4 (9.04 g, 69%) and some $[(C_5H_5)Fe(CO)_2]_2$.

Addition of isopropenyliron compound **4** (10 mg, 0.046 mmol) in 2 mL of ether at −23 °C to a stirred solution of HBF_4 (~0.08 mmol) in 2 mL of ether at −23 °C led to the immediate formation of a yellow precipitate identified spectroscopically as dimethylcarbene complex **1**. Solvent was decanted, and the yellow precipitate was washed twice with ether at −23 °C and pumped dry at −23 °C. The dry precipitate was dissolved in CD_2Cl_2 at −23 °C, and the ^1H NMR of the solution was taken at −40 °C. The ^1H NMR consisted of singlets at δ 5.66 (5 H) and 3.73 (6 H), assigned to the cyclopentadienyl and the methyl hydrogens of dimethylcarbene complex **1**. In addition, small resonances due to ether and to propene complex **9** were also seen. Reaction of $(C_5H_5)(CO)_2FeC(OCH_3)(CH_3)_2$ (**3**) with HBF_4 in ether at −23 °C also gave dimethylcarbene complex **1** as a yellow precipitate identified by low-temperature NMR.

Solutions of dimethylcarbene complex **1** decompose at −11 °C in CD_2Cl_2 with a half-life of ~70 min to give $(C_5H_5)(CO)_2Fe(CH_2{=}CHCH_3)^+BF_4^-$ (**9**) nearly quantitatively (101 ± 5% as indicated by NMR).[20,21] In a preparative reaction, **1** prepared by HBF_4 addition to **4** (127 mg, 0.628 mmol) was warmed to room temperature in 0.5 mL of CH_2Cl_2 to give **9** (150 mg, 78%) as a yellow powder.[20]

Further evidence for **1** in solution comes from trapping **1** with $P(OCH_3)_3$. Addition of several equivalents of $P(OCH_3)_3$ to a CD_2Cl_2 solution of **1** at −23 °C led to the immediate disappearance of the ^1H NMR signals assigned to **1** and to the appearance of the new resonances assigned to $(C_5H_5)(CO)_2FeC[P(OCH_3)_3](CH_3)_2^+BF_4^-$ (**10**).[22] In a larger scale reaction, $P(OMe)_3$ (0.17 mL, 1.4 mmol) was added to a suspension of **1** (420 mg, 1.37 mmol) in 5 mL of CH_2Cl_2 at −78 °C. Addition of ether (25 mL) gave yellow, crystalline **10** (470 mg, 70%).[22] The addition of nucleophiles to the carbene carbon atom of metal–carbene complexes is a characteristic reaction of electrophilic carbene complexes.[12,23]

The reaction of dimethylcarbene complex **1** with isobutylene gives a mixture of 1,1,2,2-tetramethylcyclopropane and iron–propene complex **9**. When isobutylene (~0.2 M, 1.5 equiv) was added to a 1.4:1 mixture of dimethylcarbene complex **1**/propene complex **9** in CD_2Cl_2, a reaction occurred at 0 °C to produce 1,1,2,2-tetramethylcyclopropane (δ 0.05 (2 H), 1.02 (12 H); 33% based on **1**). In addition, signals due to propene complex **9** increased, showing that there was a competition between cyclopropanation of isobutylene and thermal decomposition of **1**. In a preparative experiment, **1** prepared by HBF_4 addition to **4** (0.90 g, 4.1 mmol) was stirred with isobutylene (1.3 g, 24 mmol) in 10 mL of CH_2Cl_2 while the solution was warmed from −40 to 2 °C over 50 min. 1,1,2,2-Tetramethylcyclopropane (20% yield) was isolated by preparative gas chromatography (UCON-5/HB-280X, 60 °C) and identified by spectral and chromatographic comparison with an authentic sample.[24] Similarly, **1** prepared by HBF_4 addition to **4** (140 mg, 0.64 mmol) reacted with styrene (8 mmol) in 1.5 mL of CH_2Cl_2 upon warming from −65 to 20 °C to give 1,1-dimethyl-2-phenylcyclopropane (45% GC yield).[25] It should be noted that isobutylene and styrene were among the most reactive alkenes in cyclopropanation by $(CO)_5W{=}CHC_6H_5$[4] and that **1** gives only modest yields of cyclopropanes even with concentrated solutions of these reactive alkenes. In the case of the less reactive 1-octene, no cylcopropanation was observed upon treatment with **1**.

