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 $\mathbf{2a}^{\bullet+}$ and $\mathbf{2b}^{\bullet+}$ 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]

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(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

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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.

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(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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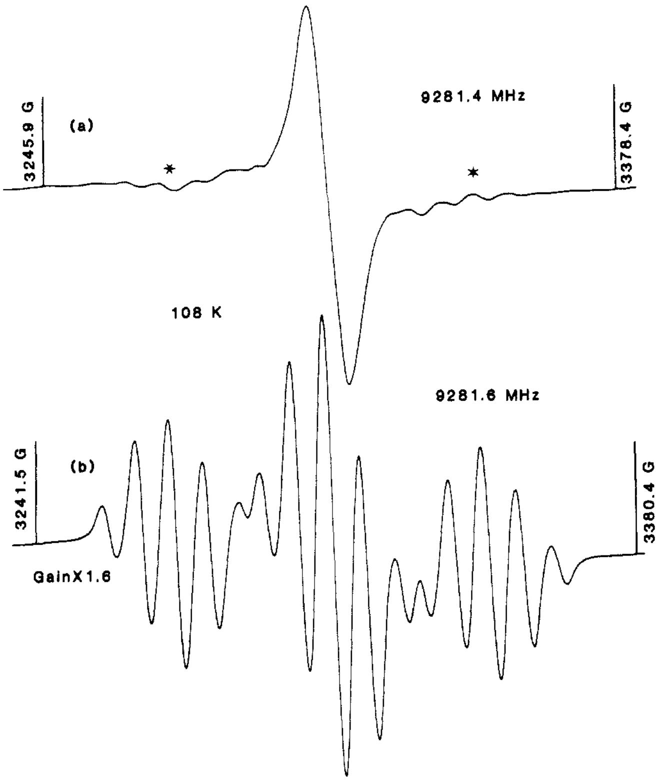
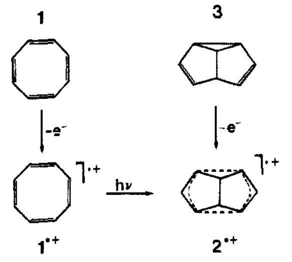


Figure 1. First-derivative ESR spectra recorded at 108 K from a 77-K γ-irradiated (dose, 0.25 Mrad) solid solution (0.5 mol %) of cyclooctatetraene in $CF_2ClCFCl_2$ (a) before and (b) after exposure to visible light (λ > 480 nm) from a tungsten lamp. The spectra in a and b are assigned to the cyclooctatetraene and bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cations, respectively. The weak signals denoted by asterisks in spectrum a occur at approximately the same line positions as the strong photoinduced signals in b.

Scheme I



in Freon matrices at 77 K.[7] The photoisomerization of $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ by exposure to visible light was then observed, both ESR and electronic absorption (EA) spectroscopy being used (vide infra) to establish that the photoisomerization product was identical with the radical cation generated directly from **3**.[5]

As shown in the top part of Figure 1, the ESR spectrum of $\mathbf{1}^{\bullet+}$ in the $CF_2ClCFCl_2$ matrix is a broad singlet (ΔH_{pp} = 8–12 G, depending on matrix and temperature) consistent with the typical line width of 3–5 G in these solids and the smaller 1.5-G hyperfine splitting to eight equivalent hydrogens observed for this radical cation in the liquid state.[2] Exposure of the sample to visible light from a tungsten lamp resulted in the extremely rapid and complete conversion of the singlet signal to the hyperfine pattern ($a(2H_\beta)$ = 36.2 G, $a(4H_\alpha)$ = 7.7 G, g = 2.0029 (3)) shown in the bottom part of Figure 1. This well-resolved spectrum is identical with that generated by the radiolytic oxidation of **3** and can be unequivocally assigned to $\mathbf{2}^{\bullet+}$.[5]

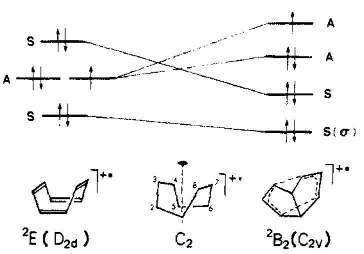


Figure 2. Orbital symmetry correlation diagram for the 1,5-closure of the cyclooctatetraene radical cation to the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation.

