Spectroscopic Observation of the Triplet Diradical State of a Cyclobutadiene

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Dedicated to Professor Roald Hoffmann on the occasion of his 80th birthday

Abstract: *Tetrakis(trimethylsilyl)cyclobuta-1,3-diene (**1**) was subjected to a temperature-dependent EPR study to allow the first spectroscopic observation of a triplet diradical state of a cyclobutadiene (**2**). From the temperature dependent EPR absorption area we derive a singlet→triplet (**1**→**2**) energy gap, E_{ST}, of 13.9 kcal mol^{-1}, in agreement with calculated values. The zero-field splitting parameters $D = 0.171$ cm^{-1}, $E = 0$ cm^{-1} are accurately reproduced by DFT calculations. The triplet diradical **2** is thermally accessible at moderate temperatures. It is not an intermediate in the thermal cycloreversion of cyclobutadiene to two acetylene molecules.*

Few molecules have fascinated chemists as continuously and consistently as cyclobutadiene (CBD). Ever since Kekulé first attempted the preparation of CBD in 1872,[1] this illusive molecule posed a challenge to experimental and theoretical chemists.[2] Owing to the high reactivity of CBD, it was not until nearly a hundred years later that CBD derivatives could be synthesized and characterized.[3] The fundamental questions that surrounded CBD dealing with its aromaticity, enthalpy of formation, reactivity in cycloaddition reactions, isomerization and ground state multiplicity led to intensive research efforts,[2,3] but some of the basic theoretically predicted properties of CBD remain without experimental support even today. One basic property which remains to be

explored, is the spectroscopic observation of CBD's low-lying triplet diradical excited state.

Theoretical studies established that the D_{2h} rectangular-singlet (RS) geometry is the minimum energy of the parent CBD and that the square-singlet (SS) geometry represents a transition state for bond isomerization in singlet CBD, that is, a transition state between the two RS geometries (Figure 1). The energy barrier for this automerization was
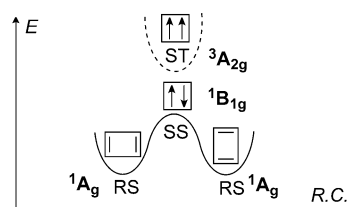

Figure 1. Lowest energy states of cyclobutadiene (CBD). R.C. = reaction coordinate.

experimentally predicted to be in the range of 1.6–10 kcal mol^{-1} while high-level multi-reference calculations found an energy barrier of approximately 6–7 kcal mol^{-1}.[4] The square D_{4h} $^3A_{2g}$ triplet (ST) CBD is energetically close to the SS $^1B_{1g}$ state (Figure 1)[5] and is predicted to prefer a square D_{4h} geometry[5], in agreement with the absence of an EPR signal of the matrix-isolated molecule. High level ab initio calculations predict that the singlet (^1A_g)—triplet ($^3A_{2g}$) energy gap (E_{ST}) ranges from 10 to 14 kcal mol^{-1}.[4,6] The experimental E_{ST} value for the *per*-alkylated CBD (a CBD fused to two seven-membered carbocycles substituted by eight methyl groups at the four α-carbon atoms) derived by flash photolysis measurements gave approximately 12.0 kcal mol^{-1}.[7] However, the triplet diradical state of CBD or of its derivatives was never directly observed spectroscopically. In one case, that of tetrakis(*t*-butyl)cyclobutadiene, crystallographic X-ray data measured at room temperature suggested a square geometry, and the authors argued that it has a triplet ground state.[8] However, no spectroscopic support for this claim (e.g. EPR) was presented and the observed chemistry of this compound did not grant a conclusive evidence for the triplet state.

In the last decades there is growing interest in the generation and properties of diradicals as these reactive intermediates play crucial roles in molecular transformations and also in materials sciences.[9] Observation of the triplet

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diradical intermediate of CBD and studying its properties is of fundamental interest and is important for understanding cycloaddition reactions—key reactions in organic synthesis.[10]

Herein, we report the first observation by EPR spectroscopy of a thermally accessible triplet state of a symmetrically substituted CBD derivative tetrakis(trimethylsilyl)cyclobuta-1,3-diene (**1**).[11] Detailed quantum chemical calculations support the triplet state assignment and suggest that the triplet diradical **2** is in thermal equilibrium with the corresponding singlet state **1** [Eq. (1)].

