

Theoretical exploration of 4 π -Photocyclization Mechanism of α -Tropone Derivatives

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Abstract

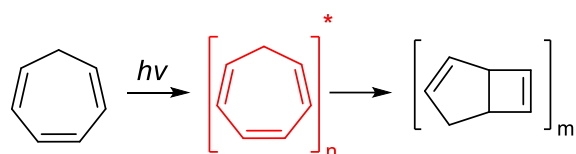
In this study, we employed ab initio methods to investigate the 4π -photocyclization process of substituted α -tropones. Our findings suggest that the initial stages of this reaction occur from low-energy excited states such as S_2 and S_3 , as the barriers in higher-energy excited states are prohibitively high. Additionally, we observed that the presence of acid catalysts or substitution of tropones with electron-donating groups reduces the energy barriers. Regarding the formation of bicyclo[3.2.0]hepta-3,6-dien-2-one derivatives, both T_1/S_0 and S_1/S_0 crossings were identified as plausible pathways for this deactivation process. Specifically, electron-donating groups on the tropones promote degeneracy between S_1 and S_0 states during the return to the ground state. Moreover, T_1/S_0 crossing systems were consistently observed across all investigated scenarios.

Keywords: Ab-initio simulations; 4π -photocyclization; α -tropones; Substituent effects

Introduction

In recent years, the photochemistry of tropone derivatives has garnered significant attention due to its wide-ranging applications in organic synthesis.¹⁻⁷ Specifically, there has been a growing focus on the production of bicyclic compounds resulting from the 4π -photocyclization reaction, owing to its provision of highly versatile building blocks applicable in synthetic methods, natural product synthesis, medicinal chemistry, and materials science.^{6,7} Generally, once tropone derivatives are irradiated (≥ 280 nm), this can lead to cyclization products following the well-known valence isomerization or 4π -photocyclization.^{2,7-10} The 4π -photocyclization involves a light-mediated

electrocyclic reaction, where 4π electrons contribute to forming a σ -sigma bond. In the case of tropone and cycloheptatriene derivatives, this photocyclization process converts the 1,3-diene substrate into cyclobutene. However, the photocyclization reaction route may compete with other processes like hydrogen migration and dimerization.^{11,12} By considering the mechanistic implications associated with the tropone derivatives photocyclization, there are no well-established notions about the reaction intermediates, energy barriers, or even a photochemical reaction mechanism for this concern. Beyond Woodward-Hoffman's standings for the 4π -photocyclization, both experimental and theoretical studies have contributed to its elucidation reaction mechanism mainly in 1,3,5-cycloheptatriene (CHT) derivatives analogous to the tropone system.¹³⁻¹⁷ These investigations suggest that the formation of photoproducts as the bicyclo[3.2.0]hepta-2,6-diene (BHD) via 4π -photocyclization (185-254 nm) occurs fundamentally from low-lying excited states. The most accepted version of this mechanism is depicted in Scheme 1.¹⁷



Scheme 1. Photochemical reaction mechanism for 4π -photocyclization of 1,3,5-cycloheptatriene

Both solution and gas-phase experiments of CHT photolysis reveal that one singlet excited state is involved in BHD derivate formation. Thus, the electronic rearrangements leading to the formation of BHD occur over only the excited reaction surface. Subsequently, the vibrationally excited BHD (or hot BHD) deactivates towards the ground state, or it quickly returns to CHT after losing its excess vibrational energy in collisions. The reaction yield of CHT \rightarrow BHD photoconversion is about 34 percent in solution since the toluene emerges as the main photoproduct. Nevertheless, in practical synthesis, tropone derivatives demonstrate significantly greater photochemical reactivity compared with their CHT counterparts.^{2,5,8,18}

Hence, the methoxytropone, tropolone, and protonated tropone are converted into corresponding bicyclo[3.2.0]hepta-3,6-dien-2-one (BHDO) analogs in short reaction times with considerable yields.^{5,8,18} The production of BHDO-like compounds from tropone primarily occurs in substituted

derivatives or protonated tropone, where electron-donating groups or Lewis's acids notably enhance yields.^{2,19,20} In contrast, the tropones with electron-withdrawing groups undergo 4π -photocyclization with low yields or its irradiation leads to the dimerization via [6+6], [6+4], [6+2], and [4+2] cycloadditions.^{10,12,21,22}

These experimental observations have contributed to elucidating 4π -photocyclization even for complex reaction systems such as colchicine photocyclization.^{23,24} Nonetheless, the specific concerns of 4π -photocyclization remain unclear, indeed its reaction mechanism is not well-established considering the nature of the electronic states involved. For example, regarding CHT photochemistry, it is presumed that a singular electronic state governs the production of the BHDO derivative.^{16,17} Conversely, the carbonyl group presence in tropone derivatives may introduce an alternative photochemical behavior. Hence, there are intersystem crossing conversions (ISC) from ($n-\pi^*$) and ($\pi-\pi^*$) triplet excited states for tropolone and 2-methoxytropone compounds^{19,23}. Note that there are several questions concerning the 4π -photocyclization mechanism in tropone derivatives that emerge from experimental observations: (i) What is the role of triplet and singlet states in forming BHDO derivatives? (ii) are there non-adiabatic transitions involved in the formation of BHDO derivatives? (iii) What is the influence of electron-donating and withdrawing groups on the formation of BHDO derivatives? The responses to this question clearly could contribute to a better understanding of the 4π -photocyclization. This work theoretically explores the 4π -photocyclization of several tropone-substituted systems through the ab initio methods. This methodology has been particularly useful in unraveling photochemical reaction mechanisms such as cycloadditions, electrocyclic, and sigmatropic rearrangements.²⁵⁻³²

Methodology

To study the 4π -photocyclization we have carried out complete-active space self-consistent calculations (CASSCF) with the Dunning double-zeta basis set cc-PVDZ using the ORCA 5.0.3 package.³³ The active space is constituted of 12 electrons distributed in 10 orbitals. Here, the electrons

selected were the 6π -electrons of cyclic fragment and the 2π -electrons of carbonyl bond along with 4π -electron corresponding to oxygen lone pairs. The reaction system comprises substituted tropone as shown in Figure 1 (panel a), including both withdrawing and electrodonating groups, as well as tropone ions derivatives. The 4π photocyclization was modeled by performing a potential energy surface calculation (PES) along the C4-C7 coordinate (Figure 1), wherein was considered four singlets and one triplet within the state-averaged approach.

