is required to enter the preorganized host; therefore, as was already pointed out,[2b] ΔG_c should contribute to K'_s favorably. However, this term, which depends on the guest volume, is expected to increase on going from CH_2Cl_2 to CCl_4, whereas the maximum stability is observed for the **2**·$CHCl_3$ complex. This fact probably means that the contribution of ΔG_c to the cavitate stabilization is relatively small. The high exothermal ΔH in the formation of the **2**·$CHCl_3$ cavitate is certainly best interpreted in terms of overall attractive host–guest interactions, which in this case should mainly consist of multipole–multipole and dispersion forces. As these interactions are strongly distance-dependent, we should conclude that effective *complementarity* between guest and host has been achieved in this complex. We simply observe that in **2** (and also in **1**), the best guest, experimentally, has a size substantially smaller than that suggested from examination of CPK models. Moreover, complementarity seems to be a very sharp requirement, if we consider that the **2**·$CHCl_3$ cavitate is stabler than the CH_2Cl_2 and $CHBr_3$ ones by $\Delta G \sim 1.0$ and 1.4 kcal/mol, respectively.

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(13) Cavity formation in solvents: see, for example: Stien, M. L.; Reisse, J. *Calorim. Anal. Therm.* **1984**, *15*, 214–219 and references therein.

Diadamantylcarbene in Solution[1]

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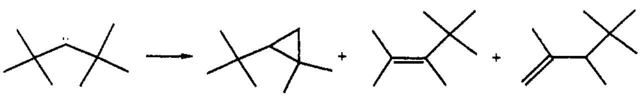
One of the substantial achievements of carbene chemistry has been the differentiation of singlet and triplet reactions. Diarylcarbenes have been the most often used vehicles for this work[6] although the parent methylene[6b] and carboalkoxycarbenes[7] have also found use. Conspicuously absent are alkyl- and dialkylcarbenes and for good reason: their chemistry is most one-sided. The reactive singlet states are effectively trapped by the available intramolecular reactions and the reactions of the lower energy, generally ground state, triplets are rendered invisible. Even when entry to the singlet–triplet manifold is gained through the triplet by photosensitized irradiation of a precursor, the reactions of the less stable singlet often win out.[6,7]

Triplet di-*tert*-butylcarbene has been observed by Gano and his collaborators[8] at 14 K. Workup produced 80% of **1** and **2**, typical products of singlet carbene reactions, but the remaining 20% (**3**) was reasonably, if tentatively, attributed to the incursion of triplet carbene. Analysis of the zero-field parameters revealed a carbene surprisingly similar to methylene as the central bond angle was ca. 143° (triplet $:CH_2 = 137°$).[9] One must always bear in mind that the determination of angles from zero-field splitting parameters alone is not very reliable.

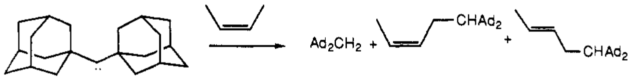


1 **2** **3**

We have found that diadamantylcarbene (**4**) not only is a triplet ground state with a wider central angle than di-*tert*-butylcarbene but shows substantial triplet reactivity even in solution at 25 °C.

Irradiation of diadamantyldiazomethane[10] labeled with ^{13}C at the central position with an unfiltered 1000-W Hg-Xe lamp at 14 K produced a persistent triplet spectrum. Curie law analysis proved the triplet to be the ground-state species. The ^{13}C hyperfine splitting could be observed and related to the central angle by using the model of Brandon et al.[11] The hyperfine components of the high-field X and Y transitions and low-field Z transition are 252, 258, and 134 MHz, respectively. This compared with 282, 281, and 177 MHz for methylene.[12] Triplet diadamantylcarbene is long-lived in ethanol matrices between 4 and 75 K. In this respect it is even less reactive than diphenylcarbene. These values lead to a value of 152°, substantially wider than that in methylene[12] and essentially the same as that in diphenylcarbene.[11] A somewhat smaller angle of 146° can also be determined. At the suggestion of a referee we have analyzed the data by taking as the isotropic hyperfine interaction the average of the anisotropic hyperfine interactions oriented along the axes of the three zero-field transitions measured in our EPR experiment.[12a] If one assumes that one of the carbene orbitals is pure 2p (?) and the other an sp hybrid, the fractional s character of the hybrid orbital can be determined by using the correlation of either Higuchi[13a] or Harrison.[13b] We suspect that the bond angle in di-*tert*-butylcarbene, reported to be 143°,[8] is really larger as the zero-field parameters of **4** ($D/hc = 0.6823$ cm^{-1}, $E/hc = 0.038$ cm^{-1}) are nearly identical with those of di-*tert*-butylcarbene ($D/hc = 0.689$ cm^{-1}, $E/hc = 0.039$ cm^{-1}).[8]

Irradiation of dry, degassed[14] solutions of diadamantyldiazomethane in *cis*-2-butene at room temperature with a Hanovia medium-pressure mercury arc led to diadamantylmethane (**5**) as the major product (16% yield, 81% relative yield). The structure was confirmed by comparison with published data[10] although the position of the central methylene protons is not reported in the literature.[10] We have confirmed the unusually high upfield position of these protons (δ 0.9) by synthesizing deuterio-**5** from α-deuteriodiadamantylcarbinyl chloride. Small amounts of 1:1 adducts (4% yield, 19% relative yield) are also produced from **4** and *cis*-2-butene. The structures are tentatively assigned as **6** and **7** on the basis of their mass and ^1H NMR spectra.



