

Unexpected photochemistry and charge-transfer complexes of $[\text{CB}_{11}\text{H}_{12}]^-$ carborane[†]

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Although the $[\text{CB}_{11}\text{H}_{12}]^-$ carborane does not exhibit an absorption band in UV, its triplet excited state can be generated upon 308 nm laser excitation; also unexpectedly carborane acts as electron donor forming a charge transfer complex with methylviologen that upon illumination gives rise to viologen radical cation.

Since the initial report of Reed and co-workers describing the superacidity of carboranes in their protonic form, there is a renewed interest in this molecule.^{1–4} Carborane $\text{CB}_{11}\text{H}_{12}^-$ results from the apical isomorphous substitution of a boron in dodecaborane with a carbon atom.⁵ As result of this substitution and the extra carbon electron, a negative charge is introduced in the system and the carborane becomes an anionic species. Carboranes are among the less nucleophilic species due to electron delocalization over the structure.^{1–4} The chemistry and properties of carboranes have recently been reviewed.^{5–9}

Carborane does not exhibit any absorption band in the UV/Vis region and, therefore, no photochemistry is expected upon irradiation in this wavelength region.⁵ Also, carborane cannot be oxidized in the potential range commonly available in conventional organic solvents,⁵ although oxidation could occur at higher potentials. In sharp contrast with these two well-known properties of $\text{CB}_{11}\text{H}_{12}^-$ carborane, herein we report the unexpected observation of photochemical activity of $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ and the formation of photoactive charge transfer complexes with a strong electron acceptor.

Optical UV/Vis spectrum of $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ in acetonitrile solution shows no peaks in the 200–800 nm range and only an absorption tail growing to shorter wavelengths is observed (Fig. 1). No transient was observed when $\text{CB}_{11}\text{H}_{12}^-$ was irradiated using 355 nm laser. However, upon 308-nm laser excitation of a N_2 -purged methanol 0.175 M solution of $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ (O.D. 0.08) a transient decaying in the microsecond time scale was recorded (Fig. 2). The transient spectrum consists of a broad band expanding from 350 to 650 nm and peaking at 420 nm. The temporal profile of the signal was coincident in the complete spectral range, this being consistent with the photochemical

generation of a single transient species (inset of Fig. 2). The signal decay fits well to a first-order kinetics with a half life of 16.2 μs . The signal from $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ generated upon the laser flash is quenched by oxygen (inset of Fig. 2). Taken together, these observations are consistent with the unexpected characterization of carborane triplet excited state.

Since carboranes do not possess absorption bands in the UV, we performed an energy-dependence study to determine whether or

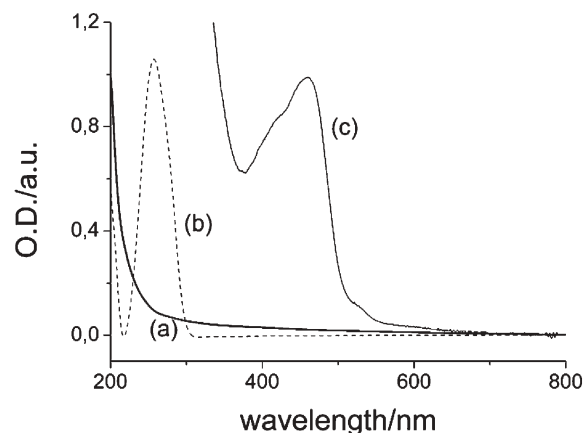


Fig. 1 UV-Vis spectra of acetonitrile solutions of: (a) $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ (0.175 M), (b) $\text{MV}(\text{PF}_6)_2$ (10^{-4} M) and (c) the charge-transfer complex formed upon mixing 0.01 M solutions of $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ and $\text{MV}(\text{PF}_6)_2$.

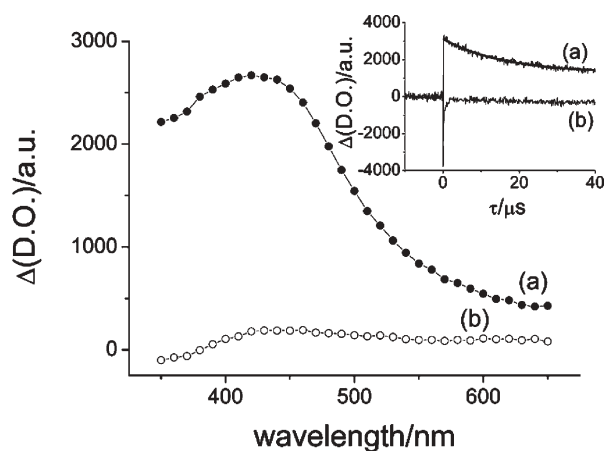
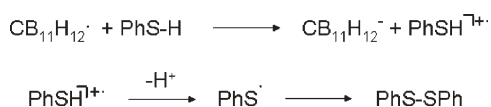


Fig. 2 UV-Vis absorption spectrum recorded 5 μs after 308-nm laser excitation of a 175 mM methanol solution of $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ purged with N_2 (a) or with O_2 (b). The inset shows the temporal evolution of the signals at 420 nm.