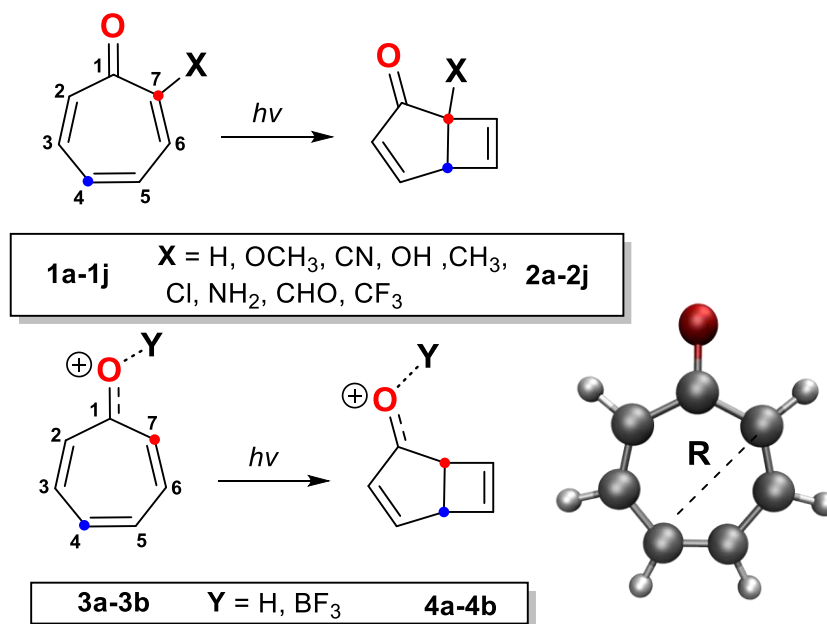


Figure 1. Reaction systems employed in the study of 4π photocyclization of substituted tropolones. Reaction system model

The energies obtained from CASSCF(12,10)/cc-PVDZ level were corrected using the NEVPT2 perturbation methods to incorporate the dynamic correlation into electronic structure modeling of 4π photocyclization. For the characterization of chemical bonding events associated with 4π photocyclization, we used the correlated version of the ELF based on the correlated approach derived by Matito *et al.*^{34,35} Thus, the second-order density matrix for ELF computation was performed from the first-order density matrix in terms of natural orbitals using the Multiwfn software.³⁶

Results and Discussion

There have been reports in the literature that the tropone derivatives undergo the 4π photocyclization reactions near 300 nm.²³ To identify the tropone excited states implied in this reaction, we have carried out excitation calculations considering the $S_0 \rightarrow S_n$ vertical transitions as shown in Table 1. Note that, for 1a and 1c derivatives the $S_0 \rightarrow S_3$ excitation corresponds to a value near 300 nm, however for 1b this wavelength is associated mainly with $S_0 \rightarrow S_2$. Interestingly, the $S_0 \rightarrow S_4$ excitation for 1a, 1b, and 1c, is near 250 nm, wherein the cycloheptatriene derivatives photochemistry is relevant.¹³

Table 1. Wavelengths associated with the $S_0 \rightarrow S_n$ excitations for the tropone (1a), 2-methoxy-tropone(1b), and 2-cyanotropone (1c).

| System | Excitation | Wavelength (nm) | focs |
|--------|-----------------------|-----------------|------|
| 1a | $S_0 \rightarrow S_1$ | 321 | 0,00 |
| | $S_0 \rightarrow S_2$ | 316 | 0,00 |
| | $S_0 \rightarrow S_3$ | 292 | 0,07 |
| | $S_0 \rightarrow S_4$ | 252 | 0,05 |
| 1b | $S_0 \rightarrow S_1$ | 316 | 0,00 |
| | $S_0 \rightarrow S_2$ | 305 | 0,00 |
| | $S_0 \rightarrow S_3$ | 285 | 0,08 |
| | $S_0 \rightarrow S_4$ | 263 | 0,06 |
| 1c | $S_0 \rightarrow S_1$ | 326 | 0,00 |
| | $S_0 \rightarrow S_2$ | 325 | 0,00 |
| | $S_0 \rightarrow S_3$ | 305 | 0,10 |
| | $S_0 \rightarrow S_4$ | 258 | 0,04 |

Following these observations, our calculations for 4π -photocyclization were conducted from the S_4 excited state. Figure 2 depicts the electron charge densities redistribution ($\Delta\rho^{i \rightarrow j}(\mathbf{r})$) resulting from the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions, wherein the electron density accumulation regions are shown in gray, whereas the depletion density regions are in green. For the $S_0 \rightarrow S_1$ excitation in the tropolone, all the C=C double bonds weaken, likewise, the C=O carbonyl bond depletes electron density. Contrarily, the C-C single bonds accumulate electron density from C=O and C=C weakening. Considering the $S_0 \rightarrow T_1$ excitation, similar electron reordering patterns that $S_0 \rightarrow S_1$ process. However, we also have calculated the atomic charge associated with the $\Delta\rho^{i \rightarrow j}(\mathbf{r})$ redistribution descriptor to differentiate the tropolone reactivity in both excited states.

