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Access to an Excited State via the Thermal Ring-Opening of a Cyclopropylidene

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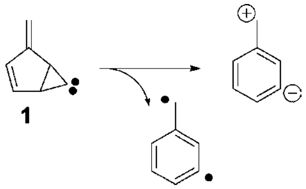
ABSTRACT

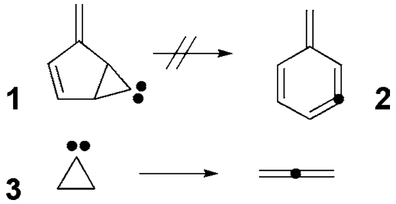


Thermal generation of singlet excited states is unusual in organic chemistry. The potential energy surface for the thermal ring-opening of 4-methylene-bicyclo[3.1.0]hex-2-ene-6-ylidene (1) was calculated at the CASSCF level of theory and found to produce α,3-didehydrotoluene in its biradical ground state (S_0) and/or its zwitterionic excited state (S_1).

The thermal generation of an excited state is not commonplace in organic chemistry. But nature affords a wonderful example in the chemiluminescence of oxyluciferin found in fireflies, where the thermal rupture of a 1,2-dioxetanone moiety produces carbon dioxide and an excited-state carbonyl.[1] 1,2-Dioxetanes are also known to produce excited-state products, primarily triplets, upon thermal fragmentation.[2] Computational studies on 1,2-dioxetane and its tetramethyl derivative show the ground-state and excited-state surfaces coming close to one another along the reaction path.[3] This communication presents computational results of a very different ring-opening that also shows ground- and excited-state surfaces coming close to each other along the reaction path, but this time it is a singlet excited state that appears to be thermally accessible.

Exploration of the ring-opening of 4-methylene-bicyclo[3.1.0]hex-2-ene-6-ylidene (**1**) was prompted by our interest in the cyclic allene 6-methylene-1,2,4,-cyclohexatriene (**2**).[4] We chose this avenue to **2** because cyclopropylidenes are known to generate both unstrained and strained allenes (Scheme 1).[5] However, the present calculations suggest that the ring-opening of the cyclopropylidene (**1**) does *not* lead to the expected cyclic allene (**2**); rather it leads to α,3-didehydrotoluene in its biradical ground state (S_0) and/or the zwitterionic excited state (S_1). This result is of particular interest because both states of α,3-didehydrotoluene have been considered as possible intermediates in the cyclization of (*Z*)-1,2,4-heptatrien-6-yne in methanol.[4,6]

Scheme 1. Ring-Opening of Cyclopropylidenes.



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(1) Lead references for luciferin chemistry: (a) White, E. H.; Roswell, D. F. *Photochem. Photobiol.* **1991**, *53*, 131. (b) Branchini, B. R.; Murtiashaw, M. H.; Magyar, R. A.; Portier, N. C.; Ruggiero, M. C.; Stroh, J. G. *J. Am. Chem. Soc.* **2002**, *124*, 2112. (c) Orlova, G.; Goddard, J. D.; Brovko, L. Y. *J. Am. Chem. Soc.* **2003**, *125*, 6962.

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The ground state of **1** at the B3LYP level is the closed-shell singlet; the triplet is 14.1 kcal/mol higher in potential energy (PE). For comparison, the ground state of **3** is also the closed-shell singlet, with the triplet calculated to be 13.8 ± 0.3 kcal/mol higher in PE.[7] Both UB3LYP and CASSCF methods[8−11] were employed to explore the ring-opening of **1**. The PE barrier was found to be 7.2 kcal/mol at the CASSCF level and 3.1 kcal/mol at the B3LYP level. These results are consistent with the computational survey of barriers to the ring-opening for various cyclopropylidenes by Bettinger et al.[12] When the reaction path (i.e., the intrinsic reaction coordinate, IRC) for the ring-opening of **1** was mapped, two interesting results appeared. First, the product was found to be the α,3-didehydrotoluene biradical rather than the cyclic allene **2**. Second, the CASSCF(8,8) IRC was found to exhibit an unusual change in slope (circled in Figure 1) shortly after the transition structure (TS). In an effort to understand this feature, state-averaged (50:50/S_0:S_1) CASSCF-(8,8) calculations were carried out on selected geometries along the CASSCF(8,8) S_0 IRC in order to estimate the energy difference between S_0 and S_1. In Figure 1, one can see that the S_0 and S_1 surfaces come close to one another near the place where the change in slope of the S_0 IRC occurs.

