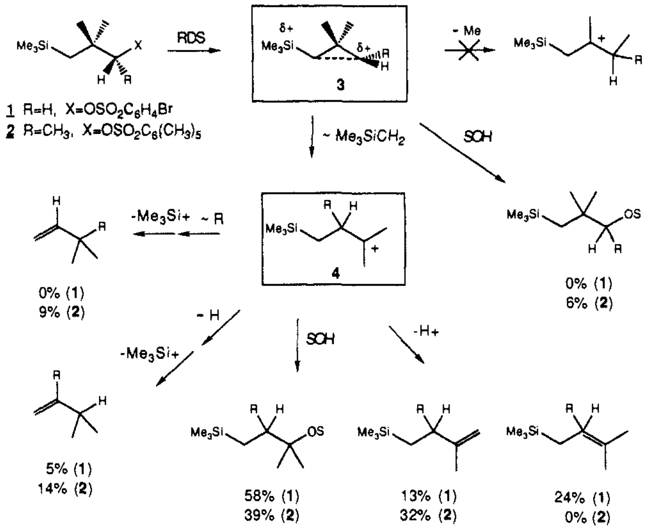
Table I. Rate Constants and Deuterium Kinetic Isotope Effects for Solvolysis at 25 °C

	solvent[a]	k, 10^{-5} s^{-1}	k_{rel}[b]	isotope rate effects α-d_1	γ-d_6[c]	γ-d_2[d]
1	80E	0.5411		1.105	0.927	0.972
	50E	4.766	2500			
	97T	14.370	21800	1.106	0.931	0.985
2	90E	2.218	500	1.119	0.985	0.985
	80E	5.936	400	1.130	0.977	0.985
	97T	707	4600			

[a] 90E, 80E, and 50E are 90, 80, and 50 vol % aqueous ethanol, respectively; 97T is 97% 2,2,2-trifluoroethanol–3% water. [b] The rate constants for the primary substrate are expressed relative to Me_3CCH_2OBs; those for the secondary substrate are relative to $Me_3CCHMeOPms$[9] (estimated OBs/OPms = 43).[10] [c] Deuteration of both γ-methyl groups. [d] Deuteration at the γ-methylene position.

Scheme I. General Mechanistic Scheme for Product Formation and Percent Yields in 80E



However, since deuterium substitution at the *γ-methylene position slows solvolysis* (Table 1), the $(CH_3)_3SiCH_2$ group *does not migrate in the rate-determining step*.[6] Further, the fact that **2** produces some unrearranged substitution, while the pinacolyl ester does not, means that the substitution reaction is also accelerated by the γ-silyl group. These facts can be accommodated by the mechanism proposed in Scheme I which involves rate-determining formation of the intermediate (**3**) which is stabilized by the same type of percaudal interaction of the Si–C_γ bond previously identified.[1] This interaction is favored by methyl substitution at C_β, as is evident from the stepwise increase in reaction rate with methyl substitution at C_β of 1:12:65 (97T) for **1** and 1:7:57 (80E) for **2**, which can be attributed to the Thorpe–Ingold or the *gem*-dimethyl effect.[7] *gem*-Dimethyl substitution serves to make the rearrangement of the intermediate **3** to the tertiary ion **4** by Me_3SiCH_2 migration, faster than nucleophilic attack on carbon or silicon. Nevertheless, the bridged ion does give a small fraction of substitution in the secondary case. In intermediate **3**, the C_β–C_γ bond is optimally oriented for rearrangement, whereas methyl migration would involve bond rotation which would break the silyl stabilization.[8]

Acknowledgment. Support from the National Science Foundation, Grant No. CHE-85-06682 (project support) and CHE-81-05004 and CHE-85-13707 (NMR instrumentation), is gratefully acknowledged.

Supplementary Material Available: Information about the preparation, physical constants, and spectra of the compounds used (**1–24**) and the isolation and identification of the products (**106–111** and **123–126**) (17 pages). Ordering information is given on any current masthead page.

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(5) (a) Tanino, K.; Hatanaka, Y.; Kuwajima, I. *Chem. Lett.* **1987**, 385-388. (b) Kuwajima, I. In *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, 1988; Chapter 7. (c) Fleming, I.; Patel, S. K.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 115-124.