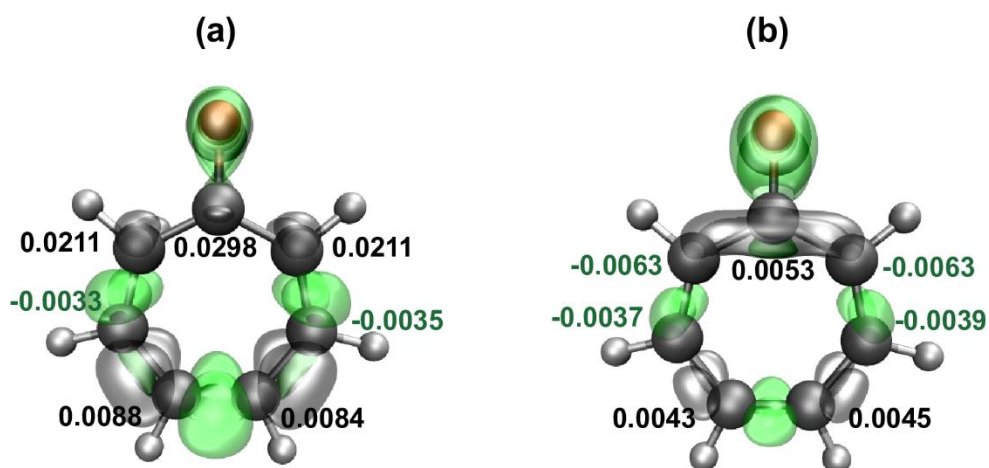


Figure 2. Isosurfaces for electron density redistribution ($\Delta\rho^{i\rightarrow j}(\mathbf{r}) = \pm 0.004$) concern the $S_0 \rightarrow S_1$ (panel a) and $S_0 \rightarrow T_1$ (panel b) transitions for tropolone, respectively. The atomic charges associated with $\Delta\rho^{i\rightarrow j}(\mathbf{r})$ also are showed.

It would be expected that upon excitation, an activation/deactivation of the carbons respectively associated with 4π -photocyclization would occur. However, this pair of carbons (C2-C5 and C7-C4 pairs) gains electron density due to the electronic state change $S_0 \rightarrow S_1$. The remaining carbons of the tropone ring deactivate by the loss of charge density. This reactivity profile allows us to explain the dimerization of tropones following, for example, [6+6] cycloaddition, as carbons with $\Delta\rho^{i\rightarrow j}(\mathbf{r}) < 0$ can interact with carbons whose $\Delta\rho^{i\rightarrow j}(\mathbf{r}) > 0$. This observation is compatible with other studies indicating that $n \rightarrow \pi$ excitation of tropone prevents them from undergoing 4π -photocyclization. Interestingly, even though the $S_0 \rightarrow T_1$ transition is not allowed, the triplet state reactivity predicts the 4π -photocyclization since both C4 and C7 carbons exhibit values of $\Delta\rho^{i\rightarrow j}(\mathbf{r})$ having inverse signs. In other words, the electron density difference between C4 and C7 carbons in the T_1 state could enhance the interaction between these atomic sites, which are directly involved in 4π -photocyclization.

The mechanistic information reference of the 4π -photocyclization is mainly the CHT \rightarrow BHD photoconversion occurring in a single excited state surface. In the case of tropolone derivatives for the S_4 state, the relative energy is essentially ascendent involving barriers of about $100 \text{ kcal mol}^{-1}$, considering the BHDO derivative formation (Figure 3). However, in the case of hydroxytropenium ion the barrier associated with this process is 32 kcal mol^{-1} following a flat behavior up to the formation of bicyclo[3.2.0]hepta-3,6-dien-2-ylideneoxonium.

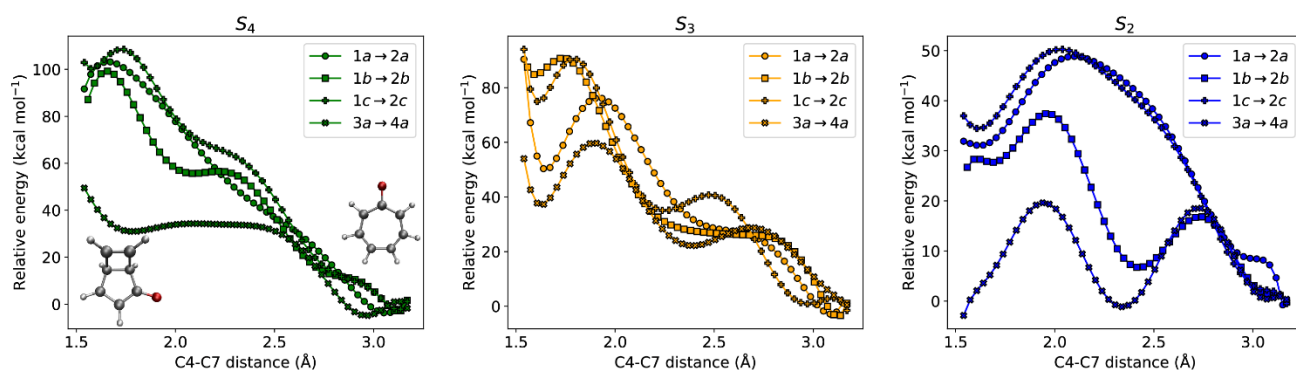


Figure 3. Relative energies for 4π -photocyclization of tropone, 2-methoxytropone, 2-cyanotropone, and hydroxytropenium ion in the S_4 , S_3 , and S_2 excited states.

By considering the S_3 state, there are two energy barriers associated with 4π -photocyclization, the first involves $40\text{--}30\text{ kcal mol}^{-1}$ ($R \approx 2.5\text{ \AA}$), and the second lies on $50\text{--}40\text{ kcal mol}^{-1}$ ($R \approx 1.9\text{ \AA}$) for all the system studied. Interestingly, energy barriers in the S_2 state for hydroxytropenium and 2-methoxytropone are lower than those observed for tropone and 2-cyanotropone. The energy barrier for both tropone and 2-cyanotropone is about 50 kcal mol^{-1} , whereas for the hydroxytropenium ion, two barriers imply both near 20 kcal mol^{-1} . In general, the energy barriers associated with the 4π -photocyclization in the S_4 , S_3 , and S_2 states for tropolone derivatives are relatively high, except for the hydroxytropenium ion. This observation agrees with the literature since the 4π -photocyclization occurs easily once the tropone is treated with a Lewis acid generating the hydroxytropenium ion. More interestingly, tropone and 2-cyanotropone photocyclizations have a reversible character which could be associated with the high barriers observed. It is important to stress that previously calculated relative energy assumes an adiabatic behavior for tropone derivatives photocyclization. However, a proper feature of photochemical processes is the deactivation funnels which implies state crossings. In Table 2 are listed the ΔE_1 and ΔE_2 which correspond to the $E(S_3) - E(S_2)$ and $E(S_2) - E(S_1)$ minimum energy differences obtained from PES calculation.