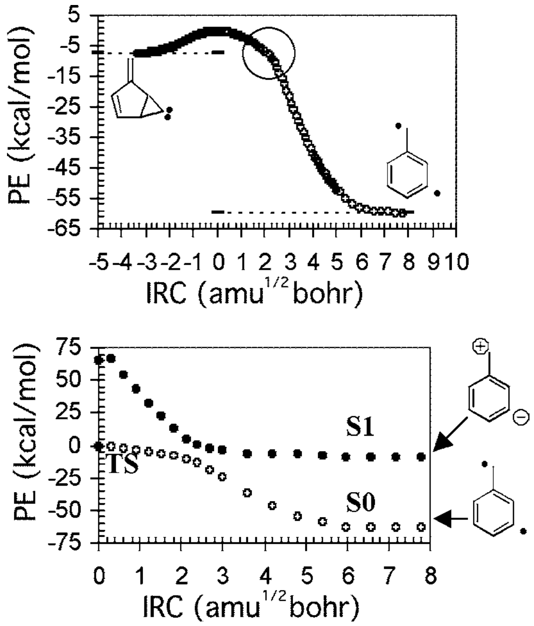

Figure 1. Top: CASSCF(8,8)/6-31G(d) IRC for the ring-opening of **1**. Bottom: State-averaged (50:50/S_0:S_1) CASSCF(8,8)/6-31G-(d) calculations along the CASSCF(8,8)/6-31G(d) IRC. Rxn means Reaction. Energies are relative to the transition structure.

The closeness of these surfaces implied a possible crossing nearby, and, in fact, a conical intersection[13] (CI) was discovered near the TS for the ring-opening. Figure 2 displays these two structures for comparison. To assess the possibility of direct access to the CI from the TS, a linear-synchronous transit (LST) from the TS to the CI was generated (Figure 3).[14] CASSCF(8,8) calculations along the LST showed a 3.1 kcal/mol barrier between the TS and the

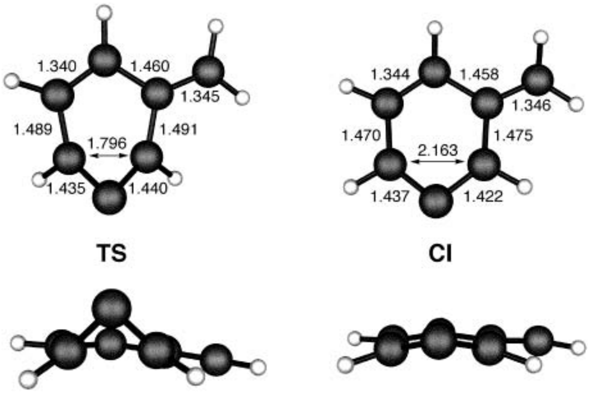

Figure 2. Comparison of geometries: the CASSCF(8,8) geometry of the cyclopropylidene transition structure (TS) and the state-averaged (50:50/S_0:S_1) CASSCF(8,8) geometry of the conical intersection (CI).

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(10) Complete active space self-consistent field (CASSCF) calculations were carried out with the Gaussian 98 and GAMESS programs. The CASSCF(8,8) active space of **1** included two bonding and two antibonding π orbitals in addition to the nonbonding π-type and σ-type orbitals. The CASSCF(8,8) active space for the cyclic allenes consisted of eight electrons in four bonding and four antibonding π orbitals. The CASSCF(4,4) active space for the cyclic allene (**1**) consisted of four electrons in two bonding and two antibonding π orbitals for the two π bonds of an allene. The CASSCF(8,8) calculations on α,3-didehydrotoluene included three bonding and three antibonding π orbitals, 1 nonbonding π-type orbital, and 1 nonbonding σ-type orbital. State-averaged calculations were performed with GAMESS. Gaussian 98 was used for calculations with Hartree−Fock (HF) and Becke's three-parameter hybrid functional with the Lee−Yang−Parr correlation functional (B3LYP).[11] All calculations used the 6-31G(d) basis set, unless stated otherwise. The conical intersection search was performed with Gaussian 98.

