, these groups were expected to generate di(9-anthryl)carbene ([3]**5**), in which the position 10 is protected so as to quench the last remaining reaction at this position.[7]

Irradiation ($\lambda > 350$ nm) of **4** in a 2-methyltetrahydrofuran (2MTHF) glass at 110 K gave ESR signals (Figure 1a) with zero-field splitting parameters ($D = 0.102$ cm⁻¹, $E = 0.00079$ cm⁻¹) very similar to those observed for di[9-(10-phenyl)anthryl]carbene [3]**1b**[5] and parent di(9-anthryl)carbene [3]**1a**.[6a] Thus, the signals are safely assignable to triplet di{9-[10-(2,6-dimethyl-4-*tert*-butylphenyl)-anthryl]}carbene [3]**5**.

The ESR signals were found to be very stable. ESR signals of [3]**5** changed very little even when the matrix was warmed to 300 K and recooled to 100 K (Figure 1b). It is to be noted that the signals of [3]**1b** started to decay at 270 K and disappeared rather quickly at 300 K.[5] In marked contrast, the signal of [3]**5** survived for hours even at 300 K.

To estimate the stability of this carbene under our standard conditions, that is, in a degassed benzene solution at room temperature, irradiation of **4** was monitored by UV/vis spectroscopy
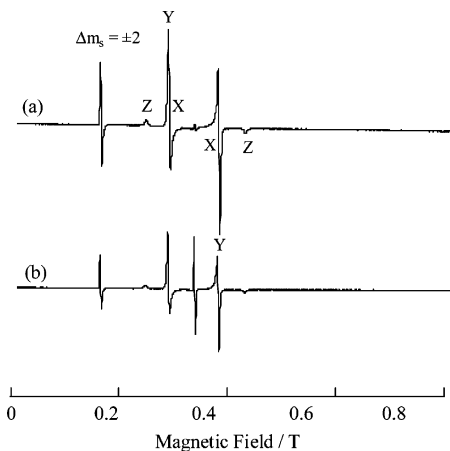
Figure 1. ESR spectra obtained by irradiation of **4** in a 2MTHF matrix (a) at 110 K and (b) same sample after warming the matrix to room temperature and refreezing to 110 K.
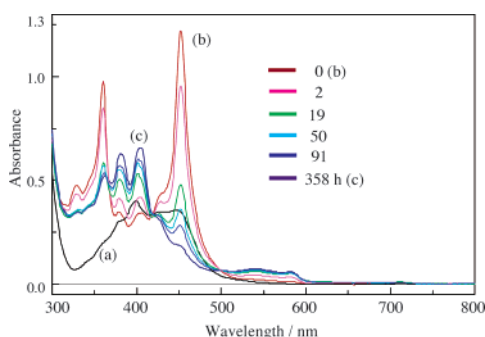

Figure 2. UV/vis spectra obtained by irradiation of **4** in benzene at room temperature. (a) Spectra of **4** in benzene at room temperature. (b) Same sample after irradiation ($\lambda > 350$ nm). (c) Same sample after standing at room temperature for approximately 15 days.

(Figure 2). Photolysis of **4** (5×10^{-5} M) resulted in the appearance of new absorption bands (330, 360, and 452 nm), which are assigned to the triplet carbene ^{3}**5** because essentially the same bands were observed when ^{3}**5** was generated in 2MTHF at 77 K.

The bands ascribable to ^{3}**5** were very stable under these conditions; the characteristic absorption bands were clearly observable even after standing for 1 week at room temperature (Figure 2c). The decay was too slow to determine the exact kinetics at this temperature. The bands did not decay at a significant rate until the temperature was raised to 70 °C. The decay curve under these conditions was analyzed by a combination of first- and second-order kinetics. At 70 °C, the main decay (77%) was fitted to first-order kinetics ($k = 1.08 \times 10^{-2}$ min^{-1}, $\tau = 93$ min), while a minor one (23%) was found to be second-order kinetics ($2k/\epsilon l = 4.24 \times 10^{-2}$ min^{-1}, $t_{1/2} = 68$ min). The Arrhenius plot of the main (first-order) decay rate is linear, which gives the following kinetic parameters: $A = 1.72 \times 10^{11}$ s^{-1}, $\Delta E = 23.7$ kcal/mol. From the plot, the decay rate at 25 °C is estimated to be 4.8×10^{-5} min^{-1}, the lifetime of ^{3}**5** at 25 °C being 14.5 days.