(6) (a) Shiner, V. J., Jr.; Tai, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 436-442. (b) Shiner, V. J., Jr. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold Co.: New York, 1970; p 151.

(7) (a) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 196-202. (b) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183. (c) Jung, M. E.; Gervay, J. *Tetrahedron Lett.* **1988**, *29*, 2429-2432 and references therein.

(8) The γ-silyl-stabilized carbocation may be formed in preference to concerted rearrangement to a β-silyl-stabilized carbocation because the latter reaction is retarded by steric interactions which hinder the "U" conformation, in which the orbitals of the C_α–X bond, the C_β–methyl bond, and the C_γ–Si bond are all parallel.

(9) Fisher, R. D. Ph.D. Thesis, Indiana University, Bloomington, IN, 1971.

(10) Ensinger, M. W. Ph.D. Thesis, Indiana University, Bloomington, IN 1987.

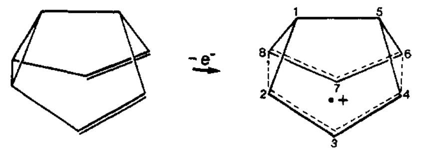
Electron Spin Resonance Evidence for the 1,4-Bishomobenzene Structure of the C_{2v} Ring-Opened Semibullvalene (Bicyclo[3.3.0]octa-2,6-diene-4,8-diyl)[†] Radical Cation

Sheng Dai, Jih Tzong Wang, and Ffrancon Williams*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Received November 24, 1989

The remarkable fact that semibullvalene (**1**)[1] undergoes a rapid degenerate Cope rearrangement on the NMR time scale at −150 °C has prompted efforts to lower the activation energy of only 4.8 kcal mol^{-1} for the parent molecule[2] to a negative value by appropriate substitution.[3,4] This exciting goal where the expected 1,4-bishomobenzene transition structure[3] would be stabilized relative to the localized semibullvalene structures has not hitherto been realized, however, even for purposely designed derivatives.[4] In contrast, we now report that radiolytic oxidation of **1** in Freon matrices generates the delocalized bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation $\mathbf{2}^{\bullet+}$ as *a stable species*.



1 $\mathbf{2}^{\bullet+}$

Bishomoaromatic radical cations of this generic type were first suggested by Roth and Abelt[5a] as the precursors responsible for the CIDNP patterns observed from the neutral recombination products in photoinduced electron transfer reactions between a series of bridged bicyclo[5.1.0]octa-2,5-dienes, exemplified by barbaralane, and various electron acceptors. Such NMR evidence[5] of radical cation structure is, of course, indirect and we are not aware of any previous *direct* spectroscopic measurements on a bishomobenzene radical cation derived from two strongly inter-

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[†] The diyl parent of the radical cation may also be named bicyclo[3.3.0]-octa-3,7-diene-2,6-diyl, these two equivalent valence-bond structures reflecting its bisallyl character.

(1) Systematic name: tricyclo[3.3.0.0^{2,8}]octa-3,6-diene. (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316. (c) Turro, N. J.; Liu, J.-M.; Zimmerman, H. E.; Factor, R. E. *J. Org. Chem.* **1980**, *45*, 3511.

(2) Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *J. Am. Chem. Soc.* **1974**, *96*, 2887.

(3) Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941.

(4) Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125.

(5) (a) Roth, H. D.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 2013. (b) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343. (c) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157.

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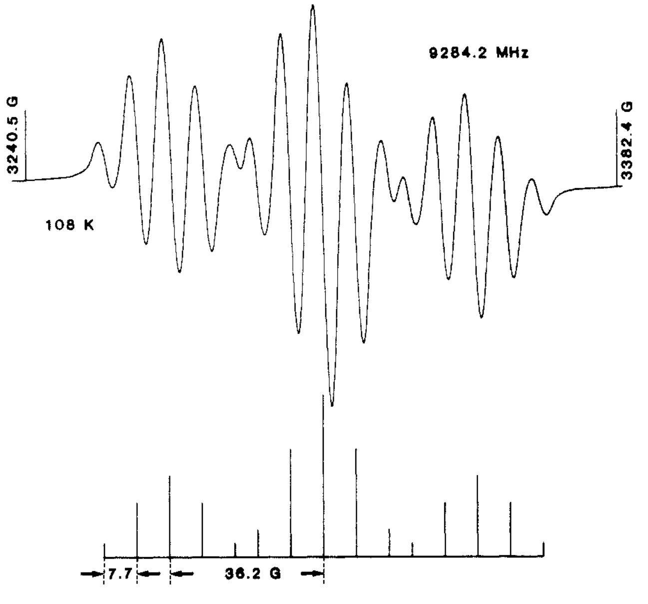
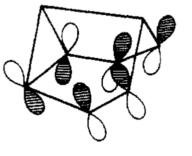


