Registry No. II, 92187-27-4; III, 4444-26-2; IV, 92187-32-1; V, 92187-33-2; HOC$^+$, 92187-28-5; HOC^{2+}, 92187-29-6; HOC^{3+}, 92187-30-9; HOC^{4+}, 92187-31-0; 2,4,6-trinitro-1,3,5-benzenetriamine, 3058-38-6.

Lifetime of a Conformationally Constrained Norrish II Biradical. Photochemistry of *cis*-1-Benzoyl-2-benzhydrylcyclohexane

Richard A. Caldwell,* S. N. Dhawan, and T. Majima

Department of Chemistry
The University of Texas at Dallas
Richardson, Texas 75080

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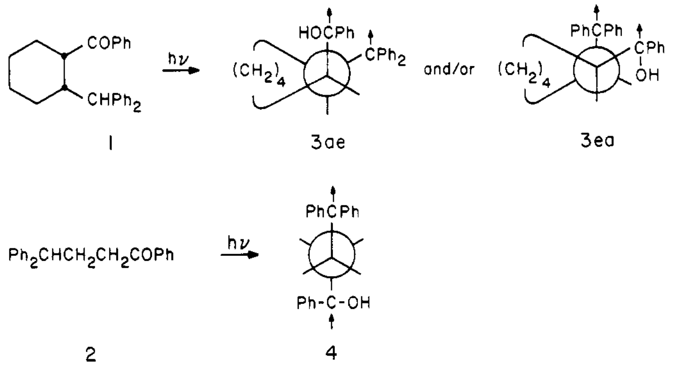
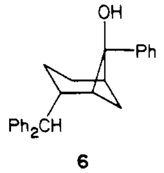
Interminal distance and orbital orientation have been suggested[1] as potentially significant factors in determining intersystem crossing rates and thus lifetimes of triplet biradicals. Scaiano[2] has suggested that a conformational dependence of intersystem crossing rate (gauche faster than trans) and a solvent-dependent conformational distribution will account for the increase of Norrish II biradical lifetimes in hydrogen-bond-accepting solvents and that the strikingly short lifetime of a Norrish II biradical with termini constrained cis on a cyclopropyl ring also may be a result of proximity of the termini. We also previously made a similar interpretation.[3] We now have prepared *cis*-1-benzoyl-2-benzhydrylcyclohexane (**1**) and compared its photochemistry and transient spectroscopy to that of γ,γ-diphenylbutyrophenone (**2**). Even though **1** affords a gauche-locked biradical **3** and **2** affords an anti-biased biradical **4**, the lifetimes (i.e., isc rates) are quite similar; in methanol, the lifetime of **3** is even longer than that of **4**. Our evidence thus suggests that the role of conformation in determining lifetimes of 1,4 biradicals may be small.



Photolysis of **1**,[4,5] mp 121–122 °C (250 mg in 50 mL of hexane, Pyrex, 450-W medium-pressure mercury lamp, 75 min), and column chromtography afforded sequentially 8 mg (3.2%) of 2-benzydryl-6-*exo*-phenylbicyclo[3.1.1]heptan-6-ol (**6**),[5] mp 215–216 °C, 15 mg (6%) of recovered **1**, and 190 mg (76%) of *cis*-7,8,8-triphenylbicyclo[4.2.0]octan-7-*endo*-ol (**7**),[5] mp 139–140 °C. Further elution afforded ca. 15 mg (6%) of polymeric material. Irradiation in methanol was incomplete in 4.5 h. In this case, elution of **6** (12 mg, 4.8%), **1** (85 mg, 34%), and **7** (90 mg, 36%) was preceded by a mixture of dienes (ca. 50 mg, 30%) with spectral properties expected for secondary photolysis products of the acyclic photofragmentation products from **1**. Quantum yields for **7** were 0.26 in hexane–benzene (4:1) and 0.12 in methanol.