(1)
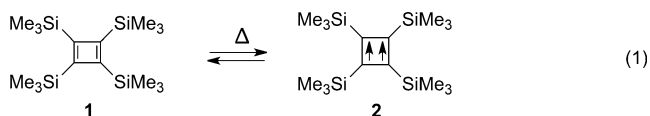
Compound **1** is a good candidate for observing spectroscopically the hypothetical thermally accessible triplet CBD diradical **2** [Eq. (1)] because of its high melting point which is required to allow its study in the solid state at relatively elevated temperatures. **1** is also thermally very stable and only decomposes to the corresponding bis(silyl)acetylene via a cycloreversion reaction at 250°C.[12] In addition, the Me₃Si groups kinetically protect the CBD ring from cycloaddition and other reactions.

A solid sample of **1** was studied by EPR spectroscopy at 350–395 K (Figure 2). At 350 K, three signals, which are typical for triplet diradical species are observed. The signal at
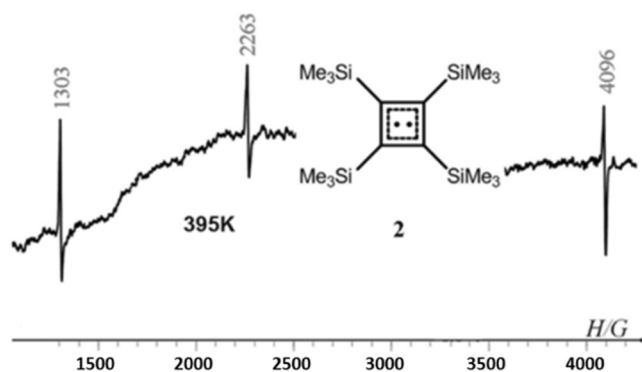
Figure 2. EPR spectrum at 395 K of a solid sample of **1** ($\Delta M_S = \pm 2$, $H_{min} = 1303$ G; $\Delta M_S = \pm 1$, $H = 2263$ G, $H = 4096$; $\nu = 9.294$ GHz).

$H_{min} = 1303$ G belongs to the $\Delta M_S = \pm 2$ transition. The signals at $H = 2263$ G and $H = 4096$ G belong to $\Delta M_S = \pm 1$ transitions. The intensity of the x, y lines in the case of high values of D is very low and they are not observed (see Supporting Information); only the z lines are observed. The coincidence of the x and y lines ($E < 0.001$) indicates plane regular polygonal symmetry.[13] The derived zero-field splitting (ZFS) parameters are $|D|_{exp} = 0.171$ cm⁻¹, $|E|_{exp} = 0$ cm⁻¹. The experimental details and the simulated EPR spectrum are given in the Supporting Information.

The area of the three transition signals (A) increases as the temperature is raised from 350 K to 395 K (Figure 3), indicating that the observed triplet diradical is not the ground
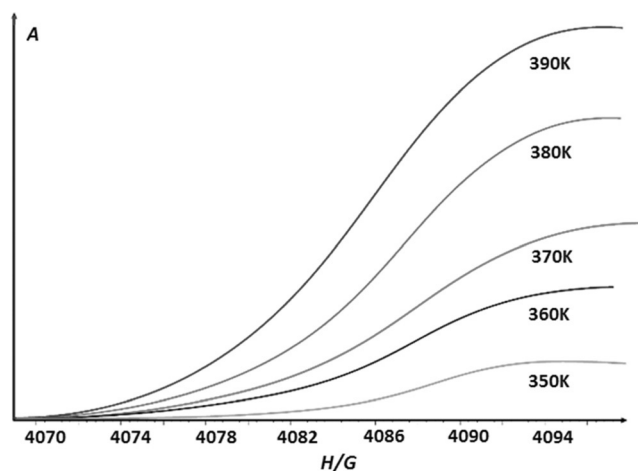
Figure 3. Selected integration curves of the absorption signal at $H = 4096$ G (A, intensity, arbitrary units) of a solid sample of **1** at 350–390 K.

state and its concentration increases at higher temperatures. Furthermore, the triplet signals intensity is temperature reversible. The $\Delta M_S = 1$ and $\Delta M_S = 2$ signals are not detected at 298 K or when the sample is irradiated with UV light.

