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Observation of a Thermally Accessible Triplet State Resulting from Rotation around a Main-Group π Bond

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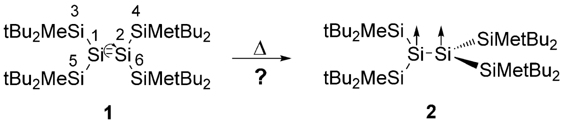
In memory of Michael Bendikov

***Abstract:** We report the first direct spectroscopic observation by electron paramagnetic resonance (EPR) spectroscopy of a triplet diradical that is formed in a thermally induced rotation around a main-group π bond, that is, the Si=Si double bond of tetrakis(di-tert-butylmethylsilyl)disilene (**1**). The highly twisted ground-state geometry of singlet **1** allows access to the perpendicular triplet diradical **2** at moderate temperatures of 350–410 K. DFT-calculated zero-field splitting (ZFS) parameters of **2** accurately reproduce the experimentally observed half-field transition. Experiment and theory suggest a thermal equilibrium between **1** and **2** with a very low singlet–triplet energy gap of only 7.3 kcal mol^{-1}.*

Rotation around the π-C=C double bond, leaving the σ-(C=C) bond intact, is one of the most fundamental processes in chemistry and is important in many chemical and biological transformations. Consequently, it has intrigued chemists for decades and has been studied extensively both experimentally and theoretically.[1–9] One approach to investigate this rotation process is to study tetrasubstituted olefins bearing large substituents that force the C=C double bond out of its preferred planar geometry, thus reducing the energy (and temperature) required for rotation,[10–18] which is about 60 kcal mol^{-1} for $H_2C{=}CH_2$.[19] Some of these highly twisted C=C double bonds exhibit a chemical behavior suggesting that they possess some diradical character; however, generally diradicals were not observed spectroscopically.[15–18] In one case, that of bis-[dibenzo[a.i]-fluorenylidene], it was claimed that the singlet ground state and the diradical triplet state resulting from rotation around the C=C double bond exist in equilibrium, but spectroscopic evidence was not provided.[15–16] Disilenes, $R_2Si{=}SiR_2$, the heavier analogs of alkenes, present an attractive opportunity to observe triplet diradicals because the barrier to rotation around Si=Si π-double bonds is about 15–25 kcal mol^{-1},[20–25] significantly lower than around C=C π-bonds. Consequently, disilenes are more easily torsionally twisted than alkenes;[25–28] for example, tetrakis(di-*tert*-butylmethylsilyl)disilene (**1**) shows a very large torsional distortion around the Si=Si double bond, with an average Si−Si=Si−Si dihedral angle (*θ*) of 55.9°.[29] One consequence of this large twisting around the Si=Si bond is the blue color of **1**, indicating a small HOMO–LUMO gap.[29] The large twisting around the Si=Si bond in **1** with π–π* transition at 612 nm, raises the possibility to observe spectroscopically the 1,2-disiladiradical **2** [Eq. (1)],



(1)

formed upon thermally induced rotation around the Si=Si π-bond of **1**. This physical behavior is unprecedented and especially intriguing if **2** exists in thermal equilibrium with its singlet electronic ground state **1**.

We report here the first direct observation, using EPR spectroscopy, of a thermally accessible triplet state resulting from a thermally induced rotation around a main-group π bond, the Si=Si bond of **1**. The experimental observations are supported by detailed theoretical calculations.

A powder sample of the blue disilene **1**[29] was studied by EPR spectroscopy at 350–410 K (experimental details are given in the Supporting Information). The most remarkable observation is a signal in the half-field region ($\Delta M_S = \pm 2$, $g \approx 4$,), which is a good indication of triplet species,[30] at $H_{min} =$ 1634.0 G ($\nu = 9.294$ GHz) with a line width of about 30.0 G. Based on quantum mechanical calculations and other evidence (see below) this signal is assigned to the rotated 1,2-disilyl triplet diradical **2** (Figure 1). In the central region of the spectrum ($\Delta M_S = \pm 1$) a narrow signal (line width 2 G, $g =$ 2.005), which is assigned to a polysilyl radical that is formed as a side product (see the Supporting Information), is observed. The absence of signals of the triplet diradical **2** in the $\Delta M_S = \pm 1$ region is not surprising. It is documented for triplet diradicals that the fine structure lines of the $\Delta M_S = \pm 1$ transitions are broadened in many cases in a non-rigid powder matrix as a result of intramolecular rotational motions and a strong dipole–dipole anisotropy and thus are difficult to detect.[30] In contrast, signals in the half-field region are