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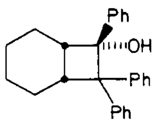

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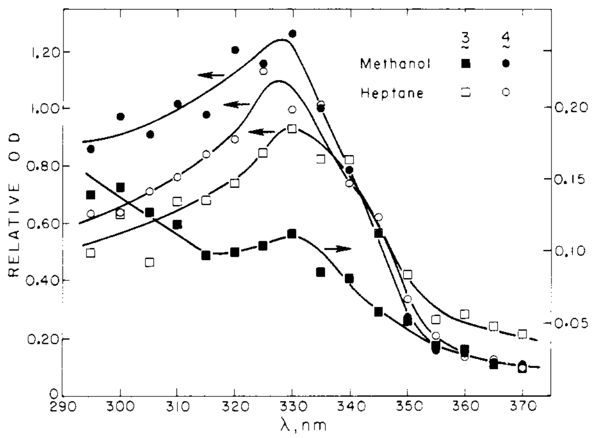

Figure 1. Transient spectra extrapolated from ca. 0.4–1 half-life back to the laser peak. OD (266 nm) = 2.06–2.14 cm^{-1}. Spectra were further normalized to the same laser dose. Note OD scale change for **3** in methanol.

In contrast, the photolysis of **2** (250 mg) afforded only the fragmentation products 1,1-diphenylethylene (120 mg, 80%) and acetophenone (80 mg, 80%) in hexane (Pyrex). Protracted elution afforded no further material; we believe that as much as 5% of a cyclobutanol would have been detected. Quantum yields for $Ph_2C{=}CH_2$ and $PhCOCH_3$ were identical and were 0.32 in hexane–benzene and 1.03 in methanol.

Transient spectroscopy was studied with a Q-switched Nd-YAG laser (266- nm fourth harmonic, 5–20 mJ/pulse, fwhm 10 ns). The transient spectra (Figure 1) are similar for **1** in heptane and **2** in both heptane and methanol. For **1** in methanol, the spectrum is much weaker and contains relatively much stronger end absorption (λ_{max} <300); however, the expected[3,6] λ_{max} 325–330 for the benzhydryl terminus is present as in the other spectra.

For **2**, assignment of the spectrum to biradical **4** from the products of photolysis is unambiguous. For **1** in heptane, assignment to biradical **3** is strongly indicated by the λ_{max} and by the high yield and quantum yield of **7**. For **1** in methanol, the altered spectral shape may reflect the intervention of an increased amount of ring hydrogen abstraction, leading to a valerophenone-like biradical absorbing at shorter wavelength.[3] The decreased intensity could be rationalized by a decreased quantum yield of biradical **3** due to the partitioning between the several H-abstraction pathways, quenching of the ketone excited states by a remote phenyl,[7] or both. In any case, the substantial yield of **7** affords confidence that lifetime measurements at an appropriate wavelength ($\lambda \geq 330$ nm) at which absorption of ring hydrogen abstraction derived biradicals is minimal[8] will give the lifetime of **3** in methanol.

Biradical lifetimes at 330 nm (nanoseconds, $\pm 2\sigma$) were, in methanol, 242 ± 14 (**3**) and 166 ± 3 (**4**) and, in heptane, 69 ± 5 (**3**) and 84 (**4**). The lifetimes for **3** are necessarily those for

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(4) Reaction of cyclohexene (3 days, 110 °C) with diphenylketene afforded *cis*-8,8-diphenylbicyclo[4.2.0]octan-7-one, cleavage of which in refluxing ethylene glycol with KOH afforded 2-benzhydrylcyclohexanecarboxylic acid, mp 151–152 °C. The acid with PhLi at −77 °C in dry ether afforded **1**. The trans isomer **5**,[5] mp 154–155 °C, of **1** could be obtained by equilibration (1:5 = 67.5:32.5) in 5% methanolic KOH.

(5) The proposed structure is suported by NMR and IR spectra, chromatographic homogeneity, and elemental analysis.

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(8) In both heptane and methanol the lifetime observed for biradical **3** is some 15% shorter at 290 nm than at 340 nm, consistent with qualitative expectation based on the shorter lifetime[3,9] of the valerophenone-derived biradical. The lifetime of **4** is independent (±2%) of wavelength in this range.

