

Generation and characterization of a fairly stable triplet carbene

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Most molecules are held together by covalent bonds—electron pairs jointly shared by the two atoms that are linked by the bond. Free radicals, in contrast, have at least one unpaired electron. In the case of carbon-based radicals, the carbon atom at the radical centre no longer makes four bonds with other atoms as it would do in its normal, tetravalent state. The presence of unpaired electrons renders such radicals highly reactive, so they normally occur only as transient intermediates during chemical reactions. But the discovery^{1,2} by Gomberg in 1900 of triphenylmethyl, the first relatively stable free radical containing a central trivalent carbon atom, illustrated that radicals with suitable geometrical and electronic structures can be stable. Compounds containing a divalent carbon atom that uses only two of its four valence electrons for bonding are usually less stable than Gomberg-type radicals with trivalent carbon^{3–5}. Although the role of these so-called carbenes in chemical reactions has long been postulated, they were unambiguously identified only in the 1950s. More recently, stable carbenes have been prepared^{6,7}, but the singlet state of these molecules^{6–12}, with the two nonbonding valence electrons paired, means that they are not radicals. Carbenes in the second possible electronic state, the triplet state, are radicals: the two nonbonding electrons have parallel spins and occupy different orbitals^{13,14}. Here we report the preparation and characterization of a triplet carbene, whose half-life of 19 minutes at room temperature shows it to be significantly more stable than previously observed triplet carbenes^{15–17}.

Triplet carbenes are usually characterized by electron paramagnetic resonance (EPR) spectroscopy. The principal information extracted from the EPR spectra of triplet carbenes are the zero-field splitting parameters, D and E (interaction energies in cm^{-1}), which measure the magnetic dipole interaction of the unpaired electrons in the absence of an external field. Usually D provides a measure of the average distance r between the unpaired electrons; in carbenes with conjugated π -systems, it thus allows for a qualitative

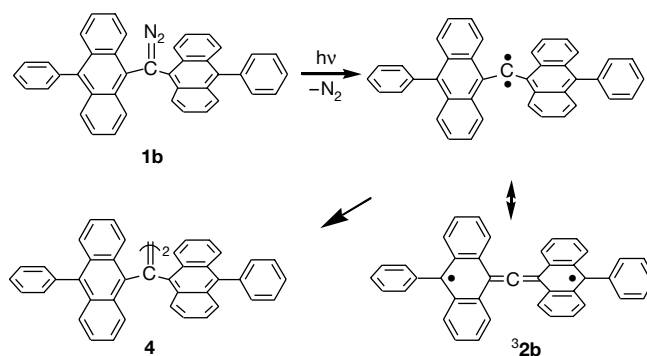


Figure 2 Structure of triplet bis(9-anthryl)carbene ($^3\mathbf{2b}$), generated by photolysis of the precursor diazomethane ($\mathbf{1b}$), and the corresponding carbene dimer ($\mathbf{4}$). The phenyl groups in $^3\mathbf{2b}$ are not expected to be in the same plane as the anthryl rings owing to the repulsion between *ortho*- and *peri*-hydrogens. This is in line with the similarity of the zero-field splitting parameters of $^3\mathbf{2b}$ to those of $^3\mathbf{2a}$. It seems that the phenyl groups effectively prevent the unpaired electrons from 'leaking out' and thus prevent reaction at position 10.

determination of the extent of electron delocalization. E provides a measure of the difference in the magnitude of magnetic dipole moment among triplet species, from which the bond angle at the carbene centre can be estimated. In the case of diarylcarbenes, E and D values are expected to decrease as the carbene bond angle expands and the unpaired electrons are more extensively delocalized^{18–21}.

Among diarylcarbenes, triplet di(9-anthryl)carbene ($^3\mathbf{2a}$) exhibits the smallest D (0.113 cm^{-1}) and E (0.0011 cm^{-1}) values reported²², indicating that it has an almost linear bond geometry at the carbene centre with extensive delocalization of the unpaired electrons onto the perpendicularly attached anthryl groups. The extensive delocalization is expected to stabilize this carbene compound thermodynamically, while the perpendicular geometry of the anthryl groups stabilizes the carbene centre kinetically, through shielding with the four *peri*-hydrogens. That is, the electronic factor and the molecular structure of the molecule seem ideal for the formation of a stable triplet carbene. In spite of those highly favourable structural factors, $^3\mathbf{2a}$ is very ephemeral²³: its lifetime in degassed benzene solution at room temperature is $0.5 \mu\text{s}$, shorter even than that of triplet diphenylcarbene.