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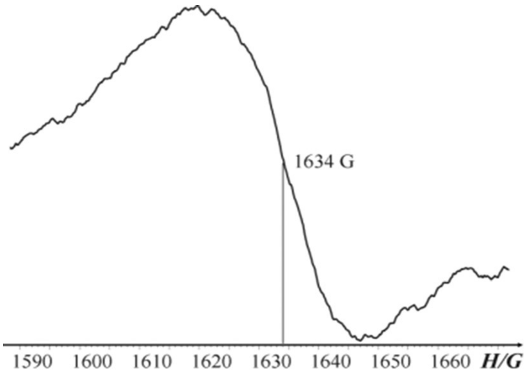


Figure 1. Expanded EPR spectrum at 390 K of **1** in the half-field region ($\Delta M_S = \pm 2$, $H_{min} = 1634.0$ G, $\nu = 9.294$ GHz).

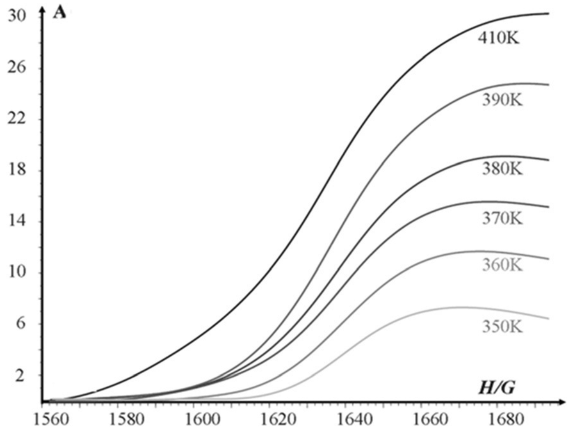


Figure 2. Integration curves of the half-field absorption signal (*A*) of a powder sample of **1** at 350–410 K.

isotropic and are not broadened and thus are easier to detect. The area of the half-field transition signal (A) increases as the temperature is raised from 350 to 410 K (Figure 2), indicating that the triplet diradical is not the ground state and its concentration increases at higher temperatures. Furthermore, the signal intensity is temperature reversible. The half-field signal is not detected at 298 K or when a frozen hexane solution of **1** is irradiated with UV light.

The absorption area of the half-field signal (A) is proportional to the magnetic susceptibility (χ).[30,31] The temperature dependence of χ is given by the Bleaney–Bowers equation [Eq. (2)],[32]

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

where T is the absolute temperature, k (cal mol^{-1} K^{-1}) is the Boltzmann constant and E_{ST} (cal mol^{-1}) is the energy gap separating the singlet and triplet states.[30–32]

Thus, taking $[3+\exp(E_{ST}/k\,T)] \approx \exp(E_{ST}/kT)$, A is proportional to $T^{-1}[\exp(1/T)]^{-1}$. A plot of $\ln(A\,T)$ versus $1/T$ (Figure 3) gives a good linear correlation ($R^2 = 0.96$) with a slope of $-E_{ST}/k$, yielding E_{ST} of 7.3 kcal mol^{-1} separating the singlet and triplet states of disilene **1**.

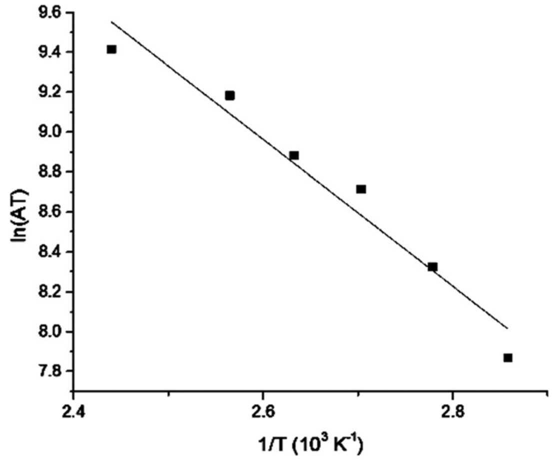


Figure 3. Dependence of the area (*A*) of the half-field transition signal of a powder sample of **1** at 350–410 K.

