structure. HMPA changed this situation dramatically.[12] In all the solvents tested, addition of 2 equiv of HMPA caused (*R*)-**1a** to exist as a chelated monomer. The ^{6}Li NMR spectrum of $[^{6}\text{Li},^{15}\text{N}_2]$-(*R*)-**1a** shows a doublet of doublets, and the corresponding ^{15}N spectrum displays two sets of triplets (Figure 2C). Addition of a large excess of HMPA (13 equiv) to the $[^{6}\text{Li},^{15}\text{N}_2]$-(*R*)-**1a** in THF-$d_8$ did not affect the five-membered chelate structure.

The asymmetric deprotonation of 4-*tert*-butylcyclohexanone (**3**) using (*R*)-**1a** (Scheme I) showed remarkable solvent effects as shown in Table I. In THF or DME, the reaction proceeded with good chemical yield and good enantioselectivity (especially in THF). On the other hand, the reaction itself did not proceed well and enantioselectivities were somewhat decreased in toluene or ether. HMPA also showed a marked effect on the reaction as an external ligand.[3a,12] In the presence of 2 equiv of HMPA, chemical and optical yields became high and independent of the solvent used. It is concluded that the five-membered chelated monomeric form of (*R*)-**1a** is higher in reactivity and gives higher enantioselectivity in deprotonation than the dimeric form of (*R*)-**1a**, and that the function of HMPA is to destroy the dimeric form and to generate the monomeric form of (*R*)-**1a**.

Acknowledgment. Partial financial support from the CIBA-GEIGY Foundation for the Promotion of Science is acknowledged.

Supplementary Material Available: Details of the diffraction analysis, plots of atom labels, and tables of atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles for the dimeric form of (*R*)-**1a** and complete ^{6}Li and ^{15}N NMR spectroscopic data of $[^{6}\text{Li},^{15}\text{N}_2]$-(*R*)-**1a** (10 pages). Ordering information is given on any current masthead page.

---

[12] Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751 and references cited therein.

A Kinetically Stable Singlet State of 1,2,4,5-Tetramethylenebenzene

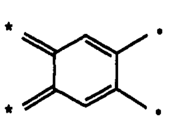
James H. Reynolds, Jerome A. Berson,*
Kristin K. Kumashiro, James C. Duchamp, Kurt W. Zilm,*
Albino Rubello, and Pierre Vogel*

Department of Chemistry, Yale University
New Haven, Connecticut 06511
Institute of Organic Chemistry, University of Lausanne
Lausanne, Switzerland CH-1005

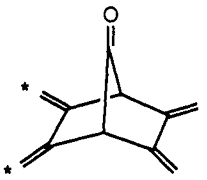
Received August 21, 1991

The atomic connectivity[1,2] of the 1,2,4,5-tetramethylenebenzene (TMB) biradical **1a** permits its two nominally nonbonding electrons to reside in "disjoint" molecular orbitals, confinable to separate spatial domains.[3] According to both semiempirical[4] and ab initio[5] theory, **1a** should have a singlet ground state. The highest level calculations done so far[5b] predict the singlet to be favored by 5–7 kcal/mol with respect to the triplet.

Previous experimental studies, however, have favored a triplet ground state for **1a**.[6] Photolysis of ketone **2a** in Ar matrix at 15 K gave rise to CO and to a UV–vis spectrum with a strong band near 480 nm (ϵ not specified) and weak bands at 530, 560, and 600 nm ($\epsilon \sim 600$, 600, and 400, respectively). The weak bands were assigned[6] to the dipole-forbidden transition at 570 nm predicted[5b] for the triplet of **1a**. A preparation of **2a** in adamantane matrix irradiated at 15 K gave a strong, narrow ESR signal near 3404 G and a weak half-field transition near 1693 G. The ESR signal intensity was linear in $1/T$ between 15 and 80 K. These observations led to the assignment of a triplet ground state for **1a**.[6] The formation of product **3** in the thermal (80 °C) reaction of ketone **2a** in solution with fumaric ester was interpreted as chemical trapping of the biradical **1a** formed by loss of CO from **2a**.[6]

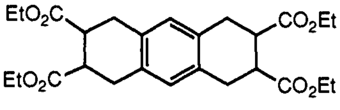


1

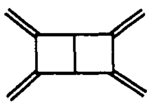


2

a: * = CH_2
b: * = $^{13}CH_2$



3



4

Our work leads to different conclusions. First, we find that the biradical **1a** is not a significant intermediate in the thermal **2a** → **3** reaction. Ketone **2a** alone is stable in benzene solution at 80 °C, and its reaction with diethyl fumarate is kinetically second-order. These observations conform to the mechanism described[7] for the reaction of **2a** with tetracyanoethylene: two successive conventional Diels–Alder reactions followed by decarbonylation.