Product analysis shows that $^3\mathbf{2a}$ forms as main product a trimer ($\mathbf{3}$) (ref. 24), in which three units of $^3\mathbf{2a}$ are connected at the C_{10}

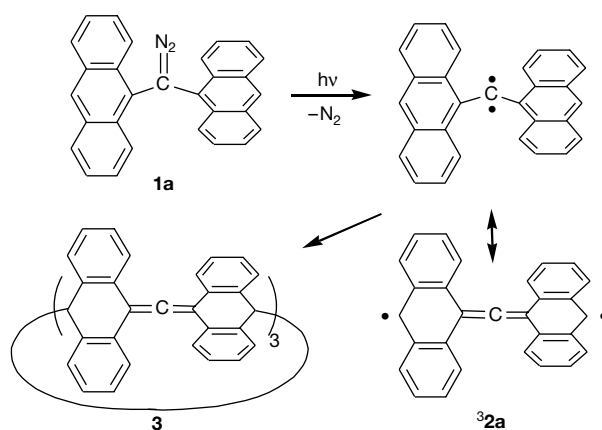


Figure 1 Structure of triplet di(9-anthryl)carbene ($^3\mathbf{2a}$), generated by photolysis of the precursor diazomethane ($\mathbf{1a}$), and the corresponding trimer ($\mathbf{3}$). In $^3\mathbf{2a}$, the carbene centre is almost linear, and there is extensive delocalization of the unpaired electrons onto the anthryl groups, which are attached in a perpendicular fashion. These electronic and

structural factors would be expected to favour the formation of a stable triplet carbene. However, $^3\mathbf{2a}$ is very ephemeral. The main decay pathway of $^3\mathbf{2a}$ is reaction at the C_{10} position of the anthryl groups in a cyclic way to form a trimer ($\mathbf{3}$).

position of the anthryl groups in a cyclic way. This behaviour suggests that delocalization of the unpaired electrons in **3a** leads to their 'leaking out' from the carbene centre to position 10, where sufficient spin density builds up for the trimerization to take place (Fig. 1). At the same time, the lack of formation of olefin-type dimers through coupling two units of **3a** at their carbene centres indicates that the carbene centre itself is indeed well shielded and stabilized.

The above observations indicate that the stability of **3a** would increase if the trimerization reaction were somehow suppressed—by, for example, the introduction of a substituent at position C₁₀ to block the reactivity there. This simple idea inspired us to synthesize **3b**, which is formally related to **3a** by substituting a phenyl group at each of the two C₁₀ positions.

Irradiation (at wavelengths $\lambda > 300$ nm) of bis[9-(10-phenyl)anthryl]diazomethane **1b** in a 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave EPR signals very similar to those observed for dianthrylcarbene **3a** (Fig. 2). The zero-field splitting parameters ($D = 0.105$ cm⁻¹, $E = 4.4 \times 10^{-4}$ cm⁻¹) derived from the signals are essentially the same as those obtained for the triplet dianthrylcarbene, indicating that the phenyl groups are not in the same plane as the anthryl rings owing to the repulsion between *ortho*- and *peri*-hydrogens. The signals of **3a** and **3b** differ only in their thermal response: when the 2-MTHF glass containing **3a** was warmed gradually, the signals due to **3a** started to disappear at around 90 K, whereas no significant decay of the signals of **3b** was observed up to 240 K. The signal of **3b** started to decay only at around 270 K ($\sim 0^\circ\text{C}$), but was still visible when heating to 300 K ($\sim 27^\circ\text{C}$) (see Supplementary Information).

The EPR signals of **3b** became sharp and shifted slightly but distinctly at around 110 K. Changes of this kind have often been observed for sterically congested triplet diarylcarbenes; they are usually attributed to the relaxation of the carbene from distorted orientations—caused by the trapping of the precursor in the frozen matrix—to the thermodynamically favourable orientation upon softening of the matrix²⁵.