Is the observed signal at $H_{min} = 1634.0$ G that of the rotated triplet diradical **2**? To answer this question, DFT[33] calculations using the ORCA 2.9 program package[34] were performed. Full details of the computational methods used and the calculations results are given in the Supporting Information.

The geometries of singlet **1** and of triplet **2** were fully optimized using the DFT-UBP86[35]/TZVP,[36] UB3LYP[37]/TZVP and UrevPBE[38]/TZVP levels of theory with D3 dispersion corrections.[39] For UrevPBE and UBP86 numerical frequencies were calculated verifying that **1**, **2** and the minimum energy crossing point (MECP) connecting them are stationary points. The calculated geometries of singlet **1** are in good agreement with the structure of **1** determined by X-ray crystallography (Table 1, the best agreement is obtained at the UB86-D3/TZVP level).[29] Singlet disilene **1** has a strongly twisted double bond with Si–Si=Si–Si dihedral angles of 48.8°(exp.) 44.4°(calc.) and 62.9°(exp.) 67.0°(calc.). r(Si = Si)

Table 1: Experimental and calculated (UBP86-D3/TZVP) geometries of **1**, **2** and the MECP for the **1**⇌**2** equilibrium. Atom numbering is given in Equation (1).

Parameter[a]	**1**, X-ray	Singlet **1**	Triplet **2**	MECP
r(1-2)	2.260	2.252	2.382	2.370
r(1-3)	2.413	2.414	2.412	2.410
r(1-5)	2.423	2.418	2.422	2.420
r(2-4)	2.417	2.414	2.411	2.408
r(2-6)	2.419	2.417	2.422	2.419
α(3-1-5)	118.2	118.2	122.2	121.6
α(3-1-2)	124.2	122.6	119.4	119.7
α(5-1-2)	117.2	118.2	117.1	117.4
α(4-2-6)	118.4	118.3	122.3	121.6
α(4-2-1)	124.7	122.6	119.3	119.7
α(6-2-1)	116.7	118.2	117.0	117.3
$\Sigma\alpha$(Si1)	359.6	359.0	358.7	358.7
$\Sigma\alpha$(Si2)	359.8	359.1	358.6	358.6
θ(3-1-2-4)	62.9	67.0	88.2	84.9
θ(5-1-2-6)	48.8	44.4	62.1	58.7
θ(3-1-2-6)	123.5	124.3	104.8	108.3
θ(5-1-2-4)	124.9	124.4	104.9	108.3

[a] r in Å, α and θ in degrees.

in **1** of 2.260 Å (exp.) 2.252 Å (calc.) is somewhat longer than regular Si=Si double bonds (2.15–2.25 Å[20–24]), but it has a significant π-bond character (Wiberg Bond Index (WBI) = 1.75).

The rotated triplet diradical **2** has a highly twisted Si=Si bond with an average Si–Si–Si–Si dihedral angle of 75.2°. The central Si–Si bond distance of 2.382 Å (WBI = 1.03) is significantly longer than in **1**, and Si1 and Si2 are nearly planar (Σα(Si1,Si2) = 358.7°, 358.6°). The spin density resides almost entirely in the two nearly orthogonal 3p orbitals of the central Si atoms.

As mentioned above, the fine EPR structure of diradical **2** could not be observed. Therefore, the zero-field splitting (ZFS) parameters, *D* and *E*, that describe the interactions of the triplet energy levels in the absence of an applied magnetic field, could not be measured directly. However, *D* and *E* are related to the position of the half-field signal ($H_{\min}$) according to Equation (3),[30]

$$H_{\min} = (2g_0\beta_0)^{-1}\{(h\nu)^2 - 4[(D^2/3) + E^2]\}^{1/2} \tag{3}$$

where *h* is the Planck constant, *ν* is the instrument frequency, β_0 is the Bohr magneton, and g_0 is the g-factor. We use $g_0 = 2.005$, which is typical for silyl radicals.[40]

Using ORCA,[34] *D* and *E* of **2** were calculated at the ROB3LYP/TZVP and ROBP/TZVP levels. These methods were previously demonstrated to give good agreement between experimentally measured *D* values and the calculated contribution of the *D* tensor arising from spin–spin coupling for various organic radicals.[41] The calculated ZFS parameters and the corresponding half-field transition [Eq. (3)] for **2** are given in Table 2.