Table 2. Minimum energy difference between S_3 - S_2 and S_2 - S_1 electronic states for the 4π -photocyclization of tropone, 2-methoxytropone, 2-cyanotropone, and hydroxytropenium ion (kcal mol^{-1}).

| Reaction | ΔE_1 | R | ΔE_2 | R |
|---------------------|--------------|------|--------------|------|
| $1a \rightarrow 2a$ | 2.37 | 2.10 | 1.76 | 3.10 |
| $1b \rightarrow 2b$ | 1.59 | 1.56 | 8.95 | 2.83 |
| $1c \rightarrow 2c$ | 2.34 | 1.71 | 8.50 | 2.55 |
| $3a \rightarrow 4a$ | 1.80 | 2.45 | 1.15 | 3.17 |

Note that the S_3/S_2 crossings associated with the S_3 reaction path involve energies less than $3.0 \text{ kcal mol}^{-1}$. However, the reaction coordinate at this crossing implies $R < 2.1 \text{ \AA}$ for the tropone derivatives except the hydroxytropenium ion, involving geometric configurations more related to the BHDO photoproducts. Therefore, before passing through the S_3/S_2 crossing, the reaction system should overcome the high energy barrier concerning the S_3 state. On the other hand, following the S_2 reaction path, the S_2/S_1 crossings are located at tropone-like configurations ($R \approx 3.0 \text{ \AA}$), wherein the relative energy is low. Nevertheless, for the 2-cyanotropone system, the crossing is located at $R \approx 2.55 \text{ \AA}$ requiring an increase in energy before it can be accessed. These results suggest that the photocyclization could occur from the S_2 state involving deactivation toward low-lying excited states, with the substitution over the tropone ring controlling the viability of the S_2/S_1 crossing. Intending to perform further analysis, Figure 4 illustrates the 4π -photocyclization reaction in the S_0 , S_1 , and T_1 states. The most distinctive feature of the reaction process in low-energy excited states is the presence of possible S_1/S_0 and T_1/S_0 state crossings at $R \approx 2.4 \text{ \AA}$, which direct the deactivation of excited tropone towards BHDO formation derivatives. By considering the T_1/S_0 crossing it is present in whole reaction systems studied involving a full degeneracy between T_1 and S_0 states. Moreover, the S_1/S_0 crossing depends on the substitution over the tropone ring and implies fundamentally nearly degeneracy. However, accessing these crossing points requires overcoming energy barriers in both the S_1 and T_0 electronic states, whereas, for the S_0 state, these crossing points are associated with energy maxima. Indeed, the S_0 barriers involving more than 60 kcal mol^{-1} ($R \approx 2.4 \text{ \AA}$) are extremely high since the BHDO formation does not occur in the ground state from tropone derivatives. In the T_1 state, the energy barriers range from 27 to 37 kcal mol^{-1} , but the energy increases from the tropone derivatives to the T_1/S_0 crossing.

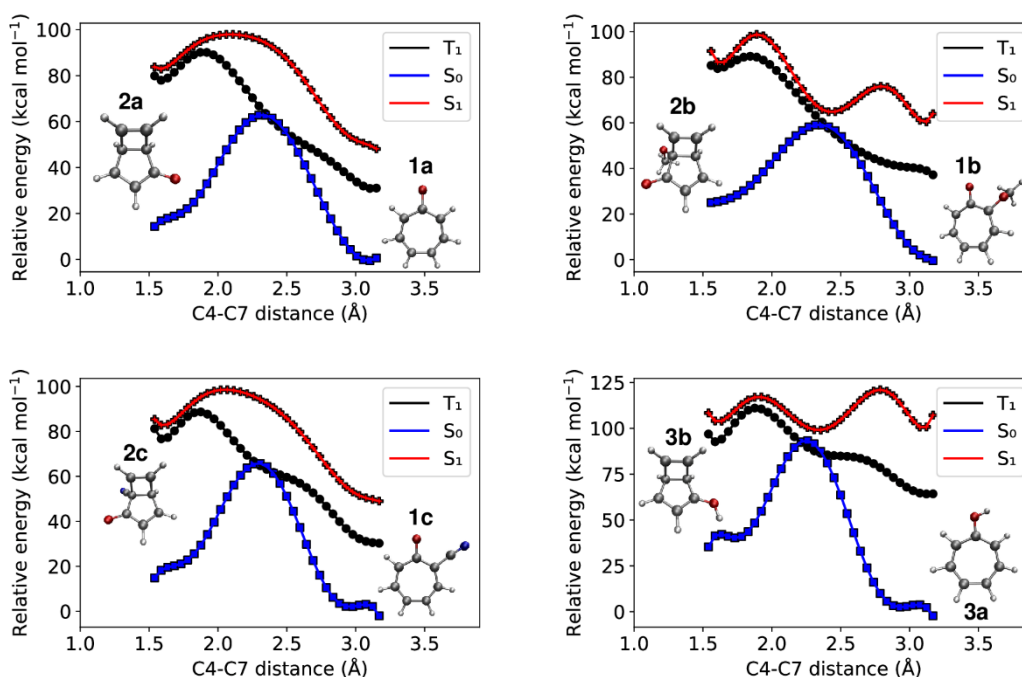


Figure 4. Relative energies for 4π -photocyclization of tropone, 2-methoxytropone, 2-cyanotropone, and hydroxytropenium ion in the T_1 , S_1 , and S_0 excited states.