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a gauche-locked conformation, though a mixture of ae and ea conformers is likely. For **4**, the absence of cyclobutanol products and the high fragmentation yield are both consistent with dominance of the anti conformation expected on simple steric grounds. The lifetime of the gauche **3** is thus actually somewhat longer than that of the anti **4** in methanol and only very slightly shorter than that of **4** in heptane.[10]

It thus appears that shortening of lifetime in a gauche conformation is not realized in this system. The expectation of such was derived from the dependence of spin-orbit coupling terms on through-space distance.[1] We have previously[6] pointed out the gross similarity of lifetime for biradicals with zero, two, and four carbons between the termini. The present experiment reinforces the lack of dependence of lifetime on through-space interminal distance and further suggests that the hypothesis that τ(gauche) << τ(anti) for biradicals[2,3] at the very least lacks generality.

Acknowledgment. This work was supported by NSF Grants CHE 7915228 and 8213637 and by the Robert A. Welch Foundation (Grant AT-532). Flash kinetic work was done at the Center for Fast Kinetics Research at the University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas. The assistance of Dr. Steven Atherton is gratefully acknowledged. S.N.D. thanks Kurukshetra University (India) for granting study leave.

Registry No. 1, 92126-53-9; **2**, 6264-81-9; **3**, 92143-40-3; **4**, 80326-03-0; **6**, 92126-54-0; **7**, 92126-55-1; hydrogen, 1333-74-0.

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(10) Somewhat longer lifetimes for **4** were reported in ref 3. Reexamination of the earlier data suggests that a cable ring caused some distortion of the temporal profile; when allowance is made for this, the earlier data are quite consistent with the present parameters. No qualitative conclusions of ref 3 need be altered thereby. Live and learn.

Rearrangement of $(C_5H_5)_2TiS_5$ Involving Migration of the Organic Fragment from Metal to Sulfur

Dean M. Giolando and Thomas B. Rauchfuss*[1]

School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801

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We report the discovery of a second structural isomer of Cp_2TiS_5 ($Cp = \eta^5\text{-}C_5H_5$) (**1**) the most heavily studied polysulfido chelate complex.[1] The structure of $\beta\text{-}C_{10}H_{10}S_5Ti$ spectacularly illustrates new bonding modes for organosulfur ligands and provides fresh insights into the pathways by which organic substrates add to sulfido ligands.

$\beta\text{-}C_{10}H_{10}S_5Ti$ (**2**) forms in 40% yield when solutions of **1** in rigorously dried and deoxygenated xylenes are heated at reflux for 24 h.[2] Compound **2** was separated from other soluble products by careful chromatography on 4% cross-linked polystyrene gel[3] and was easily obtained in analytically pure, crystalline form by hexane precipitation from dichloromethane solutions. The red color of **2** is deceptively similar to that of **1**. The ^1H NMR spectrum of **2** revealed the presence of one intact Cp group while the remaining resonances (5 H) were broad and complex, even at 360 MHz. Its ^{13}C NMR spectrum consisted of six resonances, two of which remain weak even with broad-band ^1H decoupling. Thermolysis of $(MeCp)_2TiS_5$ gave a complex mixture of products for reasons that became clear subsequent to the X-ray diffraction study on **2**.

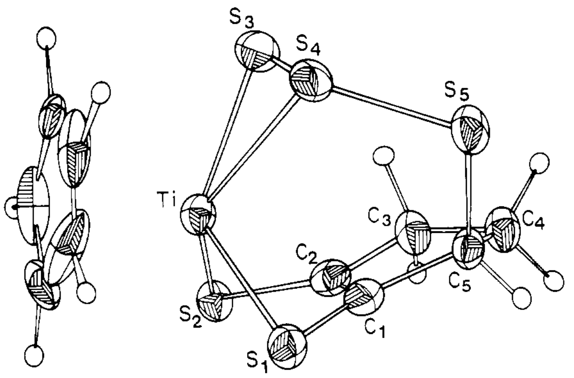

Figure 1. ORTEP plot of **2** with thermal ellipsoids drawn at 35% probability level.

