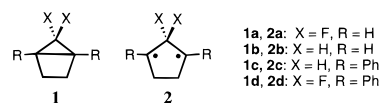


Transient Spectroscopy of a Derivative of 2,2-Difluoro-1,3-diphenylcyclopentane-1,3-diyl—A Persistent Localized Singlet 1,3-Diradical



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Substantial theoretical and experimental efforts have been made to understand the behavior of diradicals.¹ Triplet 1,3-diradicals persist on the nanosecond time scale at room temperature,² but localized singlet 1,3-diradicals typically have lifetimes of less than 1 ps.³ The preparation of a persistent, localized singlet 1,3-diradical remains a challenge.

To achieve this goal, the singlet diradical must be protected by a barrier inhibiting ring closure, and the singlet should preferably be the ground state. Electronic effects can be manipulated to achieve the desired ordering of the lowest singlet and triplet states, and electronic, steric, and strain effects all can be utilized to provide kinetic stability toward ring closure for the singlet. The goal of generating a persistent, singlet, 1,3-diradical has been attained through the use of 2,2-difluoro and 1,3-diphenyl substituents to stabilize singlet cyclopentane-1,3-diyl.

Geminal fluorine substitution profoundly affects the reactivity of a cyclopropane ring.^{4–7} For example, ab initio calculations find that the geminal fluorines in 2,2-difluorobicyclo[2.1.0]pentane (**1a**) reduce the strength of the distal cyclopropane bond by 13.5 kcal/mol from that in the hydrocarbon (**1b**).⁷ Moreover, although cyclopentane-1,3-diyl (**2b**) is known to have a triplet ground state,⁸ the geminal fluorines in 2,2-difluorocyclopentane-1,3-diyl (**2a**) are predicted to cause the lowest singlet state to fall below the triplet by 9.7 kcal/mol.⁷ Unfortunately, the direct observation of singlet diradical **2a** is expected to be extremely difficult, because the calculations predict **2a** to be the transition state for ring inversion of **1a**.

Phenyl substituents at the bridgehead carbons of **1a** should further decrease the energy difference between **1a** and **2a**. For example, the bridgehead phenyls in **1c** stabilize the radical centers in **2c** by ca. 12.5 kcal/mol each, relative to those in **2b**, and thus reduce the barrier to ring inversion in **1c** to only 12 kcal/mol.^{9a} Although diradical **2c** possesses a triplet ground state,^{9b} the existence of a short-lived ($\tau \approx 20$ ps) singlet diradical was indicated by competitive O₂-trapping kinetics, and a free energy barrier to closure of 2–3 kcal/mol was estimated.^{9c,d} If the effects of the 1,3-diphenyl and 2,2-difluoro substituents in **1d** were additive, **2d** should be a singlet diradical that is stable toward ring closure.⁷

Starting from 2,2-difluoro-1,3-diphenylpropane-1,3-dione,¹⁰ we have used the Hünig route¹¹ to prepare azoalkane **3** as a precursor of 3,3-difluoro-2,4-diphenylbicyclo[3.3.0]octane-2,4-diyl (**4**). We now report that singlet diradical **4** is spectroscopically observable and gives rise to both housane **5** and allylic cation **6**. Which reaction pathway is favored depends on the solvent polarity (Scheme 1).

Unlike the related 2,2-dimethyl-substituted azoalkanes, which afford the corresponding housanes on irradiation,¹² the preparative photolysis of azoalkane **3** in benzene, *n*-pentane, methylene chloride, or acetonitrile at ambient temperature led to cyclopentene **7**. However, at low temperatures in a 1:3 mixture of *n*-pentane and isopentane, signals for not only **7** but also housane **5** were observed by ¹⁹F (565 MHz) NMR spectroscopy.¹³ On allowing the pentane solution of **5** to warm to room temperature, these ¹⁹F resonances disappeared, and only those of **7** remained.

Pump–probe spectroscopy revealed a strong transient absorption in the visible, $\lambda_{\text{max}} = 530$ nm (Figure 1a). It appeared with a growth time constant of $\tau = 8 \pm 1$ ps after excitation of **3** with a subpicosecond pulse at 248 nm in either cyclohexane or acetonitrile. This fast growth is attributed to the formation of the diradical **4** from the n, π^* -excited singlet state of azoalkane **3** by nitrogen extrusion. The same transient was observed by excitation of **3** with a 25-ns excimer laser pulse at 248 or 351 nm, and its lifetime was 80 ± 3 ns in both degassed and oxygen-saturated *n*-pentane. An absorbance coefficient $\epsilon_{530} \approx 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was estimated, using triplet benzophenone as the actinometry standard and assuming quantitative formation of **4**.