Table 2: Calculated ZFS parameters and $H_{\min}$ of **2**.

Optimization level of **2**	ROB3LYP/TZVP	ROBP/TZVP
UBP86-D3/TZVP	$\lvert D\rvert = 0.0454$ cm^{-1} $\lvert E\rvert = 0.0009$ cm^{-1} $\boldsymbol{H_{\min} = 1632.1}$ **G**	$\lvert D\rvert = 0.0409$ cm^{-1} $\lvert E\rvert = 0.0008$ cm^{-1} $\boldsymbol{H_{\min} = 1636.6}$ **G**
UB3LYP-D3/TZVP	$\lvert D\rvert = 0.0454$ cm^{-1} $\lvert E\rvert = 0.0008$ cm^{-1} $\boldsymbol{H_{\min} = 1632.0}$ **G**	$\lvert D\rvert = 0.0411$ cm^{-1} $\lvert E\rvert = 0.0008$ cm^{-1} $\boldsymbol{H_{\min} = 1636.4}$ **G**
UrevPBE-D3/TZVP	$\lvert D\rvert = 0.0452$ cm^{-1} $\lvert E\rvert = 0.0009$ cm^{-1} $\boldsymbol{H_{\min} = 1632.3}$ **G**	$\lvert D\rvert = 0.0409$ cm^{-1} $\lvert E\rvert = 0.0008$ cm^{-1} $\boldsymbol{H_{\min} = 1636.6}$ **G**

The calculated $H_{\min}$ at both levels of theory (Table 2) are in excellent agreement with the experimentally determined value of 1634.0 G. Thus, the calculations fully support the conclusion that the observed EPR signal at $H_{\min} = 1634.0$ G belongs to triplet diradical **2**. This is the first spectroscopic observation of a triplet diradical resulting from thermal rotation around an *E*=*E* double bond, where *E* = C or Si.

A comparison of the ZFS parameters of **2** (Table 2) with other vicinal 1,2-diradicals is not available. In triplet carbenes, where the two unpaired electrons reside on the same atom, the experimental |*D*| values are in the range of 0.32–0.54 cm^{-1}.[42] Smaller |*D*| values are observed when the two unpaired electrons are further apart, for example in *m*-bis((tBu$_2$MeSi)$_2$Si$^•$)benzene diradical |*D*| = 0.013 cm^{-1},[43] in aggregated silyllithium (R$_2$Si$^•$)$_2$Li$_2$ diradical |*D*| = 0.016 cm^{-1},[44] and in some other diradicals |*D*| values are as low as 0.0035 cm^{-1}.[45] The magnitude of *D* in **2** can be expected to resemble that of 1,3-cylcopentane diradical in which the distance between the radical centers is 2.355 Å (at UBP86/TZVP level) compared with 2.382 Å in **2**. However, **2** exhibits a significantly lower *D* value of 0.041-0.045 cm^{-1} compared to 0.084 cm^{-1} in 1,3-cylcopentane diradical.[46] The lower *D* value in **2** is due to the fact that unlike in cyclic-1,3-diradicals where the two spins are nearly parallel, in **2** the spins are almost perpendicular, which diminishes the spin–spin interaction and hence lowers *D*. The resulting *D* of ~0.045 cm^{-1} is similar to that of 1,3-diphenylcyclopentane (*D* = 0.047 cm^{-1}),[46] in which the relatively low *D* is due to spin delocalization to the phenyl rings.