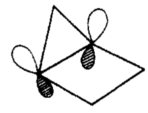
Figure 1. First-derivative ESR spectrum obtained from a solid solution of semibullvalene (<1 mol %) in $CF_2ClCFCl_2$ after γ-irradiation (dose, 0.25 Mrad) at 77 K. The stick diagram represents the line components of the C_{2v} bridged 1,4-bishomobenzene radical cation derived by the cyclopropane ring opening of the semibullvalene radical cation.

acting allyl systems, although some other biallylic radical cations have been studied by EA (electronic absorption)[6] and ESR spectroscopy[7] as well as by the CIDNP method.[5b,c]

In conjunction with an ongoing study where the ESR spectrum of $\mathbf{2}^{\bullet+}$ was needed for identification purposes,[8] previous work in this laboratory on cyclopropane radical cations[9] led us to select **1** as a suitable neutral precursor to the desired bishomobenzene radical cation. In particular, **1** is well adapted to forming a [3.3.0] bisallyl system by a weakening of the C(2)–C(8) bond upon ionization of the a′ HOMO shown below. Furthermore, a suitable precedent for this type of ring opening exists in that the cyclopentane-1,3-diyl radical cation is formed initially in the radiolytic oxidation of bicyclo[2.1.0]pentane,[10] ionization from the corresponding a′ HOMO of the latter (see below) resulting in the development of planar sp^2 carbon centers at the bridgehead positions.

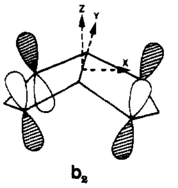


a′($\pi_1 + \pi_2 - \Delta$)

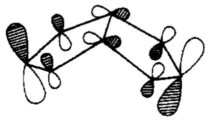


a′

An intense ESR spectrum (Figure 1) readily assignable to $\mathbf{2}^{\bullet+}$ (vide infra) was generated on γ-irradiation of Freon solid solutions containing low concentrations (<1 mol %) of **1**. The spectra obtained from $CFCl_3$, CF_3CCl_3, and $CF_2ClCFCl_2$ solutions were identical except for differing line widths, which also varied reversibly with temperature, the optimum resolution being obtained in $CF_2ClCFCl_2$ at 108 K.[11] As reconstructed in the stick diagram, the spectrum consists of a triplet (a(2H) = 36.2 G) of quintets (a(4H) = 7.7 G) with a g factor of 2.0029 (3), the unresolved hyperfine couplings (hfcs) to the two remaining hydrogens suggesting values less than the line width of ca. 3 G.



b$_2$



b$_1$

The distribution of hydrogen hfcs clearly reflects the C_{2v} point group symmetry for $\mathbf{2}^{\bullet+}$. Accordingly, the choice of SOMO is between the b$_2$ and b$_1$ representations shown herein.[12] Since the b$_1$ orbital possesses a nodal plane through the bridgehead hydrogens, the largest hfcs would necessarily be to the α-hydrogens at C(3) and C(7) but the expected values in this case would certainly be less than half the observed 36.2 G, and therefore the b$_1$ SOMO can safely be rejected. On the other hand, the measured hfcs are accommodated by the expected b$_2$ SOMO,[3] the 36.2-G hfcs being assigned to the two bridgehead β-hydrogens at C(1) and C(5) while the telltale 7.7-G coupling[13] is associated with the four allylic α-hydrogens at the C(2), C(4), C(6), and C(8) positions. Moreover, the weak couplings to the remaining hydrogens (2H$_0$) at C(3) and C(7) are only understandable from the nodal character of the xz mirror plane and would be incompatible with a pair of rapidly equilibrating $\mathbf{1}^{\bullet+}$ valence tautomers. This assignment to the $^2B_2$ state of $\mathbf{2}^{\bullet+}$ is supported by INDO calculations,[14a] which also gave hfcs of 57.2 G (2H$_\beta$), −7.1 G (4H$_\alpha$), and 3.4 G (2H$_0$), in qualitative agreement with the experimental results.[14b]