Ultraviolet–visible (UV/vis.) spectroscopic studies provided similar but more quantitative results^{21,26–28}. Irradiation ($\lambda > 300$ nm) of **1b** in the 2-MTHF matrix at 77 K resulted in the appearance of new absorption bands (343, 362 and 475 nm). As under identical conditions strong EPR signals ascribable to **3b** were observed, the UV/vis absorption bands were assigned to **3b**. When the temperature of the matrix containing **3b** was raised gradually, a

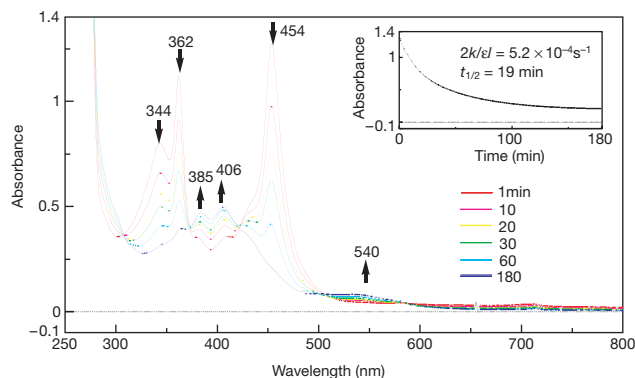


Figure 3 Ultraviolet/visible spectrum after photolysis ($\lambda = 308$ nm) of the precursor diazomethane (**1b**) in degassed benzene at 20°C . Triplet bis[9-(10-phenyl)anthryl]carbene (**3b**) showed transient absorption bands at 344, 362 and 454 nm. The spectra recorded after 1, 10, 20, 30, 60 and 180 min are shown. Inset, the decay of the transient absorption due to **3b** monitored at 454 nm. The bands due to **3b** decayed cleanly, showing isosbestic points, and persisted for more than 3 hours before disappearing completely. k , rate constant (in $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$); ϵ , molar extinction coefficient of **3b** (in $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$); l , cell-path length (in cm); $t_{1/2}$, half-life (in min).

broad absorption maximum at 475 nm became sharp and shifted to 454 nm at 110 K. As this is the temperature where the EPR signals shifted due to geometrical relaxation of **3b**, we assigned these new bands to the relaxed **3b**. When the temperature was further raised, the absorption bands decayed very slowly and cleanly, showing isosbestic points. These were observed even at 270 K, and did not disappear completely even at 300 K (see Supplementary Information). Product analysis of the spent solution showed the presence of a carbene dimer (**4**) as the main isolable product (Fig. 2).

To probe the stability and decay kinetics of **3b** at ambient conditions, **1b** was photolysed in degassed benzene at room temperature. The transient absorption bands observed were identical to those observed for the relaxed **3b** in the low-temperature matrix. The bands due to **3b** decayed cleanly, showing isosbestic points; they persisted for more than 3 hours before disappearing completely. Fitting the decay curve with second-order kinetics ($2k/\epsilon l = 5.2 \times 10^{-4} \text{ s}^{-1}$, where k is the rate constant (in $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$), ϵ is the molar extinction coefficient of **3b** (in $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$) and l is the cell-path length (in cm), a half-life for **3b** of 19 min was estimated (Fig. 3).

One of the resonance structures of **3b** can formally be regarded as two Gomberg radicals connected by an allene bond (see Fig. 4). Small D and E values and an exclusive coupling reaction at the 10 positions (in the absence of the phenyl substituents) suggest that the contribution of this structure to the actual average distribution of electrons in the molecule is important, raising the question of whether **3b** is a triplet carbene or a triplet diradical. In general, D values decrease as the unpaired electrons are delocalized. However, the information contained in the D values is insufficient to discriminate between a carbene (1,1-diradical) and a diradical (containing unpaired electrons at two discrete centres). However, we note that the measured E values indicate that **3b**, and thus also its central bond angle, is not completely linear; **3b** must therefore have some carbene characteristics.