The calculated energy gap (E_{ST}) between singlet **1** and triplet diradical **2** is 7.0, 5.1, and 6.0 kcal mol^{-1} at UBP86-D3/TZVP, UB3LYP-D3/TZVP, and UrevPBE-D3/TZVP, respectively, in good agreement with the experimentally derived E_{ST} value of 7.3 kcal mol^{-1} (Figure 3). The calculated potential energy diagram for the **1**→**2** transformation showing also the main geometrical parameters is presented in Figure 4. The calculated geometry of the MECP is intermediate between that of **1** and **2** with an average Si–Si–Si–Si dihedral angle of 71.8° compared with 55.7° in **1** and 75.2° in **2**; the central Si–Si distance is 2.370 Å compared with 2.252 Å in **1** and 2.382 Å in **2**; the central Si atoms are essentially planar (Σα(Si1,Si2) = 358.7°, 358.6°). The energy difference between **1** and the MECP is 7.2, 6.0, and 6.5 kcal mol^{-1} at the UBP86-D3/TZVP, UB3LYP-D3/TZVP and UrevPBE-D3/TZVP levels, respectively.

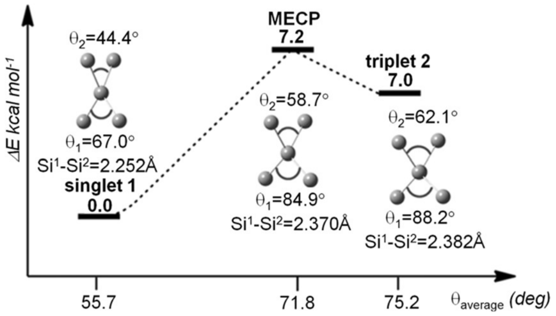
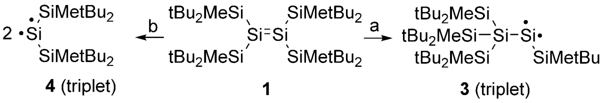


Figure 4. Calculated (UBP86-D3/TZVP) potential-energy surface for rotation around the Si=Si double bond of **1**. The structures show Newman projections along the central Si–Si bond (only Si atoms are shown).

Additional calculations were performed in order to examine the possibility, suggested by a referee, that the observed $\Delta M_S = \pm 2$ signal belongs to the triplet silylene **3** formed by 1,2-migration of a tBu$_2$MeSi group [Eq. (4) route a]



(4)

or to the triplet silylene **4** formed by Si=Si bond dissociation [Eq. (4) route b].

ZFS parameters of **3** and **4** were calculated at the UBP/TZVP//UBP86-D3/TZVP level of theory yielding $|D| = 0.6449\,\mathrm{cm}^{-1}$ and $|D| = 0.7443\,\mathrm{cm}^{-1}$ respectively (see the Supporting Information). These values are dramatically larger than that of **2** ($|D| \approx 0.04\,\mathrm{cm}^{-1}$). Moreover, the reactions that transform **1** to **3** or **4** are endothermic by $21.0\,\mathrm{kcal\,mol}^{-1}$ and $72.7\,\mathrm{kcal\,mol}^{-1}$, respectively, (at UBP86-D3/TZVP), values which are not compatible with the experimentally observed $E_{\mathrm{ST}} = 7.3\,\mathrm{kcal\,mol}^{-1}$. Thus, the calculated ZFS parameters and the calculated reaction energies rule out the possibility that the observed $\Delta M_S = \pm 2$ signal belongs to triplet silylenes **3** or **4**.

In conclusion, combination of temperature-dependent EPR spectroscopy and detailed quantum mechanical calculations indicate that the perpendicularly rotated triplet diradical state **2** of disilene **1**, can be accessed by thermal intramolecular rotation around the Si=Si π-bond. This is the first spectroscopic observation of a triplet diradical resulting from thermal rotation around an *E*=*E* double bond, *E* = C or Si. The highly twisted ground-state geometry of singlet **1** allows access to the perpendicular triplet diradical **2** at moderate temperatures of 350–410 K. The DFT calculated ZFS parameters of **2** accurately reproduce the experimentally observed H_{min}. The very low energy gap separating singlet **1** and triplet **2** of only $7.3\,\mathrm{kcal\,mol}^{-1}$ suggests that at temperatures above 350 K **1** should show significant diradical character and reactivity. Studies along this line are planned.

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Keywords: density functional calculations · diradicals · disilenes · EPR spectroscopy · zero-field splitting parameters

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