The striking photochromic effect previously reported in glassy matrices[6] was also observed in carrying out the ESR experiments in polycrystalline Freon solids ($CFCl_3$, CF_3CCl_3, and $CF_2ClCFCl_2$), and this prompted us to check the transformation from $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ by EA spectroscopy in a Freon glass.[8] In precise agreement with the band positions reported by Shida and Iwata,[6] we found that samples of $\mathbf{1}^{\bullet+}$ were bright red with a strong absorption band in the visible region (λ_{max} = 507 nm), which was replaced on photobleaching with light from a tungsten lamp by two bands with λ_{max} values at 399 and 635 nm,[9] the sample turning royal blue. Furthermore, these new bands matched the EA spectrum of $\mathbf{2}^{\bullet+}$ generated from **3**, thereby corroborating the ESR evidence for the isomerization of $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$.

The 507-nm (2.45-eV) absorption band of $\mathbf{1}^{\bullet+}$ can be assigned to the allowed transition in D_{2d} symmetry from the $^2A_1(\pi)$ ground state to the $^2E(\pi)$ lowest Koopmans excited state. Although this transition energy is almost twice as large as the 1.36-eV gap between the $5a_1$ and 7e orbital energies in the *neutral* cyclooctatetraene molecule (−8.42 and −9.78 eV, respectively, as determined from the vertical ionization potentials obtained by photoelectron spectroscopy[10]), this discrepancy can be reconciled by taking into account the changes in orbital energies introduced by the more planar geometry of the radical cation.[3] Essentially, a flattening of the cyclooctatetraene ring occurs on ionization, which stabilizes the lower orbitals (7e and especially $4b_2$) in the π manifold but destabilizes the highest $5a_1$ orbital, the resulting decrease in energy of the filled orbitals more than compensating for the destabilization of the singly occupied $5a_1$ orbital in the radical cation. As a result, the energy gap between the $5a_1$ and 7e orbitals widens on going to the radical cation. This qualitative explanation is confirmed by an MNDO calculation of the Koopmans energies for the neutral molecule at the cation geometry,[11] the λ_{max} value of 505 nm so obtained[12] for the $^2A_1 \rightarrow {}^2E$ transition being in remarkably close agreement with the experimental value of 507 nm.

The symmetry-allowed character of photoisomerization from the ^2E excited state of $\mathbf{1}^{\bullet+}$ to the $^2B_2$ ground state of $\mathbf{2}^{\bullet+}$ is illustrated by the orbital symmetry correlation diagram in Figure 2. The ^2E state of $\mathbf{1}^{\bullet+}$[10] has the π occupancy $(4b_2)^2(7e)^3(5a_1)^2$ while the $^2B_2$ state of $\mathbf{2}^{\bullet+}$[5,13] has the electron configuration $(a_1(\sigma))^2(a_1(\pi))^2(b_1(\pi))^2(b_2(\pi))^1$. The essential feature of the diagram is the recognition that the C_2 symmetry element shown in the center[14] is conserved in the process of 1,5-addition, and that this symmetry element bisects the σ bond being formed.[15] Accord-

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ingly, the orbitals are labeled as symmetric (S) or antisymmetric (A) with respect to this C_2 operation, and it is clear that the ^2E state of **1**$^{\bullet+}$ correlates adiabatically with the $^2B_2$ ground state of **2**$^{\bullet+}$. Similarly, it is readily deduced that since the $^2A_1$ ground state of **1**$^{\bullet+}$ correlates with a $^2A_1$ highly excited state of **2**$^{\bullet+}$, the ground-state reaction is state-symmetry forbidden if C_2 symmetry is maintained. Although no thermal isomerization was observed in the accessible matrix temperature range up to 150 K, a ground-state reaction at higher temperature obviously cannot be ruled out, especially since the C_2 symmetry restriction could well be relaxed in the course of such a reaction. However, AM1-UHF calculations for the ground-state radical cations indicate that **1**$^{\bullet+}$ is more stable than **2**$^{\bullet+}$ by ca. 10 kcal/mol.

Finally, we note that while the general applicability of electrocyclic processes to the photochemical isomerization of radical cations has recently been quite properly questioned,[16] the discovery of this novel reaction confirms that at least a subset of photoisomerizations can display true electrocyclic character. Specifically, the title reaction clearly accords with a concerted synchronous pathway from the *lowest* reactant excited state to the product ground state with conservation of orbital symmetry.

Acknowledgment. We thank Dr. Thomas Bally, the referees, and Professors S. F. Nelsen and T. Shida for providing helpful comments on the preprint of this paper. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-FG05-88ER13852).