The absorption area of the EPR signal (A) is proportional to the magnetic susceptibility (χ).[13,14] The temperature dependence of χ is given by the Bleaney–Bowers equation (Equation 2),[15] where T is the absolute temperature, R (cal mol⁻¹ K⁻¹) is the gas constant and E_{ST} (cal mol⁻¹) is the energy gap separating the singlet and triplet states.

$$\chi \propto T^{-1}[3 + \exp(E_{ST}/RT)]^{-1} \qquad (2)$$

Thus, taking $[3 + \exp(E_{ST}/kT)] \approx \exp(E_{ST}/RT)$,[16] the temperature dependence of A is proportional to $T^{-1}\exp(T^{-1})$, that is, $\ln(AT) \propto E_{ST}/RT$. A plot of $\ln(AT)$ versus $1000/T$ (Figure 4) gives a good linear correlation ($R^2 = 0.98$), with a slope of E_{ST}/R, yielding E_{ST} of 13.9 ± 0.8 kcal mol⁻¹ separating the singlet and triplet states of **1**.

This experimentally determined E_{ST} value is in good agreement with previously predicted theoretical values (10–14 kcal mol⁻¹) for the singlet-triplet splitting in parent CBD,
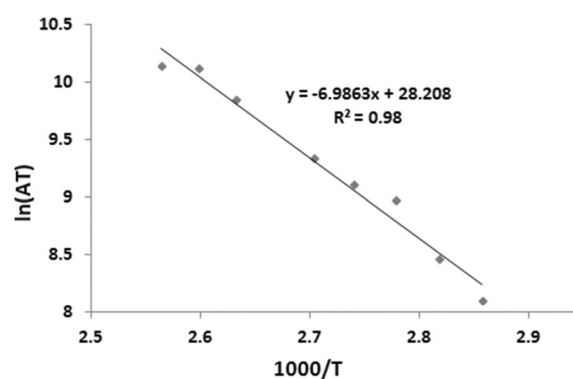
Figure 4. Dependence of the area of the $H = 4096$ G transition signal (A) of a solid sample of **1** at 350–395 K. Slope $= E_{ST}/R = -6.99$ (standard slope deviation 0.42, $R^2 = 0.98$).

and the experimental $E_{ST} = 12.0$ kcal mol^{-1} for the *per*-alkylated CBD derivative.[7] The observed $D = 0.171$ cm^{-1} resembles the D values of other thermally accessible or ground state triplet diradicals with 4π electrons such as cyclopentadienyl cation $(D = 0.19$ cm^{-1}),[17] pentaphenylcyclopentadienyl cation $(D = 0.11$ cm^{-1}),[18] and pentachlorocyclopentadiene cation $(D = 0.15$ cm^{-1}),[19] supporting the above assignment.

Based on the experimental evidence presented above and quantum mechanical calculations of both E_{ST} and the ZFS parameters (see below) we assign the observed spectrum in Figure 2 to the CBD triplet diradical **2**. The increase of the absorption peaks at higher temperatures, the temperature reversibility and the magnitude of E_{ST} suggest that the triplet state of **1** (i.e., **2**) is thermally accessible above 350 K and that the singlet and the triplet states are in thermal equilibrium.

Optimizations of the geometries of singlet and triplet CBDs bearing H, SiH$_3$, and SiMe$_3$ substituents were carried out using Density Functional Theory (DFT) at the B3LYP[20]-D3[21]/6-311 + G(d,p)[22] level (Table 1). The geometries

Table 1: Selected calculated bond lengths [Å] and E_{ST} [kcal mol^{-1}] of R-substituted CBD at the RI-MRDDCI2-CASSCF(4,4)/def2-SVP//B3LYP-D3/6-311 + G(d,p) level of theory.