At the T_1/S_0 crossing the S_1 and S_0 states also can be nearly degenerated, this feature has been reported in many photochemical reactions. Particularly, in the case of 4π -photocyclization, this phenomenon occurs mainly for α -tropones substituted with OH, OCH₃, CH₃, and the troponium ion whose experimental yields and viability reactions are considerable. In such a context, the 4π -photocyclization energy barriers in the S_1 state calculated up to the T_1/S_0 geometry for α -tropones vary depending on the nature of the substituent groups. These barriers differ between α -tropones substituted with electron-withdrawing groups and those with electron-donating groups. For example, for tropone and 2-cyanotropone, the barriers are approximately 42 kcal mol⁻¹, while for methoxytropone and the hydroxytropenium ion, the barriers are 13 and 28 kcal mol⁻¹, respectively. This trend is predominantly observed in other reaction systems, as detailed in the supporting information. Furthermore, this behavior is also demonstrated in the energy formation of T_1/S_0 whose values are reported in Table 3.

Table 3. Energy formation (in kcal mol⁻¹) of the T_1/S_0 crossing for T_1 , S_0 , S_1 , and S_2 states ($\Delta E_{fc} = E(T_1/S_0) - E(R)$). This energy was calculated considering the energy at T_1/S_0 crossing geometry $E(T_1/S_0)$ and the energy at tropone-like geometry $E(R)$.

| System | T_1 | S_0 | S_1 | S_2 |
|--------|-------|-------|-------|-------|
|--------|-------|-------|-------|-------|

| | | | | |
|---------------------|-------|-------|-------|--------|
| $1a \rightarrow 2a$ | 35.54 | 65.37 | 47.34 | 43.36 |
| $1b \rightarrow 2b$ | 24.73 | 60.43 | 2.87 | 50.29 |
| $1c \rightarrow 2c$ | 32.12 | 67.43 | 31.64 | 54.58 |
| $1d \rightarrow 2d$ | 32.17 | 69.70 | 25.65 | 38.08 |
| $1e \rightarrow 2e$ | 33.03 | 74.04 | 14.09 | 51.50 |
| $1f \rightarrow 2f$ | 37.95 | 66.51 | 46.17 | 75.28 |
| $3a \rightarrow 4a$ | 29.81 | 74.21 | -5.95 | 51.63 |
| $3b \rightarrow 4b$ | 27.14 | 93.11 | -0.29 | -13.20 |

Note that for the tropenium ions (3a and 3b), ΔE_{fc} is less than 0, whereas for 2-methoxytropone, 2-hydroxytropone, and 2-methyltropone, ΔE_{fc} ranges from 3 to 26 kcal mol⁻¹. These formation energies are relatively low compared to those of tropone, 2-cyanotropone, and 2-chlorotropone, which have ΔE_{fc} values greater than 30 kcal mol⁻¹. From a mechanistic perspective, low-lying excited α -tropones, both the barriers to S_n , T_n/S_0 crossings, and the degeneracy between S_n , T_n , and the ground states are crucial parameters for producing BHDO derivatives. Figure 5 depicts the geometry of the reaction system at $R \approx 2.4\text{\AA}$ including the gap energies between the S_0 and T_1 states ($\Delta E(S_0-T_1)$) and between the S_0 and S_1 states ($\Delta E(S_0-S_1)$). Interestingly, the S_0 - T_1 degeneracy is present in all the reaction systems studied ($R \approx 2.4\text{\AA}$, see Figure 5), wherein $\Delta E(S_0-T_1)$ is lower than 1.28 kcal mol⁻¹. This degeneracy could be associated with a T_1/S_0 intersystem crossing enabling the $T_1 \rightarrow S_0$ transition.

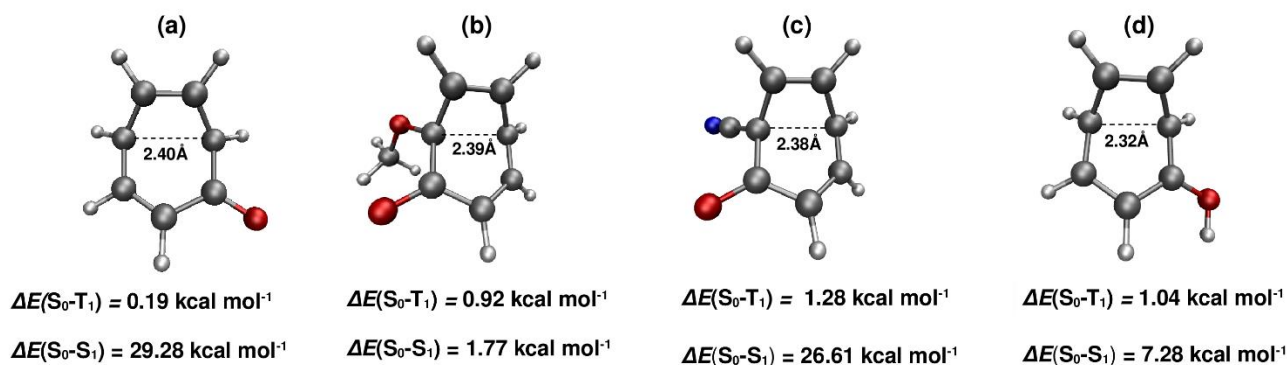


Figure 5. Relative energies for 4π -photocyclization of tropone, 2-methoxytropone, 2-cyanotropone, and hydroxytropenium ion in the T_1 , S_1 , and S_0 excited states.