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[†] Electronic supplementary information (ESI) available: Fig. S1: Dependence of the absorption at 420 nm of a $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ methanolic solution upon laser power. Fig. S2: Quenching of $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ with nitromethane. Fig. S3: ESI-MS of a coloured equimolar mixture of $\text{Cs}[\text{CB}_{11}]$ and $\text{MV}(\text{PF}_6)_2$ in acetonitrile. See DOI: 10.1039/b715303a



Scheme 2

the unirradiated sample. Formation of carborane dimer even though in small amounts is uncommon. Theoretical calculations for the $\text{CB}_{11}\text{H}_{12}^{\cdot-}$ radical indicates that the unpaired electron is mainly localized on the boron opposed to the carbon vertex.¹³ Also there are some precedents of the dimerization of decaborane and related derivatives¹⁴ as well as the permethyl substituted of carborane.⁵

In order to seek evidence for the occurrence of a photoinduced electron transfer upon excitation of the charge-transfer complex, laser flash photolysis of the solution containing $\text{CB}_{11}\text{H}_{12}^{-}$ and MV^{2+} was carried out. It is convenient to remind that previous controls commented on earlier showed that 355 nm excitation of $\text{CB}_{11}\text{H}_{12}^{-}$ does not allow recording any transient. Also another control establishes that $\text{MV}(\text{PF}_6)_2$ does not give any transient upon 355-nm excitation. In contrast to the negative results of these controls, 355 nm excitation of the charge-transfer complex gives rise to the formation of a transient (Fig. 3(B)). The transient spectrum can be interpreted as the overlapping of $\text{MV}^{\cdot+}$ radical cation (sharp absorption at 390 nm and another much broader and less intense at 600 nm) with another species. We propose that this other species corresponds to the carborane radical formed concomitantly with $\text{MV}^{\cdot+}$ in the photoinduced electron transfer. These transients are extremely long lived and did not decay in the longest time scale available to our nanosecond laser flash photolysis system (500 μs). This persistence is also compatible with the fact that at least $\text{MV}^{\cdot+}$ can be observed by steady-state optical spectroscopy.

As commented earlier, dimer formation from the $\text{CB}_{11}\text{H}_{11}^{\cdot}$ radical is most likely an unfavourable process and, thus the peak detected should correspond to a minor process. In order to seek additional evidence for the occurrence of photoinduced electron transfer we performed the irradiation of the $\text{CB}_{11}\text{H}_{12}^{-}$ and MV^{2+} charge transfer complex in the presence of thiophenol (PhSH). This compound is a good electron and hydrogen donor and if $\text{CB}_{11}\text{H}_{12}^{\cdot-}$ radical is formed, PhSH should be able to quench the carborane radical by transferring a hydrogen atom. Upon generation of PhS^{\cdot} thiyl radical, the process should lead to the

formation of 1,2-diphenyl disulfide that can be easily detected (Scheme 2).

As expected irradiation with 360 nm light gives rise to the disappearance of thiophenol and the concomitant formation of 1,2-diphenyl disulfide. A blank control under the same conditions with MV^{2+} and thiophenol but in the absence of carborane shows that the presence of carborane is responsible for an enhancement of the yield of 1,2-diphenyl disulfide from 25 to 90%.

In summary, unexpectedly in view of the absence of an absorption band in the UV above 200 nm, 308 nm laser flash excitation has allowed detection of the corresponding triplet excited state with a half life of 16.2 μs . Also unexpectedly in view of its reluctance to undergo electrochemical oxidation, carborane associates with MV^{2+} forming a charge transfer complex that can be detected by optical spectroscopy and positive ESI-MS. Upon illumination, the charge transfer complex gives rise to a charge separated state, $\text{MV}^{\cdot+}$ radical cation being indefinitely persistent in the absence of oxygen. These results can open new avenues in the chemistry and functionalization of carboranes.

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