While the above results accord with the $^2B_2$ 1,4-bishomobenzene structure, it is important to distinguish between this delocalized structure derived from two strongly interacting allyl systems and one in which the two allyl systems do not interact so strongly. A very weak interaction would be expected to result in an unsymmetrical charge distribution with separate allyl radical and cationic systems, and although a static structure of this kind on the ESR time scale is clearly excluded by the equivalent 7.7-G hfc for the four hydrogens at the termini of the allyl systems, this result does not rule out the possibility of a time-averaged C_{2v} structure

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(6) Momose, T.; Shida, T.; Kobayashi, T. *Tetrahedron* **1986**, *42*, 6337.

(7) Gerson, F.; de Meijere, A.; Qin, X.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 1135.

(8) The ESR spectrum of $\mathbf{2}^{\bullet+}$ was first generated in our laboratory by the photolysis with visible light of the radical cation produced by the radiolytic oxidation of cyclooctatetraene, the ESR spectrum of this photosensitive precursor being an unresolved singlet with a line width of 8–12 G, depending on the Freon matrix and temperature. This photoinduced rearrangement of the cyclooctatetraene radical cation (cf.: Dessau, R. M. *J. Am. Chem. Soc.* **1970**, *92*, 6356) to $\mathbf{2}^{\bullet+}$ is a symmetry-allowed electrocyclic reaction: Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.*, following paper in this issue.

(9) Qin, X.-Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301 and references therein.

(10) Williams, F.; Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835.

(11) The ESR signals from $\mathbf{2}^{\bullet+}$ persisted up to 160 K in $CFCl_3$ and to 145 K in CF_3CCl_3, these temperatures corresponding to the softening points of these matrices; in each case, no signals from daughter radicals were detected upon the decay of $\mathbf{2}^{\bullet+}$, and only the spectra of residual matrix radicals were observed at higher temperatures. In the more mobile $CF_2ClCFCl_2$ matrix, however, where ion–molecule reactions can occur quite readily (Williams, F.; Qin, X.-Z. *Radiat. Phys. Chem.* **1988**, *32*, 299) above 110 K, the decay of $\mathbf{2}^{\bullet+}$ at 115–125 K was accompanied by the growth of new ESR signals, which on better resolution at 150 K could be analyzed as a doublet (a(1H) = 35.5 G) of triplets (a(2H) = 14.4 G) with a g factor of 2.0025. This spectrum is tentatively assigned to the neutral radical produced by loss of a hydrogen atom from the C(5) position of semibullvalene, the hfcs arising from interaction with the β-hydrogens at C(1) (doublet) and C(4) and C(6) (triplet). The rigidity of this radical does not favor strong allylic resonance, so the spin population is expected to be localized primarily on C(5).

(12) (a) The b$_1$ orbital described here corresponds to the a$_2$ orbital in ref 5a. The latter designation is incorrect irrespective of the choice of x and y axes, which only interconvert the b$_1$ and b$_2$ representations in C_{2v} symmetry. (b) The b$_2$ SOMO of $\mathbf{2}^{\bullet+}$ and the a′ HOMO of **1** are both symmetric in the yz plane. Since this symmetry element bisects the C(2)–C(8) bond in **1**, the thermal isomerization of $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ is *state-symmetry allowed*, in keeping with the experimental result reported here.

(13) As expected for the radical cation of two delocalized allyl systems, this 7.7-G coupling is slightly larger than half the value of 14.8 G for the corresponding exo hydrogens in the allyl radical: Berndt, A. In *Landolt-Börnstein*; New Series, Group II, *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, 1977; Vol. 9, Part b, pp 345–353.

(14) (a) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970. A factor of 540 G was used to convert hydrogen 1s spin populations to hfcs. Geometry optimization was done by the AM1 method (Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902). (b) INDO calculations appear to systematically overestimate β-hydrogen coupling constants by a factor of ca. 1.5; see, e.g.: Dai, S.; Pappas, R. S.; Chen, G.-F.; Guo, Q.-X.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1989**, *111*, 8759.

produced by rapid electron transfer between radical and cation moieties.