By irradiation at 77 K of ketone **2a**, prepared by either of the literature[6,7] routes, in glassy media or in adamantane matrix prepared by cosublimation, we observe an intense purple color and a UV–vis spectrum (major absorption near 490 nm, $\epsilon \sim 4200$) essentially the same in all features as that reported.[6] Purple samples from **2a** show an ESR signal near 3280 G at a microwave frequency of 9.27 GHz whose intensity is variable and is not correlated with that of the UV–vis absorption. At 77 K, a half-field signal near 1650 G is not visible, even at 1.8 mM concentration of the biradical. Allowing the matrix to thaw results in complete destruction of ketone **2a** and disappearance of the purple color. Refreezing and rephotolyzing this sample give the same ESR signal as before, but the purple color and the UV–vis spectrum featuring the 490-nm band are absent. The implication is strong that the carrier of the ESR signal is not the species responsible for the purple color and the UV–vis spectrum.

Ketone precursor **2**-2,3-*di*-$^{13}CH_2$ (**2b**) was synthesized as described elsewhere.[8] Figure 1A shows the solid-state CP MAS ^{13}C NMR spectrum of **2b** immobilized in 2-methyltetrahydrofuran (MTHF) glass at 77 K. Irradiation at 310 nm produces a new species with a resonance at 113 ppm (Figure 1B). This chemical shift corresponds well to that expected[9] for a singlet biradical (compare the shifts of the terminal CH_2 carbons of 3,4-dimethylenefuran[9a] and 3,4-dimethylenethiophene,[9b,c] $\delta = 102$ and 105 ppm, respectively) and cannot be attributed to a triplet, which would not be observable under these conditions.[9] Integration of the difference spectrum (1B − 1A) shows that the decrease in

---

[1] (a) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 497. (b) Misurkin, I. A.; Ovchinnikov, A. A. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 967.

[2] See, for example: Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251 and references cited therein.

[3] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

[4] (a) Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273. (b) Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 958.

[5] (a) Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4362. (b) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072.

[6] Roth, W. R.; Langer, R.; Bartmann, M.; Stevermann, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 256.

[7] Rubello, A.; Vogel, P. *Helv. Chim. Acta* **1988**, *71*, 1268.

[8] See supplementary material.

[9] (a) Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567. (b) Zilm, K. W.; Merrill, R. A.; Webb, G. G.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1533. (c) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A.; Merrill, R. A.; Duchamp, J. C.; Zilm, K. W. *J. Am. Chem. Soc.* **1991**, *113*, 2318.

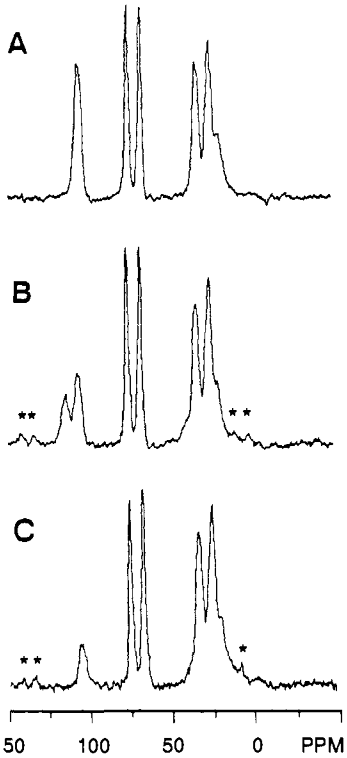


Figure 1. (A) Solid-state CP MAS ^{13}C NMR spectrum of 98% isotopically enriched ketone **2b** in MTHF at 77 K. The four lines between 0 and 80 ppm are MTHF resonances. The line at 105 ppm is the signal of the labeled exocyclic methylene groups of **2b**. (B) Spectrum obtained after irradiation of the above sample at 310 nm at 77 K. The purple color of **1b** is visible. (C) Spectrum obtained by annealing sample of B to 120 K and then recooling to 77 K. Sample C is colorless. Spinning sidebands in each trace are marked with asterisks.

intensity of the **2b** resonance is matched quantitatively (≥95%) by the increase in intensity of the 113 ppm resonance, and the extent of photoconversion (~40% in this experiment) is in good agreement with the growth in the UV–vis optical density expected from a species having the extinction coefficient reported[6] for TMB biradical **1a**. Experiments in toluene glass[8] confirm the observation in MTHF that only one new NMR resonance appears. This 113 ppm resonance is that of a transient species, since it disappears (Figure 1C) when the sample is annealed at 120 K. The data indicate that only one photoproduct is formed and that its symmetry cannot be lower than that of the precursor **2b**.