We next set out to prepare $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}C(CH_3)_2^+BF_4^-$ (**2**) with the expectation that the electron-donating triphenylphosphine ligand would increase the stability of the dimethylcarbene complex and allow its isolation at room temperature. Photolysis of **8** (1.5 g, 6.1 mmol) and $P(C_6H_5)_3$ (1.6 g, 6.1 mmol) in hexane–benzene produced $(C_5H_5)(CO)[(C_6H_5)_3P]FeC(CH_3){=}CH_2$ (**11**) (1.39 g, 51% yield).[26] Protonation of **11** (0.55 g, 1.2 mmol) with HBF_4 (4.0 mmol) in diethyl ether at 0 °C led to the precipitation and isolation of $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}C(CH_3)_2^+BF_4^-$ (**2**) (0.61 g, 93%) as a yellow crystalline solid.[27] **2** is stable as a solid at room temperature and decomposes upon heating in CD_2Cl_2 with a half-life of ~30 min at 88 °C.[28] The ^1H NMR (270 MHz) of **2** consists of a singlet at δ 3.13 for the equivalent methyl groups of the dimethylcarbene ligand, a singlet at δ 5.13 for the C_5H_5 unit, and a multiplet at δ 7.5 for the protons of the $P(C_6H_5)_3$ ligand. The single CO ligand of **2** gives rise to an intense band at 1993 cm^{-1} in the IR spectrum (CH_2Cl_2).

Acknowledgment. Research support from the National Science Foundation is gratefully acknowledged.

Registry No. 1, 81939-62-0; **2**, 81939-64-2; **3**, 81939-65-3; **4**, 38960-10-0; **5**, 81939-66-4; **6**, 81939-67-5; **7**, 12108-22-4; **8**, 81939-68-6; **9**, 37668-14-7; **10**, 81939-70-0; **11**, 70569-00-5; 1,1,2,2-tetramethylcyclopropane, 4127-47-3; 1,1-dimethyl-2-phenylcyclopropane, 36825-29-3; isobutylene, 115-11-7; styrene, 100-42-5; $Na^+[(C_5H_5)Fe(CO)_2]^-$, 12152-20-4.

---

(20) **9**: ^1H NMR (acetone-d_6) δ 5.75 (s, 5 H), 5.3 (m, 1 H), 4.01 (d, J = 8 Hz, 1 H), 3.59 (d, J = 14 Hz, 1 H), 1,85 (d, J = 6 Hz, 3 H). **9** has previously been reported: Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *88*, 101.

(21) When solid **1** was warmed to room temperature for 15 min, low-temperature ^1H NMR indicated that decomposition to a 1:1 mixture of **1**/**9** had occurred.

(22) **10**: ^1H NMR (CD_2Cl_2) δ 4.98 (s, 5 H), 3.15 (d, J_{P-H} = 10 Hz, 9 H), 1.45 (d, J_{P-H} = 22 Hz, 6 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 214.9, 86.3, 58.7 (J_{C-P} = 10 Hz), 30.0, 21.8 (J_{C-P} = 100 Hz); IR (CH_2Cl_2) 2023, 1984 cm^{-1}.

(23) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262.

(24) An authentic sample of 1,1,2,2-tetramethylcyclopropane was prepared by addition of ICH_2ZnI to $(CH_3)_2C{=}C(CH_3)_2$: Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057. Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

(25) 1,1-Dimethyl-2-phenylcyclopropane was isolated by preparative gas chromatography (20% SE-30, 135 °C) and identified by spectral and chromatographic comparison with an authentic sample[4] prepared by reaction of 1-phenyl-3-methylbut-2-en-1-one with hydrazine and NaOH.

(26) **11** can also be obtained by photolysis of **4** and $P(C_6H_5)_3$. **11** has been prepared previously by hydride addition to a cationic iron–allene complex: Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

(27) Anal. Calcd for $C_{27}H_{26}BF_4FeOP$: C, 60.04; H, 4.85; P, 5.73. Found: C, 60.09; H, 5.01; P, 5.85.

(28) The $CF_3SO_3^-$ salt related to **2** is substantially less stable and decomposes with a half-life of 15 min at 40 °C.