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Shape-Selective Cleavage of tRNA$^{\mathrm{Phe}}$ by Transition-Metal Complexes

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In order to determine the biological and chemical functions of RNA molecules, an understanding of the tertiary folding patterns of these molecules is required. At present, there is a considerable amount of information on the three-dimensional conformations of small transfer RNA molecules based upon crystallographic[1-4] and NMR[5] characterizations. In contrast, little is known about the folding patterns of other RNA molecules. Enzymatic and chemical probes are becoming increasingly more important to detect structural variations, yet the number of structure-specific reagents for mapping RNA is limited.[6-8] In our laboratory, there has been considerable effort in the design of shape-selective probes of DNA structure.[9] In particular, the complexes tris(1,10-phenanthroline)ruthenium(II) [Ru(phen)$_3^{2+}$], tris(3,4,7,8-tetramethylphenanthroline)ruthenium(II) [Ru(TMP)$_3^{2+}$],[10] tris(4,7-diphenyl-1,10-phenanthroline)rhodium(III) [Rh(DIP)$_3^{3+}$],[11] and bis(phenanthroline)(9,10-phenanthrenequinone diimine)rhodium(III) [Rh(phen)$_2$phi^{3+}][12] have been shown to target local variations in conformation along the DNA helix and, upon photoactivation, to induce DNA strand scission, thereby marking sites of alternate structure. We report here that these transition-metal complexes are capable also of shape-selective cleavage of natural, structured RNA. This cleavage involves the same chemical schemes as found with DNA and follows the same patterns of recognition, matching the shape of the metal complex to the nucleic acid structure.

Cleavage by the metal complexes was assayed on yeast tRNA$^{\mathrm{Phe}}$, a well-characterized[1-3] RNA. Fragmentation patterns are shown in Figure 1. At added ruthenium concentrations of 2.5 μM and irradiation in the MLCT band for 20 min, the ruthenium complexes efficiently cleave RNA, but only after treatment with aniline. Reactions with Ru(TMP)$_3^{2+}$ and Ru(phen)$_3^{2+}$ (Figure 1A) reveal cutting preferentially at guanine residues. HPLC analysis[12] does not show the liberation of free bases after aniline treatment, and high-resolution electrophoresis points to the production of 5′-phosphate and 3′- or 2′-phosphate termini.[13] These cleavage results are equivalent to those obtained on DNA[10] and are consistent, as with DNA, with attack on the nucleic acid base (with guanine most reactive) in a reaction mediated by singlet oxygen, generated by photoexcitation of the ruthenium complex. The cleavage chemistry differs considerably for the rhodium complexes. As shown in Figure 1B, at a 2.5 μM Rh(DIP)$_3^{3+}$ concentration, cleavage is observed after 2 min of irradiation at 313 nm; with 10 μM Rh(phen)$_2$phi^{3+}, cleavage is found after 4 min of irradiation at 365 nm. No preferred base composition is apparent in cleavage; aniline is not required for fragmentation; and HPLC analysis[12] shows the release of free nucleic acid bases. After cleavage with these complexes, high-resolution experiments also indicate both 5′-phosphate and 3′- or 2′-phosphate termini.[13] Also, specificity in cleavage on the RNA molecule is evident. Based upon these data, photoinduced cleavage by the rhodium complexes, therefore, appears to occur through a direct oxidative path, and the target is the nucleic acid sugar, also consistent with results found earlier with DNA.[9,12] In all cases, no RNA cleavage was observed in the presence of light or metal alone. Competition experiments also indicate that cleavage on tRNA by the metal complexes is comparable in efficiency to cleavage on double-stranded DNA.

The site selectivities associated with this cleavage chemistry can be understood by superimposing the results onto the three-dimensional structure of the tRNA.[1] Figure 2A displays cleavage results for the ruthenium complexes. Somewhat different patterns of cleavage are observed for the two ruthenium complexes, despite the fact that they share a $^1O_2$-mediated reactivity.[14] The different site selectivities must then necessarily be determined by their different binding characteristics, which are governed only by their different molecular shapes.[15] All guanine residues except G24[16] are cleaved upon photolysis with Ru(phen)$_3^{2+}$. Ru(phen)$_3^{2+}$ also

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(13) The presence of 5′- and 3′- or 2′-phosphate termini is based upon the comigration of cleaved fragments with products of chemical sequencing reactions (diethylpyrocarbonate or hydrazine followed by aniline treatment) and the lack of correspondence to fragment mobilities following alkaline hydrolysis.

(14) Ru(TMP)$_3^{2+}$ and Ru(phen)$_3^{2+}$, at higher concentrations ($\geq$10 μM), cleave all guanine residues. Understandably, under such conditions, the local singlet-oxygen concentration becomes greater, increasing the rate of reaction at all guanine sites.

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