It is important to stress that the T_1/S_0 crossing exhibits a geometry more like photoproducts than tropone derivatives, involving the out-plane rotation of the C5-C6 bond and the strengthening of the C4-C7 distance. On the other hand, the S_0-S_1 degeneracy is not observed in all reaction systems. For instance, for the tropone and 2-cyanotropone systems, the S_0-S_1 gap is higher compared with the values of 2-methoxytropone and the hydroxytropenium ion systems which exhibit nearly degeneracy. This finding is relevant since the 4π -photocyclization reaction does not occur for all the tropone derivatives, requiring the modification of the tropone ring or using a Lewis catalyst. In such a context, the presence of S_0-S_1 degeneracy could be an important parameter of prediction and/or rationalization of 4π -photocyclization occurrence. Regarding the S_0-T_1 degeneracy in the 4π -photocyclization reaction, it should be mentioned that the $T_1 \rightarrow S_0$ transition is prohibited, indeed experimental studies for CHT photocyclization exclude the involvement of triplet states as deactivation pathways to the ground state. Nonetheless, the C=O group of tropones could imply the participation of triplet states in the BHDO derivatives formation. In this sense, the UV-vis spectrum of 2-methoxytropone, tropolone, and colchicine reveals that the absence of phosphorescence for these compounds could be associated with the rapid deactivation from the T_0 state. Thus, Figure 6 shows the spin-orbit couplings (SOCs) considering the $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ transitions respectively, following the C4-C7 reaction coordinate.

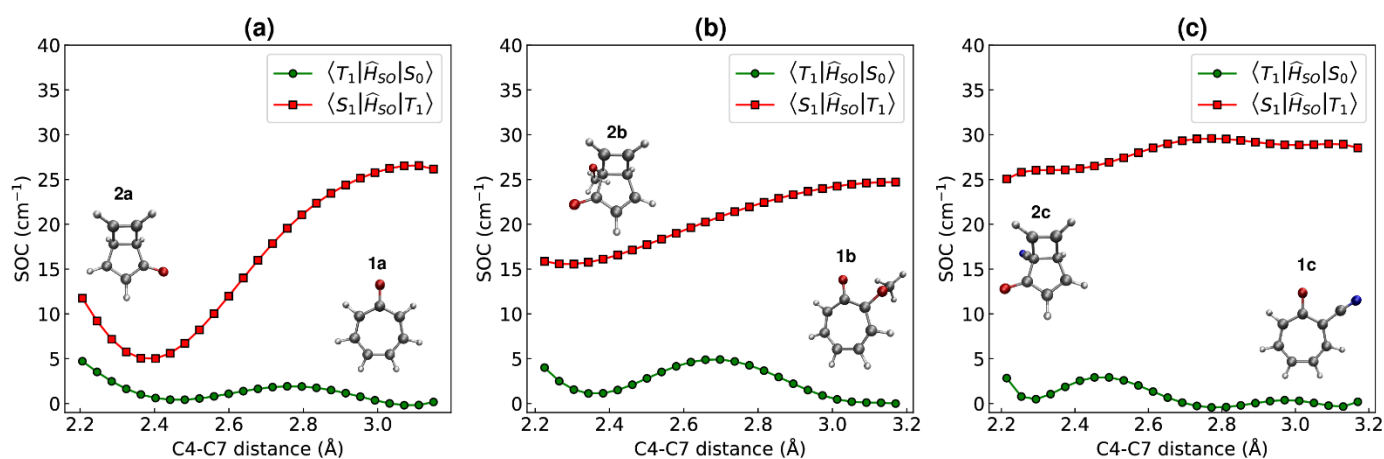


Figure 6. Spin-orbit couplings associated with $T_1 \rightarrow S_0$ and $S_1 \rightarrow T_1$ transitions calculated for 4π -photocyclization of tropone, 2-methoxytropone, 2-cyanotropone.

Note that, the SOC values observed for $S_1 \rightarrow T_1$ transitions are considerably higher than the $T_1 \rightarrow S_0$ one's values. More interestingly, the SOC values are larger with more similar geometries to those of

tropone-type reagents. These values of SOCs oscillate between 5-30 cm^{-1} for $S_1 \rightarrow T_1$, which are considerable values for organic molecules. Notably, at $R \approx 2.4 \text{ \AA}$ the SOC values are high for 2-methoxytropone and 2-cyanotropone compared to tropone. On the other hand, regarding the $T_1 \rightarrow S_0$ transition the SOCs values are relatively small ranging between 1-5.0 cm^{-1} even at $R \approx 2.4 \text{ \AA}$. These values suggest that for 4π -photocyclization, the photoproduct formation via the T_1/S_0 crossing could be unfavored. However, the T_1/S_0 crossing is observed for each reaction system studied here involving a full S_0 - T_1 degeneracy. Furthermore, the experimental photophysical properties of tropone derivatives suggest the triplet states involvement in its deactivation routes. Likewise, some photochemical reactions occurring via $T_1 \rightarrow S_0$ transitions exhibit low values of SOCs.

In addition to the energetical analysis of the 4π -photocyclization reaction, we have carried out a chemical bonding analysis concerning the reaction system at $R \approx 2.4 \text{ \AA}$. The purpose of this exploration is to connect the energetical observations with Lewis's notions of chemical bonding³⁷ phenomena in 4π -photocyclization. In such a context, we used the ELF to obtain a reasonable pair-electron representation³⁷⁻⁴² of the reaction system at both T_1/S_0 and S_1/S_0 crossings. Table 4 reports the electron populations for C-C and C-O bonds at $R \approx 2.4 \text{ \AA}$ for S_1 and T_1 states.