The preceding ambiguity is nicely resolved, however, by reference to the Whiffen effect for delocalized structures.[15] Thus, since the coefficients of the b_2 SOMO at C(2) and C(8) are equal and have the same sign, the hfc to the bridgehead β-hydrogens should be given by $B(0.25^{1/2} + 0.25^{1/2})^2 \cos^2 \theta$ for the delocalized structure whereas the corresponding relation for the unsymmetrical structure is $B(0.50^{1/2} + 0.00^{1/2})^2 \cos^2 \theta$, the numerical values referring to the local spin populations in the 2p orbitals at C(2) and C(8). The dihedral angle θ between the 2p axes at C(2) and C(8) and the C(1)–H_β bond can be taken as 30° for planar five-membered rings in this [3.3.0] bisallyl system, and with 48 G for the constant B in these Heller–McConnell relations,[16] β-hydrogen hfcs of 36 and 18 G are thus expected for the delocalized and unsymmetrical structures, respectively.[17] The experimental β-hydrogen hfc of 36.2 G therefore establishes the delocalized structure corresponding to the $^2B_2$ state, the representations **2a**$^{\bullet+}$ and **2b**$^{\bullet+}$ shown herein constituting *mesomeric* rather than equilibrating structures.

2a$^{\bullet+}$ **2b**$^{\bullet+}$

Another measure of the interaction between the two allyl systems is given by the energy of the charge resonance interaction responsible for the long-wavelength band in the EA spectrum. This band is centered at 635 nm (1.95 eV) for $\mathbf{2}^{\bullet+}$,[8] and therefore the interaction is substantially greater than that in the radical cations of dicyclopentadiene,[5c,6] where the corresponding bands have energies of 1.46 and 1.67 eV for the exo and endo isomers.[6]

Finally, we point out that the inverted relationship between the curvatures of the potential energy surfaces for the ground-state structures of **1** and $\mathbf{2}^{\bullet+}$ implies an energy requirement, namely, that the difference between the lowest vertical ionization potentials, I, of **1** and the transition state **2** must exceed the enthalpy of activation for the degenerate rearrangement of **1**, i.e., $I(\mathbf{1}) - I(\mathbf{2}) > \Delta H^{\ddagger}(\mathbf{1} \rightarrow \mathbf{2})$. In order to satisfy this relation, $I(\mathbf{2})$ must be less than $I(\mathbf{1})$ (=8.5 eV)[18] by at least 0.21 eV, which is intuitively reasonable, considering that the b_2 HOMO of the transition state[3] is largely nonbonding whereas the a′ HOMO of **1** has significant bonding character in the cyclopropane ring; in fact, recent calculations by Halevi and Rom[19] bear out this proposition, the orbital energies ($-I$) of **2** and **1** being −7.33 eV and −9.37 eV, respectively, at a CI level of computation. As a general rule, therefore, we can surmise that the potential energy surface for a radical cation is likely to become inverted from that of its neutral molecule only when the HOMO of the latter develops appreciable nonbonding character in the transition state of a degenerate rearrangement. *Diyl* transition states for neutral Cope reactions exemplify this principle, both in the present case and for the prototypal degenerate rearrangement of 1,5-hexadiene,[20] where the chair form of the cyclohexane-1,4-diyl radical cation[21] represents the stable positive hole of the likely neutral transition state.[22]

Acknowledgment. We thank Professor R. M. Pagni for providing experimental facilities, Professors R. G. Bergman and S. F. Nelsen for valuable discussions, and the referees for helpful comments. This research was supported by the Division of Chemical Sciences, Office of Basic Sciences, U.S. Department of Energy (Grant DE-FG05-88ER13852).

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(15) (a) Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223. (b) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *38*, 773; *39*, 2147. (c) Snow, L. D.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1982**, *104*, 2062. (d) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456.

(16) Gordy, W. *Theory and Applications of Electron Spin Resonance*; Wiley: New York, 1980; Chapter VI, p 198.

(17) Allowance for the presence of negative spin densities resulting in higher spin populations of 0.30 (4 C) and 0.60 (2 C) at the respective α-carbons of the delocalized and unsymmetrical [3.3.0] bisallyl structures would lead to expected hfcs of 43.2 and 21.6 G. Despite the less impressive agreement with experiment in this case, the delocalized structure is again clearly supported. A similar conclusion is also reached by comparison with the β-hydrogen hfcs of 22.7 G for the cyclopentenyl radical.[13]

(18) Askani, R.; Gleiter, R.; Heilbronner, E.; Hornung, V.; Musso, H. *Tetrahedron Lett.* **1971**, 4461.