ESR Study of 2-Adamantyl and 2-(Trimethylsiloxy)-2-adamantyl Radicals[1]

Mitsuo Kira, Mieko Watanabe, Michiko Ichinose, and Hideki Sakurai*

Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

Received November 10, 1981
Revised Manuscript Received February 8, 1982

In spite of a number of ESR studies on 2-adamantyl radicals in adamantane matrix[2] as well as in solution,[3] the hfs parameters have not been determined accurately to date; γ irradiation of adamantane studied by different groups has produced conflicting results.[2,4] We now report the first detailed analysis of the ESR spectra of 2-adamantyl and 2-(trimethylsiloxy)-2-adamantyl radicals in solution. The present results offer definitive evidence that the 2-(trimethylsiloxy)-2-adamantyl radical is nonplanar and inverts at rates comparable to the difference in its γ hydrogen hyperfine splitting constants (hfsc), while the 2-unsubstituted

---

(1) Chemistry of Organosilicon Compounds, 157.

(2) (a) Gee, D. R.; Fabes, L.; Wan, J. K. S. *Chem. Phys. Lett.* **1970**, *7*, 311. (b) Ferrell, J. R.; Holdren, G. R., Jr.; Lloyd, R. V.; Wood, D. E. *Ibid.* **1971**, *9*, 343. (c) Lloyd, R. V.; Rogers, M. T. *Ibid.* **1972**, *17*, 428. (d) Hyfantis, G. J.; Ling, A. C. *Can. J. Chem.* **1974**, *52*, 1206. (e) Migita, C. T.; Iwaizumi, M. *Chem. Phys. Lett.* **1980**, *71*, 322. (f) Lloyd, R. V.; DiGregorio, S.; DiMauro, L.; Wood, D. E. *J. Phys. Chem.* **1980**, *84*, 2891.

(3) (a) Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 4727. (b) Conlin, R. T.; Miller, R. D.; Michl, J. *Ibid.* **1979**, *101*, 7637. (c) Ieli, S. *Chim. Acta Turc.* **1979**, *7*, 261.

(4) For a review, see: King, F. W. *Chem. Rev.* **1976**, *76*, 157.

0002-7863/82/1504-3762$01.25/0

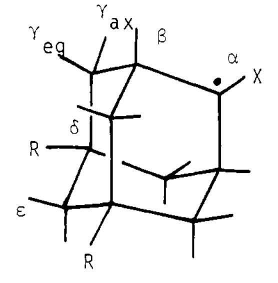
Table I. Observed and Calculated ^{1}H hfsc's of 2-Adamantyl Radicals

proton	1a (−137 °C)	1b (−133 °C)	1a INDO[a]	2a (−12 °C)	2b (−8 °C)	2b (−137 °C)	3a INDO[b]
α	20.73 (d)	20.55 (d)	−20.48				
β	1.93 (t)	1.93 (t)	1.16	5.07 (t)	4.94 (t)	5.07 (t)	3.18
γ-ax	0.98 (q)	0.94 (q)	0.96	0.93 (q)	0.93 (q)	1.24 (t), 0.62 (t)	−1.15, −0.79
γ-eq	4.06 (q)	3.90 (q)	−1.41	2.33 (q)	2.23 (q)	4.42 (t), 0.04 (t)[c]	3.62, −1.01
δ	2.78 (t)		4.07	1.88 (t)			4.04, 1.62
ϵ	0.12 (t)		−0.15	0.10 (t)			−0.10

[a] Standard C–C and C–H bond lengths and tetrahedral H–C–H and C–C–C bond angles were used.[7] The C–C–C bond angle around the radical center is assumed to be 109.5°. The calculated hfsc's did not depend seriously on the C–C_α–C angle. [b] The adamantane ring structure was assumed to be the same as the parent 2-adamantyl radical. The angle that the C-O bond makes to the ring was taken as 36° from the ab initio study of 1-hydroxycyclohexyl radical.[13] The hydroxy hydrogen was placed at the eclipsed position for the front-side lobe of the singly occupied orbital. [c] Calculated by assuming that the average value of two γ-eq hfsc's at −137° evens up the γ-eq hfsc (q) at −8 °C.

2-adamantyl radical is nearly planar. The barrier of pyramidal inversion correlated with the trimethylsilyl group rotation of the former radical was estimated by analysis of the marked temperature dependence of the ESR spectra.