Table 4. Electronic populations of C-C and C-O bonds and C non-bonding centers in tropone derivatives at $R \approx 2.4 \text{ \AA}$ in T_1 and S_1 states involved in 4π -photocyclization.

| <i>Reaction</i> | <i>State</i> | C5-C6 | C6-C7 | C7-C1 | C1-O | C1-C2 | C2-C3 | C3-C4 | C4-C5 | C7 | C4 |
|-----------------------------------|--------------|-------|-------|-------|------|-------|-------|-------|-------|------|------|
| <i>3a</i> \rightarrow <i>4a</i> | T_1 | 3.24 | 2.28 | 2.67 | 1.96 | 2.43 | 3.08 | 2.28 | 2.20 | 0.43 | - |
| | S_1 | 3.16 | 2.24 | 3.00 | 1.81 | 2.24 | 3.80 | 2.42 | 2.26 | - | - |
| <i>1c</i> \rightarrow <i>2c</i> | T_1 | 3.40 | 2.16 | 3.26 | 2.22 | 2.60 | 2.39 | 2.22 | 2.14 | 0.44 | - |
| | S_1 | 3.40 | 2.15 | 2.22 | 2.06 | 3.33 | 2.30 | 3.31 | 2.13 | 0.47 | - |
| <i>1b</i> \rightarrow <i>2b</i> | T_1 | 3.40 | 2.16 | 2.43 | 2.31 | 2.43 | 2.90 | 2.16 | 2.16 | 0.85 | - |
| | S_1 | 3.38 | 2.19 | 2.84 | 2.26 | 2.82 | 2.72 | 3.16 | 2.15 | - | - |
| <i>1a</i> \rightarrow <i>2a</i> | T_1 | 3.31 | 2.17 | 2.20 | 2.12 | 2.27 | 3.28 | 2.31 | 2.21 | 0.42 | 0.58 |
| | S_1 | 3.24 | 2.20 | 2.70 | 2.31 | 2.50 | 3.20 | 2.39 | 2.23 | 0.51 | - |

According to Table 4, the electronic pair structure of the reaction system depends on both the electronic state and the substitution over the tropone ring. However, a common feature in all reaction systems in the S_1 and T_1 states is the C5=C6 double bond formation before returning to the ground state. This is because its electronic population ranges between 3.2e and 3.4e, characteristic values of

double bonds according to ELF topological analysis.⁴⁰ Another distinctive feature is the appearance of non-bonding centers on the C4 and C7 carbons, with populations between $0.4e$ and $0.85e$. This feature is reported in the literature as typical in excited state reactions. In such reactions, centers showing a radicaloid^{43–46} character are formed as a step before the C-C bond formation.

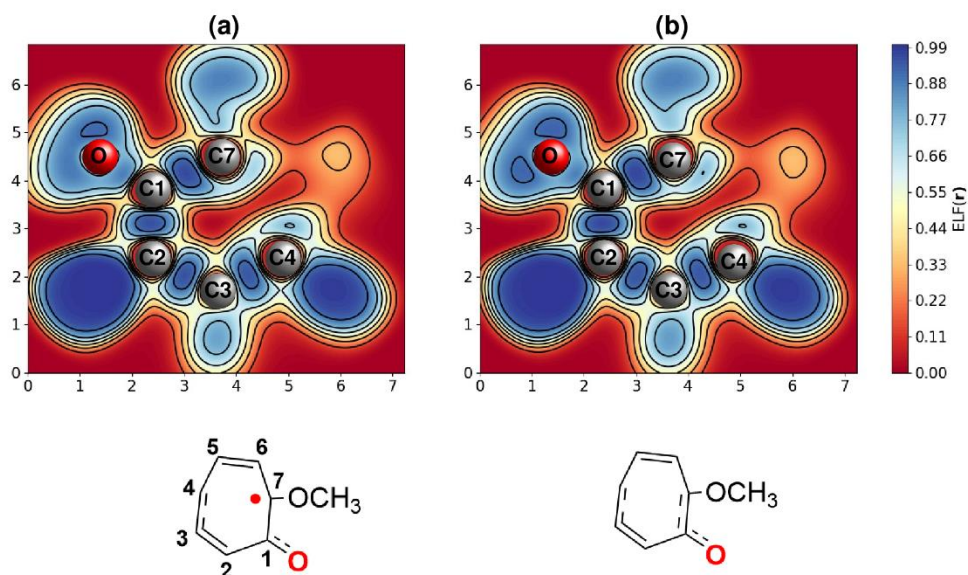


Figure 7. ELF contour plots of the 2-methoxy tropone reaction system at $R=2.4 \text{ \AA}$ illustrate the pair electron density distribution in electronic states T_1 and S_1 (panels a and b) respectively. The ELF values are depicted for the plane formed by the C7, C2, and C4, atoms.

However, according to the data in Table 4, these centers appear mostly in the T_1 state compared to the S_1 state. For the hydroxytropenium ion and 2-methoxytropone, these centers are not observed in S_1 . Interestingly, the non-bonding does not form in the tropone and 2-cyanotropone systems without S_1 - S_0 degeneracy. Figure 7 depicts the contour plots of the ELF function calculated along the plane containing the C7-C2-C4 atoms. Herein are visible regions with high pair localization probability over C7 and C4 atoms corresponding with the non-bonding centers. Note that, such regions are distinguishable in both states, however only for the T_1 state is it possible to associate these with pair probability maxima. Overall, we propose a version of the 4π -photocyclization in α -tropones depicted in Figure 8 based on ab initio calculations.

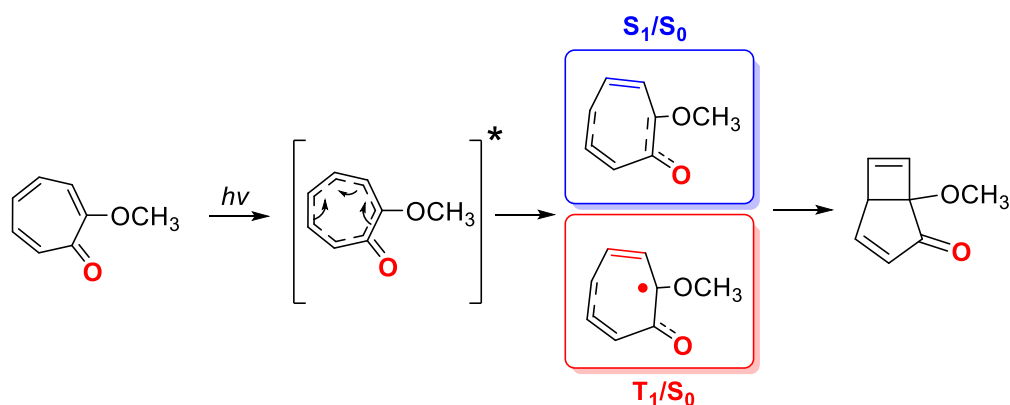


Figure 8. Lewis pair representation for the 4π -photocyclization of 2-methoxytroponone obtained from ELF topological analysis.