R	**1** ($r_{C=C}$, r_{C-C}, r_{C-R})	**2** (r_{C-C}, r_{C-R})	E_{ST}
H	1.333, 1.577, 1.081	1.440, 1.080	12.4
SiH$_3$	1.353, 1.589, 1.867	1.457, 1.866	13.5
SiMe$_3$	1.359, 1.599, 1.886	1.463, 1.883	11.8

obtained by optimizations at B3LYP-D3/6-311 + G(d,p) are in good agreement with high level ab initio calculations (see Supporting Information). The parent singlet state CBD adopts rectangular geometry with r(C—C) of 1.577 Å and r(C=C) of 1.333 Å. In the SiH$_3$ and SiMe$_3$ substituted CBD these bonds are slightly longer, r(C—C) = 1.589 Å, 1.599 Å and r(C=C) = 1.353 Å, 1.359 Å, respectively. The triplet diradical state (**2**) adopts a square geometry with equal C—C ring bond lengths of 1.440 Å in the parent CBD and slightly longer bonds of 1.457 Å and 1.463 Å in the H$_3$Si- and Me$_3$Si-substituted CBD, respectively. There is no significant shortening of the C—R bonds upon going from the singlet to the triplet diradical state. This suggests that in the triplet state there is no stabilizing hyperconjugation between the Si-H and Si—Me bonds of the silyl substituents and the p orbitals of the ring carbons. NBO analysis confirms this interpretation, as there are virtually no donor–acceptor interactions between the carbon p orbitals with the silyl substituents. Mulliken spin density analysis shows that in **2** 1.90 e$^-$ of the two unpaired electrons reside on the ring carbons (Figure 5) so there is only minor delocalization of the spin density to the silyl substituents.

Because of the multi-reference nature of the singlet and triplet states accurate computation of singlet–triplet energy gaps of diradicals is a challenging problem when using DFT.[23] For example, in parent cyclobutadiene B3LYP yields E_{ST} of approximately 5 kcal mol^{-1} compared to 10–14 kcal mol^{-1} predicted by high-level ab initio calculations.[4,6] Therefore, most computational studies involving diradicals utilize multi-
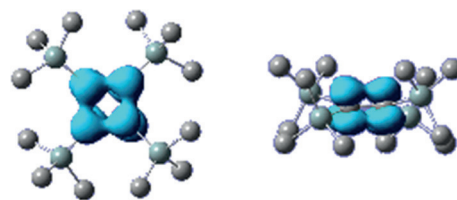

Figure 5. Mulliken spin-density plot of triplet diradical **2**, top view (left) and side view (right).

reference ab initio methods, such as complete active space self-consistent field (CASSCF),[24] complete active space with second-order perturbation theory,[25] or multi-reference coupled cluster theory.[26] Consequently, we carried out single-point calculations of the B3LYP-D3/6-311 + G(d,p) optimized geometries with multi-reference difference dedicated configuration interaction method with two degrees of freedom and resolution of identity approximation (RI-MRDDCI2)[27] over CASSCF(4,4)/def2-TZVP. These calculations give E_{ST} of 12.2, 13.5 and 11.8 kcal mol^{-1} for H-, H$_3$Si- and Me$_3$Si-substituted CBD, respectively. These E_{ST} for the H and H$_3$Si-substituted CBD, are in good agreement with previously calculated values,[4,6] and with coupled cluster calculations (see Supporting Information), verifying that the RI-MRDDCI2-CASSCF(4,4)/def2-SVP//B3LYP-D3/6-311 + G(d,p) method gives meaningful results for cyclobutadiene systems. Using this method E_{ST} of the per-alkylated CBD[7] was calculated to be 13.8 kcal mol^{-1} in good agreement with experimental $E_{ST} = 12.0$ kcal mol^{-1}. The RI-MRDDCI2 calculated $E_{ST} = 11.8$ kcal mol^{-1} for the **1**→**2** energy gap is in a good agreement with the EPR experimentally determined value of 13.9 kcal mol^{-1}.

Only a few quantum chemical methods are available for reliable prediction of ZFS parameters. Although it was shown that an accurate DFT calculation of triplet organic systems is possible,[28] applying DFT to polyacenes and other delocalized triplet diradicals resulted in significant underestimation of the absolute D values.[28] Having that in mind we applied the UNO-B3LYP/TZVP method[28,29] to calculate the D tensor of **2**, obtaining $D = 0.1054$ cm^{-1}—significantly lower than the experimentally observed $D = 0.171$ cm^{-1}. The UNO-B3LYP/TZVP method was used to examine other related thermally accessible or ground state triplet diradicals (**a**–**k**) (Table 2).