Arrhenius parameters, $E_a = 7.8 \pm 0.5$ kcal/mol and $\log(A/s^{-1}) = 12.8 \pm 0.4$, were determined from the rate constants for disappearance of the transient absorption in the temperature range of 257–313 K in cyclohexane (18 measurements). The high activation energy for the disappearance of diradical **4** provided the opportunity to study **4** in frozen EPA (2:5:5 ethanol:*n*-pentane: ether) and 2-methyltetrahydrofuran (MTHF) solutions at low

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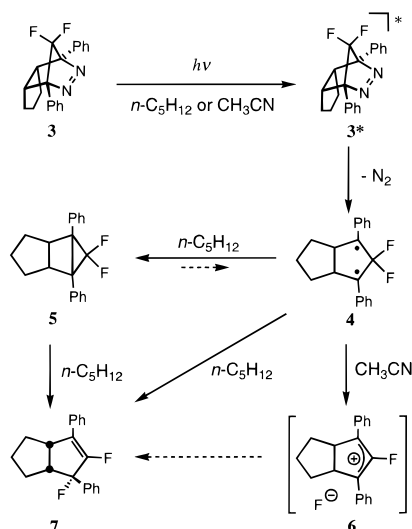
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(13) At 135 K the ¹⁹F resonances for **7** appeared at $\delta = -131$ (dd, $J = 29$ and 7 Hz, 1F) and -156 ppm (dt, $J = 29$ and 11 Hz, 1F), those for **5** appeared at $\delta = -119$ and -126 ppm, with $J_{\text{FF}} = 218$ Hz. The geminal fluorine coupling constant J_{FF} in **5** is unusually large in magnitude for a *gem*-difluorocyclopropane, but a large value ($J_{\text{FF}} = -202$ Hz) is also seen in the *gem*-difluorohousane derivative with bridgehead methyl, instead of phenyl groups.

Scheme 1^a

^a The actual pathway for the formation of **7** from **5** is postulated to involve ring opening of **5** to **4**, and allylic cation **6** is presumably the precursor of **7** in both polar and nonpolar solvents. These proposed reaction pathways are indicated by dashed arrows.

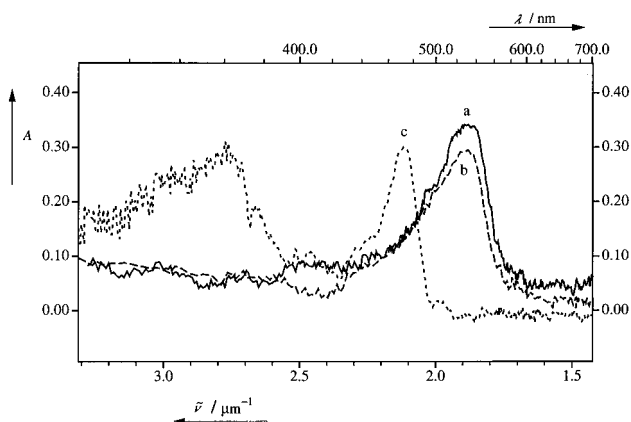


Figure 1. (a) Transient spectrum of diradical **4** in degassed *n*-hexane solution at 10 ps delay (—). (b) UV spectrum of **4** in an EPA glass at 77 K (---). (c) Transient spectrum of allylic cation **4** in acetonitrile at 50 ns delay (· · ·).

temperatures. The UV absorption spectrum of the frozen glasses (Figure 1b) matched well that of the transient species (Figure 1a), observed by flash photolysis.

The identification of the transient intermediate as singlet diradical **4** rests on the following observations: (1) The lifetime of the transient is insensitive to oxygen, $k_{O_2} < 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Triplet cyclopentane-1,3-diylium react with oxygen with rate constants on the order of $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,^{14a} whereas, singlet diradicals react with oxygen orders of magnitude more slowly.^{14b} (2) The Arrhenius parameters are reasonable for the spin-allowed ring closure to afford housane **5**, whereas $\log(A/\text{s}^{-1})$ values in the range of 6–9 are common for the spin-forbidden reactions of related triplet diradicals.^{9d} (3) No EPR signal was detected from frozen solutions that were intensely colored by the red species **4**. The lifetime of transient **4** was about a day at 77 K, indicating that the singlet state is the ground state of **4**.¹⁵