Because spectroscopic methods seem unable to discriminate between a carbene and a diradical species, we use chemical reactivity to probe whether the unpaired electrons are localized on one carbon

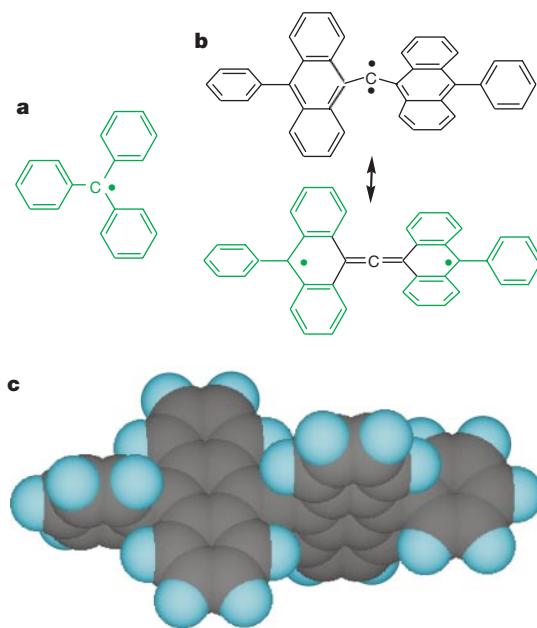


Figure 4 Structure of **3b** and Gomberg's radical. **a**, Structure of Gomberg's radical. **b**, Resonance structures of **3b**. The lower of these structures can be regarded as two Gomberg radicals connected by an allene bond. **c**, Space-filling model of **3b**, showing how well the carbene centre is shielded by two anthryl groups.

centre (carbene) or localized on two different atoms within the molecule (diradical). One of the best known reactions of triplet carbenes is their interaction with oxygen to form the corresponding ketones, which involves carbonyl oxide formation. In contrast, diradicals react with oxygen to give oxidation products mainly derived from the corresponding peroxides. When **1b** was irradiated in the presence of oxygen, bis [9-(10-phenyl)anthryl]ketone was formed. Laser flash photolysis studies showed the presence of a broad transient absorption at 505 nm ascribable to the carbonyl oxide. Moreover, whereas **3a** aggregated into a trimer, **3b** produced a carbene dimer (**4**) through coupling of two molecules at their carbene centres. These observations, and the fact that we observed the main decay pathway of persistent triplet carbenes in solution to be dimerization, suggest that even though the free electrons in **3b** are extensively delocalized, it is considered more appropriately as a carbene than a diradical.

Although the conceptual ideas underpinning this work were developed more than a century ago, the present findings may still affect modern materials science because triplet carbene units can serve as a useful source of electron spins in high-spin organic molecules that act as models for purely organic ferromagnetics²⁹. To date, the highly transient nature of these species has prevented further development of such systems into usable magnetic materials, but the relatively stable triplet carbene described here may point to new strategies for developing organic ferromagnetic materials. □

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Normal faulting in central Tibet since at least 13.5 Myr ago

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Tectonic models for the evolution of the Tibetan plateau interpret observed east–west thinning of the upper crust to be the result of either increased potential energy of elevated crust¹ or geodynamic processes that may be unrelated to plateau formation^{2–6}. A key piece of information needed to evaluate these models is the timing of deformation within the plateau. The onset of normal faulting has been estimated to have commenced in southern Tibet between about 14 Myr ago⁷ and about 8 Myr ago⁸ and, in central Tibet, about 4 Myr ago⁹. Here, however, we report a minimum age of approximately 13.5 Myr for the onset of graben formation in central Tibet, based on mineralization ages determined with Rb–Sr and ⁴⁰Ar–³⁹Ar data that post-date a major graben-bounding normal fault. These data, along with evidence for prolonged activity of normal faulting in this and other Tibetan grabens, support models that relate normal faulting to processes occurring beneath the plateau. Thinning of the upper crust is most plausibly the result of potential-energy increases resulting from spatially and temporally heterogeneous changes in thermal structure and density distribution within the crust and upper mantle beneath Tibet. This is supported by recent geophysical and geological data^{10–17}, which indicate that spatial heterogeneity exists in both the Tibetan crust and lithospheric mantle.

The Tibetan plateau consists of several continental fragments (Fig. 1a) that were accreted to the southern margin of Eurasia during the Palaeozoic and Mesozoic eras. Although crustal thickening due to these collisions may have raised portions of the plateau¹⁸, most of the plateau's current elevation is attributed to the India–