Well-resolved ESR spectra of 2-adamantyl radicals **1a** and **1b**



1a, X = H; R = H
1b, X = H; R = CH_3
2a, X = $OSi(CH_3)_3$; R = H
2b, X = $OSi(CH_3)_3$; R = CH_3
3a, X = OH; R = H

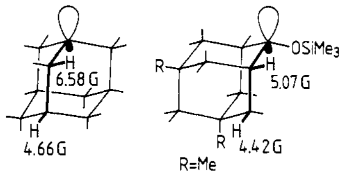
were obtained by the photolysis of a mixture of the corresponding 2-bromoadamantane, trimethylsilane, di-*tert*-butyl peroxide,[5] and cyclopropane in an ESR cavity at low temperature. Similarly, 2-(trimethylsiloxy)-2-adamantyl radicals **2a** and **2b** were generated by addition of the trimethylsilyl radicals to the corresponding adamantanone.

All the hydrogen hfsc's and the assignments are listed in Table I. Complex splitting patterns of these spectra were well reconstructed by computer simulation with the listed parameters. The assignments of the two larger triplets in **1a** and **2a** were ensured by comparing the splitting patterns with those of the 5,7-dimethyl derivatives. The ϵ-hydrogen triplets of both **1a** and **2a** could not be resolved in **1b** and **2b**. The only ambiguity may remain on the assignment of the two quintets for **1a**, **1b**, **2a**, and **2b**. We have assigned the larger hfsc's tentatively to the γ-equatorial hydrogens since they are in a W arrangement with the half-occupied orbital.[6]

Very small β-hydrogen hfsc values for both **1a** and **1b** suggest strongly a planar geometry around the radical centers with the β hydrogens lying near the nodal plane of the half-occupied orbital on C_α. The values of the α-hydrogen hfsc of **1a** and **1b** (20.73 and 20.55 G, respectively) are consistent with INDO values[7] for the planar 2-adamantyl radical. Moreover, negative temperature gradients of the absolute values of the α-hydrogen hfsc's (-4.5×10^{-3} and -3.6×10^{-3} G/°C for **1a** and **1b**, respectively) are also compatible with the planar configuration.

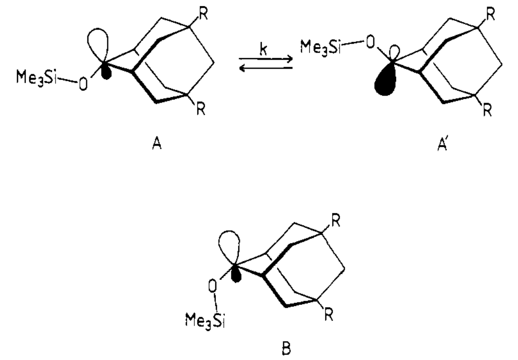
The ESR spectra of both **2a** and **2b** show interesting temperature dependences. An ESR spectrum corresponding to five pairs of equivalent hydrogens was observed for **2b** at −137 °C, although the smallest hfs was hidden in the line width. However, as the solution warmed to −8 °C, the splitting pattern of the spectrum changed to a triplet split further into a quintet of quintets (Table I). Apparently, two pairs of triplets for γ-axial (1.24 and 0.62 G) and γ-equatorial (4.42 and 0.04 G) hydrogens at −137 °C are averaged into two quintets at −8 °C (0.93 and 2.23 G, respectively). The β-hydrogen hfsc of **2b** is significantly larger than those of **1a** and **1b**, indicative of partial eclipsing of the C_β–H bond with the half-occupied orbital on C_α.

It is interesting to compare the hfsc values of β- and γ-equatorial hydrogens of **2b** at −137 °C with those of the *pyramidal* 1-adamantyl radical.[8] The β- (6.58 G) and γ-hydrogen (4.66 G) hfsc's of the 1-adamantyl radical correspond rather nicely with those of **2b**.



In addition, the observed hydrogen hfsc's of **2b** at −137 °C are in good agreement with INDO calculations for the pyramidal 2-hydroxy-2-adamantyl radical (**3a**). Therefore, **2b** may be taken as pyramidal to an extent comparable with the 1-adamantyl radical; there is a wealth of ESR data supporting the nonplanarity of mono-, di-, and trialkoxyalkyl radicals.[9]

The trimethylsilyl group in **2b** may exist in two possible rotational conformations, A and B, in which the Si–O bond eclipses



---

(5) (a) Hudson, A.; Hussain, H. A. *Mol. Phys.* **1969**, *16*, 199. (b) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *90*, 7155.