The simplest interpretation of the facts is that the carriers of the UV–vis signal (λ_{max} 490 nm, $\epsilon \sim 4200$) and the NMR signal are the same species, a kinetically stable singlet state of TMB. The values of λ_{max} and ϵ so derived are in good agreement with those ($\lambda_{max} > 417$ nm, $\epsilon \sim 3600$) calculated[5b] for the $^1A_g \rightarrow {}^1B_{3u}$ transition of singlet TMB. An alternative but less satisfactory hypothesis would assign the NMR signal to 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane (**4**) and the UV–vis spectrum to a small amount (≤5%) of the biradical TMB. In this hypothesis, the UV–vis extinction coefficients of the biradical would have to be ≥20 times as strong as previously[6] reported. The strong absorption at 490 nm then would have $\epsilon \geq 84\,000$, corresponding to $f \sim 1.7$, which lies beyond the Kuhn–Thomas[10] approximate theoretical limit of oscillator strength. Even if that is disregarded, the "weak" long-wavelength bands now would have $\epsilon \sim 8000$–$12\,000$, so that the previous assignment[6] to the forbidden triplet transition would become inappropriate.[11]

We note that the major photoproduct, the TMB singlet species **1a** or **1b** (monitored by UV–vis and CP MAS ^{13}C NMR spectroscopy), persists at 77 K for >17 days, behavior expected of the theoretically predicted singlet ground state.[12]

Acknowledgment. We thank the National Science Foundation (Grants 8820073 and 9018455) and the Swiss National Science Foundation for support of this work.

Supplementary Material Available: Details of the synthesis of **2b**, description of photochemical equipment, and CP MAS NMR spectra in toluene glasses (10 pages). Ordering information is given on any current masthead page.

---

(10) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley, New York, NY, 1966; p 172.

(11) The third formal hypothesis, that **4** is the only photoproduct, necessarily would imply that TMB has not been generated under the present or previous[6] conditions. In that case, the proposed[6] conflict with theory would vanish also.

(12) Since we can provide no direct assurance that an equilibrium distribution of spin states exists in these experiments, we prefer to call our major photoproduct a "kinetically stable singlet". None of our results so far permit an assignment of our ESR signals to triplet species. In the absence of further evidence, it is conceivable that the carrier of the previously reported[6] triplet ESR signal may be a small amount of triplet TMB which is not in rapid equilibrium with the singlet species observed here.

Electrochemical Intercalation of Lithium into Solid C_{60}

Yves Chabre,[*,†] David Djurado,[†,‡] Michel Armand,[§]
William R. Romanow,[‖] Nicole Coustel,[‖,⊥]
John P. McCauley, Jr.,[‖,#] John E. Fischer,[‖,⊥] and
Amos B. Smith, III[‖,#]

Laboratoire de Spectromētrie Physique
Universitē Joseph Fourier
Grenoble I BP 87
F-38042 St. Martin d'Hères, France
Laboratoire d'Ionique et d'Electrochimie du
Solide de Grenoble
ENSEEG, INPG, BP 75
F-38042 St. Martin d'Hères, France
Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6272
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323
Department of Materials Science
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6272

Received August 16, 1991
Revised Manuscript Received November 19, 1991

We have succeeded in intercalating fullerite electrodes with lithium using all-solid-state electrochemical cells and polymer electrolytes. This method offers several advantages over previous studies of fullerenes in solution[1-3] and fullerite films in liquid electrolytes.[4] First, polymer electrolytes generally exhibit larger electrochemical stability windows than liquid electrolytes, especially at negative potential, while avoiding dissolution of the working electrode, the possibility of solvent co-intercalation, and problems associated with limited solubility of neutral, ionized, or

---

[†] Universitē Joseph Fourier.

[‡] Permanent address: Laboratoire de Chimie des Solides, Universitē Blaise Pascal, F-63177, Aubiere, France.

[§] ENSEEG.

[‖] Laboratory for Research on the Structure of Matter, University of Pennsylvania.

[⊥] Department of Materials Science, University of Pennsylvania.

[#] Department of Chemistry, University of Pennsylvania.

(1) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Cuifollini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 9634.

(2) Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

(3) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

(4) Jehoulet, C.; Bard, A. J.; Wudl, R. *J. Am. Chem. Soc.* **1991**, *113*, 5446.

0002-7863/92/1514-764$03.00/0