The marked stability of ^{3}**5** is also shown in its reaction toward typical triplet carbene quenchers. The decay rate of ^{3}**5** increased dramatically when it was generated in the presence of oxygen, and a new broad band with a maximum at 505 nm appeared at the expense of the absorption band due to ^{3}**5**. The spent solution was found to contain dianthryl ketone (**7**) as the main product. It is well-documented that diarylcarbenes with a triplet ground state are readily trapped by oxygen to generate the corresponding diaryl ketone oxides (e.g., **6**), which show a broad absorption band centered at 400–500 nm.[8,9] Thus, the observation can be interpreted

as indicating that ^{3}**5** is trapped by oxygen. The quenching rate constant of the reaction of ^{3}**5** by oxygen, k_{O_2}, was obtained from the slope of a plot of the observed rate constant of the formation of the oxide against [O$_2$] and was determined to be 5.5×10^4 M^{-1} s^{-1}, which is about 1/15 of that observed for triplet (2,6-dibromo-4-*tert*-butylphenyl)[2,6-bis(trifluoromethyl)-4-*iso*-propylphenyl]carbene (^{3}**9**), the most stable triplet diphenylcarbene ($k_{O_2} = 8.6 \times 10^5$ M^{-1} s^{-1}).[10]

On the other hand, when a degassed solution of **4** containing 1,4-cyclohexadiene (CHD) was excited, a new species, with its maxima at 382 and 407 nm, was formed as the bands due to ^{3}**5** decayed. The decay was again found to be kinetically correlated with the growth of the new species. Thus, this new band was attributable to the dianthrylmethyl radical **8**[11] formed as a result of H abstraction of ^{3}**5** from the diene, because it is also well-documented that triplet arylcarbenes generated in good hydrogen donor solvents, such as the diene, undergo H abstraction, leading to the corresponding radicals.[12] The absolute rate constant for the reaction of ^{3}**5** with the diene, k_{CHD}, was also obtained from the slope of a plot of the pseudo-first-order rate constant of the formation of the radical against [CHD] and determined to be 0.02 M^{-1} s^{-1}, which is some 3 orders of magnitude smaller than that observed for ^{3}**9** ($k_{CHD} = 1.0 \times 10$ M^{-1} s^{-1}).[10]

A simple modification of triplet di(anthryl)carbene, thus, results in a rather unexpectedly large increase in the stability.

Supporting Information Available: Experimental details, figures showing decay of ^{3}**5** at 75 °C, Arrhenius plot for decay of ^{3}**5**, trapping of ^{3}**5** by oxygen and 1,4-cyclohexadiene, and X-ray crystal structure of **7** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Inspection of the X-ray crystal structure of the corresponding ketone (**7**) clearly indicates that the phenyl group at the C$_{10}$ position is perpendicular to the anthryl ring and hence methyl groups at the ortho positions are hanging over the C$_{10}$ position of the anthryl ring where a significant amount of nonbonded electrons resides in ^{3}**5**.

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(10) Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1999**, *121*, 10213. The difference is not so large when compared with ^{3}**1b** ($k_{O_2} = 9.5 \times 10^4$ M^{-1} s^{-1} and $k_{CHD} = 0.047$ M^{-1} s^{-1}). This can be interpreted as indicating that the origin of the increased lifetime of benzene is not mainly due to an intrinsic decrease in the reactivity of the carbene center but to the decrease in the decay from the C$_{10}$ position.

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