Firstly, the C=C double bonds in the troponone ring weaken, followed by out-plane distortion of the ring. The deactivation towards the ground state could be from S_1/S_0 and T_1/S_0 crossings, wherein the T_1 - S_0 degeneracy could be independent of substitution. Contrarily, the S_1 - S_0 degeneracy depends strongly on substitution over the troponone ring, enhanced through electrodonating groups such as OCH_3 or OH . The formation new C=C bond takes place on the excited state surface, whereas the C-C bond forming the bicyclic compound occurs after deactivation to the ground state. If this deactivation occurs from a triplet state, non-bonding centers or radicals may appear. By contrast, if it happens from the S_1 state, these would not form in excited states.

Conclusions

The theoretical exploration of the 4π -photocyclization mechanism of α -troponone derivatives presented in this study provides significant insights into the photochemical behavior of these compounds. Using complete-active space self-consistent field (CASSCF) calculations, we reported the potential energy surfaces of photoconversion of α -troponone into bicyclo[3.2.0]hepta-3,6-dien-2-one derivatives and electronic transitions involved in the reaction pathways. Thus, energy barrier calculations indicate that substituted α -tropones exhibit high barriers in the S_4 , S_3 , and S_2 states considering its 4π -photocyclization. However, the electron-donating presence groups or the formation of hydroxytropenium ions significantly lowers these barriers, thereby making 4π -photocyclization more feasible. Moreover, the occurrence of S_1/S_0 and T_1/S_0 crossings, suggests potential non-adiabatic

transitions that facilitate excited state deactivation towards the ground state. Our findings indicate that the 4π -photocyclization of α -tropone derivatives primarily proceeds via low-lying excited states, with substituent effects notably influencing reaction pathways and energy barriers. Specifically, electron-donating groups on the tropone rings enhance photochemical reactivity by affecting the S_1 - S_0 degeneracy, thereby promoting the formation of bicyclo[3.2.0]hepta-3,6-dien-2-one (BHDO) derivatives. Additionally, our results suggest the involvement of triplet states in BHDO derivative formation through T_1/S_0 intersystem crossings, although further investigation is needed due to the low spin-orbit couplings observed. Finally, this comprehensive theoretical investigation into the 4π -photocyclization of tropone derivatives clarifies the complex mechanistic pathways involved and underscores substituents' critical role in modulating photochemical reactivity.

Acknowledgments

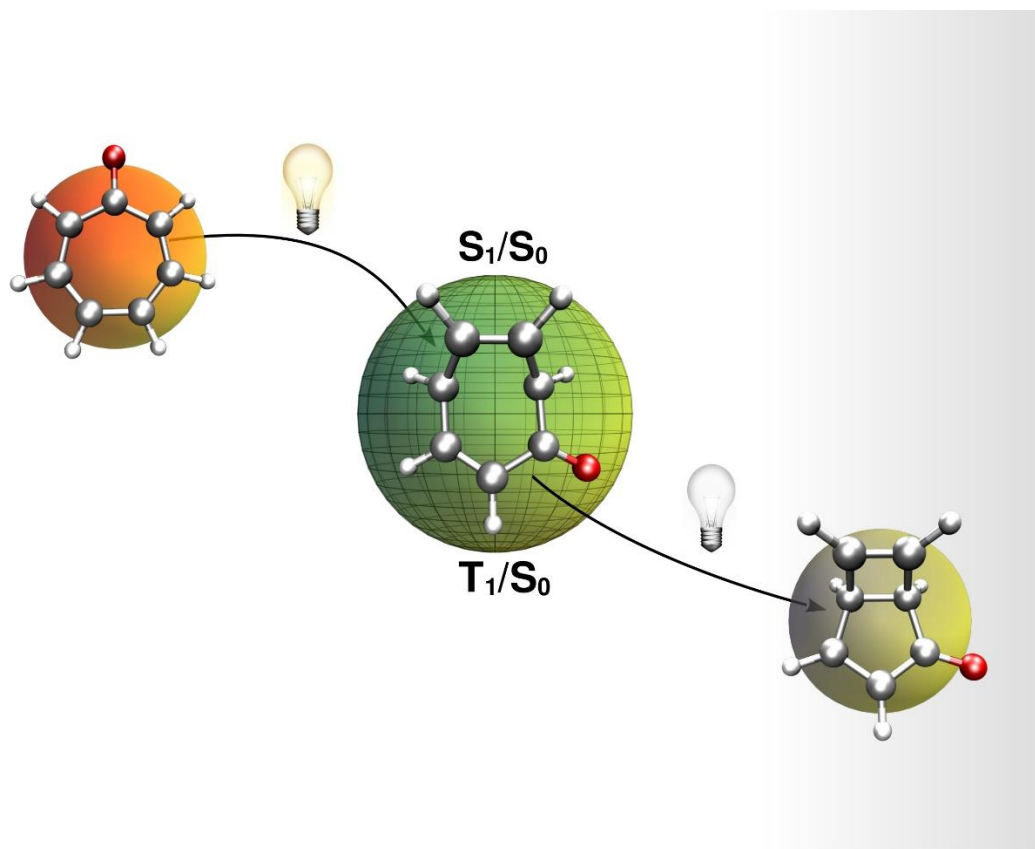
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We employed ab initio methods to investigate the 4π -photocyclization of substituted α -tropones. Our findings reveal that acid catalysts and electron-donating groups reduce energy barriers, facilitating the formation of bicyclo[3.2.0]hepta-3,6-dien-2-one derivatives via T_1/S_0 and S_1/S_0 crossing.