4 = $Ad_2C:$ **5** **6** **7**

Diadamantylmethane is surely a product of triplet carbene. Abstraction products are not reported for singlets[6b] but have been

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[1] Support from the National Science Foundation through Grants CHE-8318345 (Princeton) and CHE-8210710 (Ohio State) is gratefully acknowledged. Reactions of diadamantylcarbene in the gas phase have already been described: Sellers, S. F.; Klebach, T. C.; Hollowood, F.; Jones, M. Jr.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 5492.

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[3] Princeton University.

[4] The Ohio State University.

[5] Camille and Henry Dreyfuss Fellow.

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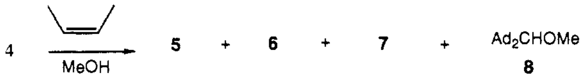
found from triplet reactions with hydrocarbons.[16] Similarly, sensitivity to oxygen is a well-known triplet trait.[15] Thus **4** becomes the first alkylcarbene to react as a triplet in solution. One may legitimately wonder why. Triplets are favored by wide central angles. Thus triplet methylene has an angle of 137° and the singlet only 103°.[9] Perhaps triplet **4** is exceptionally favored relative to the singlet state. In addition, singlet reactivity, which requires formation of two bonds will be disfavored relative to triplet reactivity which initially permits but one bond to form.[17] The wide angle of **4** and steric requirements of the adamantyl groups would surely favor a process requiring only one bond to form.

The singlet state of diphenylcarbene can be detected by characteristic reactions. This is also the case for **4**. Irradiation of diadamantyl diazomethane in *cis*-2-butene doped with methanol led to **5** and a product attributed to singlet **4**, diadamantylmethyl methyl ether, **8**. As little as 0.25% of the powerful singlet trap methanol led to a relative yield of 77% **8**. Diadamantylmethane (21%) and adducts (2%) were still formed. An analysis of the relative ratios of these products with varying concentrations of methanol leads to the tentative conclusion that **7** and **8** are products from the singlet carbene.



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Biomolecules in the Gas Phase.
1. Multiphoton-Ionization Mass Spectrometry of Native Chlorophylls

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We present here the results of a new technique by which it is possible to vaporize large, thermally unstable biomolecules, like native chlorophylls, into a molecular beam and subsequently study them by mass spectrometry. The chlorophylls have been obtained by methanolic extraction of the cyano-bacterium *Spirulina geitlerie*[1] and are investigated without further purification.

The laser vaporization in the first stage of our instrument is analyzed by multiphoton ionization (MPI) mass spectra obtained from the reflectron-time-of-flight mass spectrometer (RETOF-MS) in a second stage. This separation of the vaporizing and ionizing process is one special feature of our technique, yielding intense signals of pure intact molecular ions as opposed to all other previous vaporization techniques.[2] A second feature is the injection of the vaporized neutral molecules into a supersonic beam of a carrier gas which leads to intensive cooling of those molecules. This cooling provides small kinetic energy distributions and thus high mass resolutions in time-of-flight mass spectrometers. For conventional vaporization of ions from a solid surface, broad kinetic energy distributions are a fundamental problem for TOF mass spectrometers, even for energy-correcting RETOF mass spectrometers.

Most bimolecules have only a minimal vapor pressure or alternatively decompose if heated to attain an appreciable vapor pressure. Different approaches have been made to form supersonic beams with large molecules.[4] Recently two new adoptions have been published. One method[5] is a combination of the thermospray method[6] with the formation of a supersonic jet. The other method[7] uses laser desorption from a solid sample into the supersonic jet.

In our method a low-power CO_2 laser is focused on a probe tip, mounted just before the jet generating valve, thus, producing a mixture of the carrier gas and vaporized molecules. The supersonic beam is then introduced into the ion source of our RETOF instrument.[8] It should be noted that in our experimental setup only neutrals but no charged particles can enter the ion source. The MPI spectrum is produced with an eximer pumped frequency doubled dye laser running at a wavelength of 2750 Å. The mass spectrum is recorded with a transient recorder and is an average of 10 laser shots. The RETOF is running in a medium-resolution mode, even then yielding a resolution of 2900.

Intact chlorophylls have been previously investigated by several different methods.[9-12] In all these techniques vaporization and ionization are a combined process. Due to this simultaneous process the resulting mass spectra give not only the pure molecular ions but also quasi-molecular adduct ions formed either in the vaporization step or in the matrix on the sample holder. These so formed cluster ions often interfere in the peak pattern of the pure molecular ion, thus complicating the interpretation of the mass spectra. Sometimes molecular ions are not formed at all.

Multiphoton ionization has been proven to be a soft ionization method.[13] Depending on the laser power, it is possible to obtain all ranges of decomposition from only molecular ions to total fragmentation, thus giving all possible information with only one method. In Figure 1 the resulting mass spectrum is shown, demonstrating very clearly the softness of the MPI-process. This proves unequivocally not only that native chlorophyll *a* can be soft-ionized but more importantly that the intact chlorophyll *a* has survived the vaporization process and is present in a molecular beam. The ions in the high-mass region are extraordinary intense and very little fragmentation occurs. In this region three different compounds can be identified. The signal group at mass 892

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(1) Generously supplied by Prof. Dr. H. Scheer, Botanisches Institut, Universität München.

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