Table I. Selected Bond Distances (Å) and Angles (deg) for One of the Two Molecules of **2** in the Asymmetric Unit[a]

Ti–S(1)	2.355 (3)	S(2)–C(2)	1.745 (9)
Ti–S(2)	2.358 (3)	S(1)–C(1)	1.738 (9)
Ti–S(3)	2.474 (3)	S(5)–C(5)	1.845 (9)
Ti–S(4)	2.537 (3)	S(1)–Ti–S(2)	90.8 (1)
Ti–C(1)	2.421 (8)	S(3)–Ti–S(4)	47.7 (1)
Ti–C(2)	2.483 (8)	Ti–S(3)–S(4)	67.8 (1)
Ti–Cp(av)	2.328	Ti–S(4)–S(5)	111.3 (1)
C(1)–C(2)	1.362 (11)	S(3)–S(4)–S(5)	112.8 (2)
S(3)–S(4)	2.025 (3)	C(5)–S(5)–S(4)	107.1 (3)
S(4)–S(5)	2.061 (3)		

[a] In comparing the two molecules in the asymmetric unit, it was found that no bond lengths differed significantly from the weighted mean values and the largest angular deviation was 0.7°.

The structure[4] of **2** is shown in Figure 1; the two crystallographically independent molecules in the asymmetric unit are quite similar. Chiral **2** consists of a CpTi moiety coordinated to four sulfur atoms of 1,2-dimercapto-3-(mercaptodithio)cyclopentene. The four coordinated sulfur atoms define a plane (±0.02 Å), 0.92 Å above which lies the titanium atom. The dithiolene is coordinated in an unusual manner as the Ti–C(dithiolene) distances are 2.42 and 2.48 Å which may be compared to the 2.32 Å Ti–C(Cp) distances (Table I).[5] As such **2** can be described as an example of an η^4-dithiolene complex. The η^2-attachment of the trisulfido group is unprecedented and the Ti–S(3) and Ti–S(4) distances indicate the absence of significant S to Ti π-bonding, unlike the case for **1**. The first examples of η^1-trisulfides have very recently been reported by Shaver and ourselves.[6,7] In the absence of S to Ti π-donation, **2** assumes a 16e configuration.

The mechanism for the rearrangement of **1** to **2** is undoubtedly complex and is probably related to the facile conversion of Cp_2VS_5 to $Cp_2V_2S_5$.[8,9] The short C···β–S contacts, noted by Dahl and

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(2) Anal. C, H, S, Ti. ^1H NMR (200 MHz, $CDCl_3$) δ 6.42 (S, 5 H), 5.39 (m, 1 H), 3.27 (m, 1 H), 2.99 (7, 1 H), 2.75 (m, 1 H), 2.30 (m, 1 H); FD MS, *m/e* 338 (M^+); ^{13}C NMR (360 MHz, $CDCl_3$) δ 155.7, 142.2, 111.1, 59.4, 34.9, 32.3.

(3) Compound **2** and a number of related titanium sulfides are insufficiently robust to withstand adsorption chromatography on silica gel or alumina. Gel permeation chromatography using the less aggressive Sephadex SH-20 or, in this case, Biobeads X-4 is a more useful separation technique.

(4) A platy crystal (0.02 × 0.22 × 0.50 mm) was obtained by vapor diffusion of hexanes into a $C_2H_4Cl_2$ solution of **2**. Cell data: monoclinic, $P2_1/c$ (C^5_{2h}), $a = 18.60$ (2) Å, $b = 7.508$ (7) Å, $c = 18.66$ (1) Å, $\beta = 92.18$ (7)°, $Z = 8$, μ(Mo K$\bar{\alpha}$) = 13.98 cm^{-1}. 4757 unique intensities from the $\pm h+k+l$ quadrant having $2\theta < 50.0°$ (γ(Mo K$\bar{\alpha}$) = 0.71069 Å) were measured at 25 °C on a Syntex $P2_1$ four-circle diffractometer with graphite monochromator and were numerically corrected for absorption (min/max transmission factors, 0.738/9.792). 2197 reflections had $I > 2.58\ \sigma(I)$ and only these were used. The structure was solved by MULTAN-80 and refined by SHELX-76 to give $R = 0.054$ and $R_w = 0.046$, where non-hydrogen atoms were varied anisotropically, and hydrogens were fixed in calculated positions. The final difference Fourier map was featureless.

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