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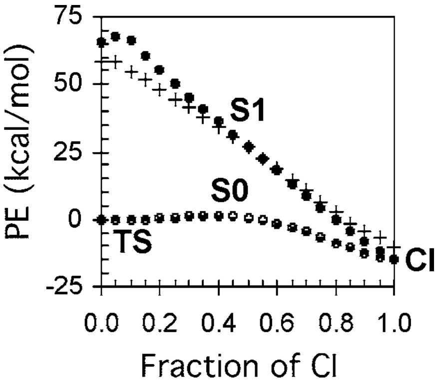

Figure 3. Linear-synchronous transit from the TS to the CI. Open (S_0) and filled (S_1) circles are the state-averaged (50:50/S_0:S_1) CASSCF(8,8)/6-31G(d) results. Dashes and pluses are the UB3LYP (S_0) and TDUB3LYP (S_1) results.

CI. State-averaged (50:50/S_0:S_1) CASSCF(8,8) calculations reduced this barrier to 1.4 kcal/mol, while UB3LYP calculations found it to be only 0.4 kcal/mol.[15] Given that the LST is not necessarily the lowest energy pathway and that the estimated barrier along the LST is quite small, it seems plausible that a barrierless pathway from the TS to the CI exists.

The principal electronic configuration of the carbene in its lowest singlet state is like that of singlet methylene, i.e., one in which the divalent carbon has a lone pair in the plane of the three-membered ring and an empty p-like orbital perpendicular to the ring. If the ring opening were to occur with this configuration persisting as the principal contributor, the product would be the zwitterionic excited state of α,3-didehydrotoluene. However, since the ground state of α,3-didehydrotoluene is the biradical, the system encounters a surface crossing during the reaction, hence the conical intersection.

The shapes of the IRC (Figure 1) and the LST (Figure 3) suggest that the conical intersection is sloped.[13,16] This detail is important because a sloped conical intersection (Figure 4) can allow for access to the S_1 surface from the S_0 surface.[16] Consequently, the ring-opening of 4-methylene-bicyclo-[3.1.0]hex-2-ene-6-ylidene apparently has the potential to generate α,3-didehydrotoluene in its biradical ground state and/or zwitterionic excited state.

If all of the reactive trajectories for the ring opening passed exactly through the conical intersection, then a Landau−Zener analysis[17] would predict formation of the zwitterionic state with unit efficiency, since, by definition, the energy gap between the crossing diabats is zero at that point. However, in reality, the molecular distortions due to normal vibrational motion will cause most trajectories to pass through the CI region with geometries that lift the exact degeneracy and thereby reduce the efficiency of generation of the excited state. It consequently seems likely that thermal ring opening of **1** will afford both electronic states of α,3-didehydrotoluene, but the ratio is hard to predict without a nonadiabatic dynamical simulation.

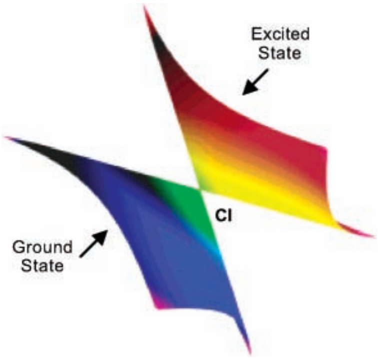

Figure 4. Sloped conical intersection.

The failure to form cyclic allene **2** from the ring-opening of **1** was investigated further by carrying out CASSCF calculations with geometry optimizations at several levels up to CASSCF(8,8)/6-311G(d). None of these calculations resulted in a local minimum corresponding to structure **2**.[18] Instead, all converged to the α,3-didehydrotoluene biradical.

This result prompted re-examination of the RB3LYP calculations that had led to the proposal of **2** as a local minimum.[4] It was found that the wave function derived from the RB3LYP density was unstable with respect to unrestricted symmetry breaking. A UB3LYP geometry optimization again converged to the biradical state of α,3-didehydrotoluene. Thus, the present calculations and earlier experiments[4] now seem consistent in ruling out cyclic allene **2** as an interceptible intermediate.