(19) Halevi, E. A.; Rom, R. *Isr. J. Chem.* **1989**, *29*, 311.

(20) Doering, W. von E.; Roth, W. R. *Tetrahedron* **1962**, *18*, 67. Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

(21) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1988**, *110*, 1974. Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B. K. *J. Am. Chem. Soc.* **1989**, *111*, 4133.

(22) It should be noted that destabilization of the HOMO enters the above expression as a favorable driving force for geometry change in the radical cation *since the process is considered relative to the corresponding change in the neutral molecule*, the increase in energy resulting from the destabilization of the half-filled HOMO (SOMO) in the radical cation being less than that for the filled HOMO in the neutral molecule. In order for the geometry change to be exoergic in the radical cation, however, the binding energy lost by destabilization of the SOMO must be more than recouped through stabilization of the fully occupied subjacent orbitals (HOMO-1, HOMO-2, etc.). It is, of course, the concurrent stabilization of these lower orbitals that provides the actual positive driving force for the rearrangement in the radical cation.

Photoinduced Electrocyclic 1,5-Closure of the Cyclooctatetraene Radical Cation to a Bridged 1,4-Bishomobenzene (Bicyclo[3.3.0]octa-2,6-diene-4,8-diyl†) Radical Cation

Sheng Dai, Jih Tzong Wang, and Ffrancon Williams*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Received December 26, 1989

Cyclooctatetraene (**1**) is well-known to have a tub-shaped (D_{2d}) geometry with alternating double bonds,[1] and its radical cation ($\mathbf{1}^{\bullet+}$) evidently also possesses a nonaromatic and nonplanar structure.[2,3] Here we describe a novel photoisomerization in which $\mathbf{1}^{\bullet+}$ undergoes *homoaromatization*[4] by 1,5-closure to yield the bridged 1,4-bishomobenzene (bicyclo[3.3.0]octa-2,6-diene-4,8-diyl) radical cation[5] $\mathbf{2}^{\bullet+}$ at temperatures as low as 80 K, a symmetry-allowed reaction in which the excited state of $\mathbf{1}^{\bullet+}$ correlates adiabatically with the ground state of $\mathbf{2}^{\bullet+}$. This photoisomerization is responsible for the previously reported photochromic effect in this system.[6]

Scheme I outlines the protocol of the experiments in which the radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ were first generated independently by the radiolytic oxidation of **1** and semibullvalene (**3**), respectively,

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† The diyl parent of the radical cation may also be named bicyclo[3.3.0]-octa-3,7-diene-2,6-diyl, these two equivalent valence-bond structures reflecting its bis(allyl) character.

(1) Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125 and references therein.

(2) Dessau, R. M. *J. Am. Chem. Soc.* **1970**, *92*, 6356.

(3) Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* **1969**, *91*, 7521.

(4) A referee has objected to the use of the terms *aromaticity* and *homoaromaticity* for radical ions on the grounds that cyclic delocalization of an uneven number ($4n + 1$ or $4n + 3$) of π electrons does not entail aromatic stabilization of the type found in systems containing cyclic arrays of $4n + 2$ electrons. The advantage of such a strict definition, however, must be balanced against the apparent usefulness of these terms for describing spectroscopic and chemical studies of open-shell systems related to aromatic or homoaromatic molecules through oxidation or reduction, as judged by a considerable body of extant literature on this subject. We feel that the latter consideration outweighs the former, and elect to follow current practice in this respect.

(5) Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1973**, *95*, 3473. These authors briefly conjectured that the photochromism of $\mathbf{1}^{\bullet+}$ reported in Figure 16 of their detailed paper on the electronic spectra of aromatic hydrocarbon radical ions could be due to a conformational change of the cyclooctatetraene radical cation (e.g., from the tub to the crown shape). A further photobleaching effect on the product radical cation (now identified as $\mathbf{2}^{\bullet+}$) was also described and has been confirmed in the present work. We thank a colleague and a referee for kindly bringing this report to our attention.

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