The high intensity and long wavelength of the transition at 530 nm are remarkable. The first intense absorption band of related

triplet diradicals lies at ca. 340 nm. It is possible that the strong 530-nm band in **4** arises from CF_2 -induced mixing of the weak, parity-forbidden transitions near 460 nm in benzyl radicals with the allowed transitions at higher energies.¹⁷ This mixing should shift the parity-forbidden transitions to lower energies and increase their intensities. To test this proposal, we have generated the ketyl radical of α,α,α -trifluoroacetophenone by hydrogen abstraction from 1-phenyl-2,2,2-trifluoroethanol. The fluorinated radical shows a strong absorption band in the visible, $\lambda_{\text{max}} = 520 \text{ nm}$, whereas the first strong absorption band of the parent ketyl radical lies at $\lambda_{\text{max}} = 370 \text{ nm}$.¹⁸ Thus, trifluoro substitution at the α -position does, indeed, induce a 150-nm red shift of the first strong absorption in this model system.

In the conventional kinetic flash photolysis of **3** in cyclohexane solution at room temperature, the slow, first-order growth of an absorbance at 250 nm with a time constant $\tau = 225 \pm 20 \mu\text{s}$ was observed. If this absorbance is attributed to **7**, then an intermediate other than **4** must be involved in the formation of **7**, because diradical **4** disappears 3000 times faster than **7** appears. It seems highly likely that this intermediate is **5**; but since housane **5** hardly absorbs in the near-UV region, its formation cannot be monitored directly by flash photolysis. Nevertheless, the low-temperature ¹⁹F NMR data presented above provide strong evidence for the intermediacy of **5**.¹⁹

In acetonitrile, singlet diradical **4** behaved quite differently than in the hydrocarbon solvents. The 530-nm transient decay had a lifetime of 6 ns and was accompanied by the growth of a transient absorption with $\lambda_{\text{max}} = 470 \text{ nm}$ (Figure 1c), which we assign to allylic cation **6**.²⁰ This assignment was confirmed by the finding that nucleophilic trapping of **6** by azide is essentially diffusion-controlled, $k_{\text{N}_3^-} = (1.7 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. In the absence of azide, the decay of **6** followed clean second-order kinetics and, with a half-life of 135 μs , led to **7**. Formation of **7** in hydrocarbon solvents presumably proceeds via an ion pair ($\text{6}^+\text{F}^-$) that is too short-lived to be detected. The reaction sequences that are proposed to occur in polar and nonpolar solvents are summarized in Scheme 1.

In conclusion, localized singlet 1,3-diradical **4** is generated by irradiation of azoalkane **3**. In contrast to other cyclopentane-1,3-diylium, the 2,2-difluoro-substituted diradical **4** has a singlet ground state. It is, nevertheless, remarkably persistent due to a substantial barrier inhibiting its closure to housane **5**.²¹

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(19) If, as seems likely, **4** is an intermediate in the rearrangement of **5** to **7**, the steady-state approximation may be used for [4] during the relatively slow decay of **5** to **7**. This yields $k_{(5 \rightarrow 7)} = k_{(5 \rightarrow 4)}k_{(4 \rightarrow 7)}/(k_{(4 \rightarrow 5)} + k_{(4 \rightarrow 7)}) = 1/(225 \mu\text{s})$. From this equation, combined with $k_{(4 \rightarrow 5)} + k_{(4 \rightarrow 7)} = 1/(80 \text{ ns})$, the following expression for the equilibrium constant $K = [4]/[5]$ can be derived: $K = k_{(5 \rightarrow 4)}/k_{(4 \rightarrow 5)} = (80 \times 10^{-3}/225)(1 + R)^2/R$, where $R = k_{(4 \rightarrow 5)}/k_{(4 \rightarrow 7)}$ is the ratio that defines how diradical **4** partitions between **5** and **7**. Experimentally, $R \approx 1$, which gives $K \approx 10^{-3}$; but K is not very sensitive to R , and $R = 10$ and 0.1 both give $K = 4 \times 10^{-3}$. Perhaps fortuitously, the CASPT2N/6-31G* energy difference of 3.2 kcal/mol that is computed between the divinyl analogues of **1d** and **2d** is in excellent agreement with the value of $\Delta G = 4 \text{ kcal/mol}$ between **4** and **5** that corresponds to $K \approx 10^{-3}$ at room temperature.

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(15) The existence of a lower lying, but kinetically inaccessible triplet state is unlikely, because the conformational flexibility, to which very slow intersystem crossing in another diradical has been attributed,¹⁶ is not present in **4**.