This conclusion stands in interesting contrast to the results of the calculations by Engels et al. on the apparently similar

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[13] Robb, M. A.; Garavelli, M.; Olivucci, M.; Bernardi, F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2000; Vol. 15, pp 87−146.

[14] Linear combination of the CASSCF(8,8) geometry of the cyclopropylidene transition structure and the state-averaged (50:50/S_0:S_1) CASSCF-(8,8) geometry of the conical intersection was generated in steps of 0.1 to create the LST in Figure 3.

[15] UB3LYP (S_0) and TDUB3LYP (S_1) qualitatively reproduced the shape of the CASSCF surface, which is consistent with the results of: Fantacci, S.; Migani, A.; Olivucci, M. *J. Phys. Chem. A* **2004**, *108*, 1208.

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[17] (a) Landau, L. D. *Phys. Z. Sowjetunion* **1932**, *2*, 46. (b) Zener, C. *Proc. R. Soc. (London)* **1932**, *A137*, 696.

[18] CASSCF(2,2)-optimized cyclic allene[4] was used for the initial geometry of a CASSCF(4,4) optimization. The CASSCF(4,4)-optimized geometry was then used as an initial geometry for a CASSCF(8,8)-constrained optimization where two dihedral angles (C1−C6−C5−C4 and C3−C4−C5−C6) were frozen to the CASSCF(4,4) values (15.593 and 10.102°, respectively). The geometry from the constrained optimization was used as the initial geometry for a full optimization at the CASSCF(8,8) level. This optimization led to a planar geometry, i.e., the biradical. A CASSCF(8,8) optimization with a triple-ζ basis set, 6-311G(d), starting from the CASSCF(4,4)-optimized geometry, also led to a planar geometry, the biradical. A CASSCF(8,8) transition structure search from the CASSCF-(8,8)-constrained geometry led to distorted structures and was not close to convergence after 100 optimization steps. A stability analysis of the cyclic allene from the RHF and RB3LYP calculations demonstrated that the restricted wave functions were unstable. For the RHF-optimized cyclic allene, there was an open-shell wave function ($\langle S^2 \rangle = 1.504$) that was lower in energy by 28.4 kcal/mol. For the RB3LYP-optimized cyclic allene,[4] there was an open-shell wave function ($\langle S^2 \rangle = 0.501$) that was lower in energy by 1.81 kcal/mol.

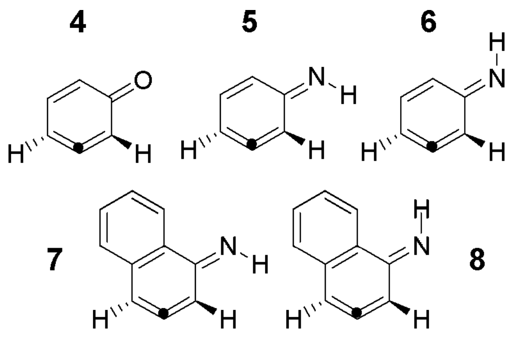

Figure 5. Substituted cyclic allenes.

structure 2,3,5-cyclohexatrienone (**4**), which *is* found to be a local minimum on the PE surface.[19] Apparently, the balance between planar biradical and nonplanar cyclic allene structures is close in this class of molecules. The former acquires the benefit of aromaticity at the price of assigning two electrons to effectively nonbonding orbitals, whereas the latter enjoys a more-or-less closed-shell electronic structure at the cost of strain and loss of aromatic stabilization. The computational results on **2** and **4** suggest that the strength of the π bond to the exocyclic substituent may be sufficient to tip the balance one way or the other, with the stronger π bond of the carbonyl favoring the cyclic allene structure. UB3LYP calculations on the corresponding imines **5** and **6** (Figure 5) suggest that the C═N π bond is not strong enough to have the same effect, since no local minima corresponding to these structures could be found. However, by decreasing the benefit of aromaticity through benzannelation, the cyclic allenes, **7** and **8**, appear as local minima.

In summary, this communication has presented a prediction that the thermal ring opening of **1** should provide access to the first singlet excited state of α,3-didehydrotoluene and has outlined a possible rationale for the lack of a local minimum for cyclic allene **2**.

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Supporting Information Available: Cartesian coordinates, absolute energies, frequencies, and details for Figures 1 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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