(6) (a) Russell, G. A. "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Interscience: New York, 1968; pp 87 ff. (b) Russell, G. A. *Sciences, N.Y.* **1968**, *161*, 423 and references cited therein.

(7) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

(8) Krusic, P. J.; Rettig, T. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 995.

(9) (a) Fessenden, R. W. *J. Phys. Chem.* **1967**, *71*, 74. (b) Livingston, R.; Dohrman, J. K.; Zeldes, H. *J. Chem. Phys.* **1970**, *53*, 2448. (c) Krusic, P. J.; Meakin, P.; Jesson, J. P. *J. Phys. Chem.* **1971**, *75*, 3438. (d) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. A* **1971**, 124. (e) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 786. (f) Kobayashi, S. O.; Simamura, O. *Chem. Lett.* **1973**, 695, 699. (g) Brunton, G.; Ingold, K. U.; Roberts, B. P.; Beckwith, A. L. J.; Krusic, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 3177. (h) Gaze, C.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1161. (i) Malatesta, V.; McKelvey, R. D.; Babcock, B. W.; Ingold, K. U. *J. Org. Chem.* **1979**, *44*, 1872.

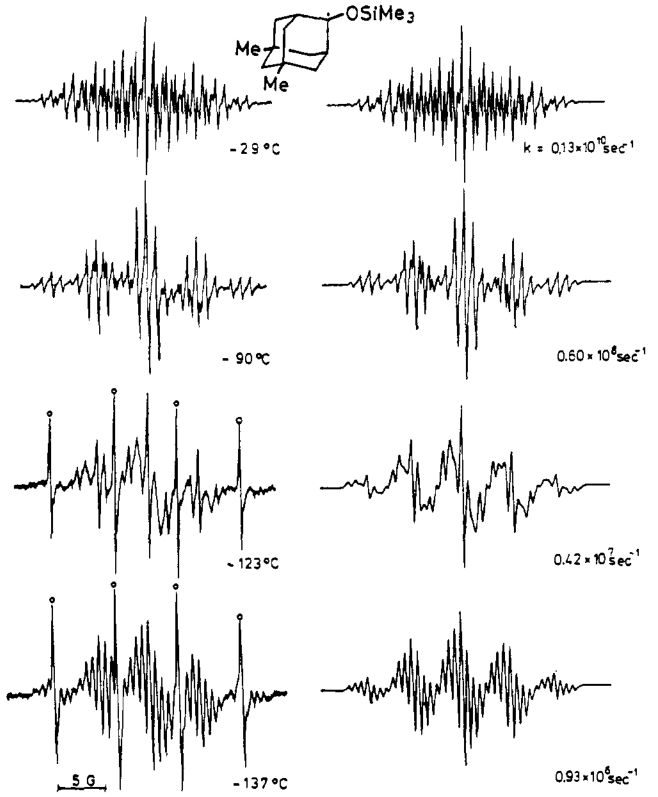


Figure 1. ESR spectra of **2b** at various temperatures: left, experimental; right, simulated with specified rate constants. Signals denoted with a small open circle in the experimental spectra are those of $Me_3Si\cdot$.

the half-occupied orbital on C_α due to hyperconjugation and steric hindrance.[10] The folded conformation B should be much higher in energy than A if the radical is pyramidal as inferred above. These two conformations are compatible with the equivalence of the β-hydrogen hfsc observed even at −137 °C and also with the temperature dependence of the spectrum. Since we have detected only one isomer of **2b** at the lowest temperature, the temperature-dependent behavior of the hfs pattern and the line-width alternation in the ESR spectrum (Figure 1) may be explained in terms of an exchange between the two equivalent structures A and A′[11] at rates of nearly the same order of magnitude as the difference in the hyperfine splittings for the two pairs of γ hydrogens expressed in frequency units.

The exchange rates were determined by comparing the experimental spectra with the simulated spectra obtained by solving the modified Bloch equations for the two-jump system[12] (Figure 1). From a plot of ln (k/T) vs. $1/T$, the following Eyring parameters for **2b** were obtained: $\Delta H^* = 4.2$ kcal/mol; $\Delta S^* = 1.2$ eu. A similar temperature dependence observed in the ESR spectrum of **2a** was complicated by an additional modulation due to the δ hydrogens.