Table 2: Experimental and calculated D values of triplet diradicals **a**–**k**.

Compound	$|D_{exp.}|$ [cm^{-1}]	$|D_{calcd}|$ [cm^{-1}]
a cyclopentadienyl$^+$	0.1897	0.1307
b pentachlorocyclopentadienyl$^+$	0.1495	0.0866
c pentaphenylcyclopentadienyl$^+$	0.105	0.065
d hexachlorobenzene^{2+}	0.1012	0.0506
e triphenylene^{2-}	0.0458	0.0293
f coronene^{2-}	0.0539	0.0392
g 1,3,5-triphenylbenzene^{2-}	0.042	0.028
h decacyclene^{2-}	0.025	0.020
i coronene^{2+}	0.0591	0.0409
j hexasilylbenzene^{2-}	0.0963	0.0556
k 2,4,6-triphenyl-sym-triazine^{2-}	0.0561	0.0376

Similarly to **2** the calculated *D* values of **a**–**k** are significantly lower than the experimental values (Table 2). However, a good linear correlation ($R^2 = 0.96$) is obtained between the experimental *D* values and the calculated *D* arising from spin-spin coupling (UNO-B3LYP/TZVP//B3LYP-D3/TZVP), (see Figure S2 in the Supporting Information). Using the obtained calibration curve the calculated *D* of **2** is 0.166 cm^{-1}, and the calculated *E* is 0.000 cm^{-1} in a good agreement with the experimental $D = 0.171 \text{ cm}^{-1}$ and $E = 0 \text{ cm}^{-1}$.

Thus, both the calculated E_{ST} and ZFS parameters fully support the conclusion that the observed EPR spectrum (Figure 2) belongs to the thermally accessible triplet state of **1**, that is, to diradical **2**.

Upon heating, **1** undergoes a cycloreversion reaction to produce two molecules of bis(trimethylsilyl)acetylene.[12] The concerted [2+2] cycloreversion reaction of singlet **1** is thermally forbidden. Is the observed triplet diradical **2** an intermediate in the cycloreversion? To answer this question the potential energy surfaces of the cycloreversion for both the singlet and triplet states were studied by quantum mechanical methods at the B3LYP and CCSD(T) levels. Full details are given in the Supporting Information. The computational results suggest that the cycloreversion of CBD to the corresponding two acetylene molecules proceeds in a stepwise fashion via consecutive C−C bond cleavages. The predicted rate determining step of this reaction is the first C−C bond cleavage to produce an open chain RC≡CR−CR≡CR diradical. The transition states for the singlet diradical rate determining steps are 18, 16, and 13 kcal mol^{-1} lower than the corresponding triplet diradical transition states for H, SiH$_3$, and SiMe$_3$ substituted CBD, respectively. Thus, quantum mechanical calculations suggest that the observed thermally accessible triplet diradical **2** is *not* an intermediate in the cycloreversion of **1**, and that the reaction proceeds via a stepwise singlet diradical pathway. Even on the singlet surface the barriers for cycloreversion are quite high— CCSD(T) (B3LYP) 55.3 (43.0), 42.6 (36.5), and (32.0) kcal mol^{-1} for R = H, SiH$_3$, SiMe$_3$, respectively.

In conclusion, combination of temperature-dependent EPR spectroscopy and detailed quantum mechanical calculations demonstrate that the square triplet diradical state **2** of rectangular singlet tetrakis(trimethylsilyl)cyclobuta-1,3-diene (**1**) can be accessed thermally. For the first time a triplet state of a cyclobutadiene derivative was observed by EPR spectroscopy. The measured **1**→**2** singlet-triplet energy gap of 13.9 kcal mol^{-1} is in agreement with previously predicted values. The ZFS parameters of **2** and the **1**→**2** singlet-triplet energy gap are reproduced by quantum chemical calculations. A correction factor was derived for DFT calculated ZFS parameters of thermally accessible and ground state delocalized organic diradicals. Experimental and theoretical mechanistic studies suggest that triplet diradical **2**, which is in equilibrium with the singlet state, is not an intermediate in the [2+2] cycloreversion reaction, which proceeds via singlet diradicals.

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