Although the exchange should include two modes of motion, pyramidal inversion and silyl-group rotation, these motions are most probably strongly correlated and will avoid the high-energy conformation B. While the observed barrier to exchange should be taken as that for this rather complex motion,[11] it is noteworthy that the barrier is very similar to the inversion barrier (3.5 kcal/mol) for the 1-hydroxycyclohexyl radical calculated by ab initio methods.[13]

Registry No. 1a, 21517-94-2; **1b**, 81814-95-1; **2a**, 75890-76-5; **2b**, 81814-96-2; **3a**, 81814-97-3.

---

[10] Edge, D. J.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 182.

[11] If the radical is more planar than we have estimated with β-hydrogen hfsc's, the exchange between A and A′ (or between A and B) should represent essentially the hindered internal rotation about the C–O bond. However, if the rotational barrier of the Si–O bond would be very small, the experimental activation energy could represent a pyramidal inversion barrier. Thus, strictly speaking, the observed barrier should be considered as the upper limit of both pyramidal inversion and internal rotation. We thank a referee for useful comments on this point.

[12] Sullivan, P. D.; Bolton, J. R. *Adv. Magn. Reson.* **1970**, *4*, 39. The simulation program was modified for our specific spin system.

[13] Lloyd, R. V.; Causey, J. G.; Momany, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 2260.

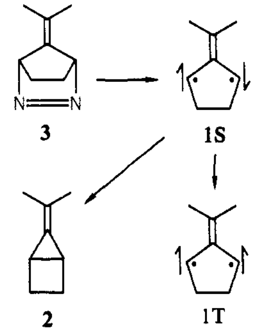
Direct Observation of a Hydrocarbon Singlet 1,3-Biradical by Picosecond Fluorescence Spectroscopy

David F. Kelley,[1] P. M. Rentzepis,*[1,2] Mark R. Mazur,[2,3] and Jerome A. Berson*[2]

Bell Laboratories, Murray Hill, New Jersey 07974
and Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received December 7, 1981

Recent experiments indicate that a finite energy barrier (2–3 kcal/mol) opposes the ring-closure of the planar singlet state of 2-isopropylidenecyclopentane-1,3-diyl (**1S**) to 5-isopropylidenebicyclo(2.1.0)pentane (**2**).[4-6] Moreover, the spin-retarded intersystem crossing (ISC) of **1S** to the more stable triplet biradical (**1T**) is only 10^{-5} times as fast as a molecular vibration.[6] These findings imply that **1S** is a local minimum on the reaction pathway, not a transition state. The present paper reports the direct spectroscopic observation of an excited state of **1S**.



The transients are generated by picosecond excitation[7] of the diazene **3**[6] in hexane solution and are monitored by their fluorescence. The radiative lifetime of the planar singlet **1S*** is expected[8] to be longer by at least 10^3–10^5 than the lifetimes observed in the present experiments, so that quenching of the fluorescence signal intensity strongly indicates the occurrence of some other chemical or physical process that consumes excited species.

Figure 1 shows the fluorescence decay beyond 310 and 380 nm. For both spectral ranges, the emission decay is found to be biphasic with two resolvable processes with lifetimes of 38 and 280 ps. The 280-ps component intensity is affected only slightly by restricting the observed fluorescence to longer than 380 nm. This restriction

---

[1] Bell Laboratories, Murray Hill, NJ 07974.

[2] Yale University, Department of Chemistry, New Haven, CT 06511.

[3] Humphrey Chemical Co. Fellow, 1981.

[4] (a) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 684. (b) *Ibid.* **1982**, *104*, 2217.

[5] (a) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091. (b) Rule, M.; Mondo, J. A.; Berson, J. A. *Ibid.* **1982**, *104*, 2209.

[6] (a) For reviews, see: Berson, J. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982. (b) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

[7] Barbara, P. F.; Brus, L. E.; Rentzepis, P. M. *Chem. Phys. Lett.* **1980**, *64*, 447.

[8] The $^1A_1 \leftarrow {}^1E'$ transition for parent trimethylenemethane has been calculated[9] to occur at 289 nm with an oscillator strength $f \sim 0.1$. The Einstein probability of spontaneous emission for such a species gives rise to a lifetime of about 10 ns.[10]

[9] Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 4242.

[10] (a) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; p 174. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; pp 91 ff, 147.

0002-7863/82/1504-3764$01.25/0