Regular Article

Towards the understanding of the photochemical ring opening and closing mechanisms for spiropyrans using 2H-pyran and the maximum overlap method

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Abstract. A first principle study on 2H-pyran has been carried out to elucidate the photochemical ring opening and closing mechanism of spiropyrans. A systematic study on relative energies using Hartree-Fock, density functional and post-Hartree-Fock methods was carried out to determine an appropriate level of theory for these systems. Second order Møller–Plesset perturbation theory (MP2) shows good agreement with the CCSD calculations, converges at the 6-31+G($2df, p$) basis set level and predicts the closed ring structure as the most stable. The maximum overlap method (MOM) was used to calculate the excited states of both 2H-pyan and the open ring structure 2,4-pentadienal. Excitation of the planar form of 2H-pyran at 189 nm leads to direct photochemical ring opening. Excitation of the open-ring structure at 283 nm causes the reverse process, ring closing, to occur. Our excited state calculations indicate that thermal conversion of the more stable puckered structure of 2H pyran into the planer form needs to take place before the photochemical ring opening can occur.

1 Introduction

During the last 40 years, spiropyrans have attracted intense investigation due to their photochromatic properties. In their ring-closed form, spiropyrans consist of two planer heterocyclic moieties, a pyran and indoline, joined orthogonally via a tetrahedral carbon atom (spirocarbon). This spiro-carbon prevents the conjugation of the two π systems. Upon irradiation with ultraviolet light the pyran ring can open yielding a single conjugated π system with a strong absorption in the visible region.

The reversibility of the photochemical ring-opening was first reported by Bercovici et al. [1] and since then there have been several experimental studies [2–14], including many on substituted spiropyrans and benzopyrans, which were considered as simplified models of spiropyrans. Recently, Buback et al. [11] reported that the ring opening and closing processes of 6,8-dinitro-2′-3′-3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline] (6,8-dinitro BIPS), as shown in Scheme 1, are reversible on a picosecond time scale, and this may lead to applications of spiropyrans as molecular switches.

In contrast to the many experimental studies, there have been relatively few theoretical studies attempting to elucidate the mechanisms for ring opening and closing. This is due, in part, to the difficulty of studying the excited electronic states of such large systems and theoretical work on the excited states of spiropyrans has been limited to a few semi-empirical studies. In 1979, Le Beuze

et al. [15] reported the relative positions of singlet and triplet states of 2H-chromenes at the ground state equilibrium geometry using CNDO/S-CI. More recently, the potential energy surfaces of the ground and lowest excited states of pyrans and chomenes have been studied along the C-O bond cleavage coordinate using constrained geometry optimizations [16,17].

Studies using more accurate methods have focused on using simplified models of spiropyrans including pyran, the ground state of which has been extensively studied [18–21], and benzopyran. In 1997, Celani et al. [22] used CASSCF calculations to propose a conical intersection mechanism for the photochemical ring opening of benzopyran compounds. Their study looked at the first excited singlet state and its potential energy surface along the intrinsic reaction coordinate (IRC). They matched this with the ground state branch of the potential energy surface of pyran and proposed that the photochemical conversion takes place through the intersection of these two branches. A similar explanation for the ring closing mechanism was proposed by Gómez et al. [23] using the ring-opened structure of benzopyran, and a more recent CASSCF study on the ring opening process of pyran by Wang et al. [24] also has proposed a conical intersection mechanism.

Besides these studies on model compounds, Sheng et al. [25] suggested two reaction mechanisms, one singlet and one triplet pathway, for 6-dinitro-BIPS (a substitution of a nitro group in a 6 position) in their TD-DFT

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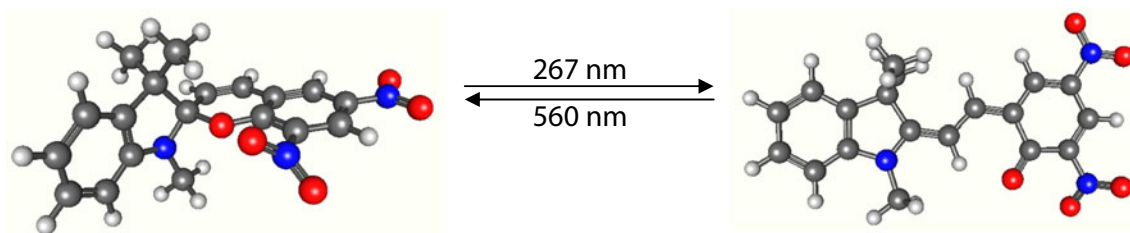
Scheme 1. Schematic for the photochemical ring opening of 6,8-dinitro-BIPS (left) and its ring-opened form (right).

Table 1. Energy differences between the fully optimized trans-2,4-pentadienal (trans-conformer 1) and puckered 2H-pyran structures. A negative energy indicates the closed structure is more stable.

	HF	B3LYP	MP2	CCSD
6-31G	−20.3	−22.7	−37.0	−29.8
6-31G(d)	−23.8	−15.7	−5.2	−8.2
6-31+G	−23.0	−28.9	−38.2	−29.7
6-311G	−20.6	−24.7	−31.8	−25.5
6-31+G(d)	−26.1	−21.4	−6.1	−8.8
6-31+G(d,p)	−26.9	−22.1	−6.3	
6-31+G($2d$)	−33.3	−24.0	−8.3	
6-31+G($2d,p$)	−34.4	−24.9	−6.8	
6-31+G($2df,p$)	−29.6	−22.3	+5.5	
6-31+G($2df,2p$)	−29.6	−22.3	+5.8	
6-31+G($3df,2p$)	−27.3	−19.9	+6.3	

calculations on equilibrium geometries, but the triplet pathway was not observed by Buback et al. [11].

Despite these attempts, the photochemical ring-opening pathway of spiropyrans still remains to be fully understood. In this paper we use the Maximum Overlap Method [26] for computing excited states to study 2H-pyran as a model for the ring-opening and ring-closing mechanisms of spiropyrans. The pyran moiety was considered, as this is the ring that opens and is responsible for the photochromism of spiropyrans.

2 Computational method

In order to determine an appropriate level of theory, an extensive study was undertaken to determine the relative stabilization between the lowest energy closed and open structures. The possible structures of 2H-pyran and 2,4-pentadienal are shown in Figure 1. Initial geometries were computed at the B3LYP/6-31G* level with frequency calculation confirming a minimum energy structure. The planar form of 2H-pyran is a transition structure between the two equivalent puckered forms. Isomers 1 and 2 (both cis and trans) also have C_s symmetry, whereas the remaining structures twist out of plane and consequently have C_1 symmetry. The lowest-energy closed and open structures (puckered and trans-isomer 1) were then re-optimized using Hartree-Fock, B3LYP, MP2 and CCSD theory and various Pople basis sets, as tabulated in Table 1. In all
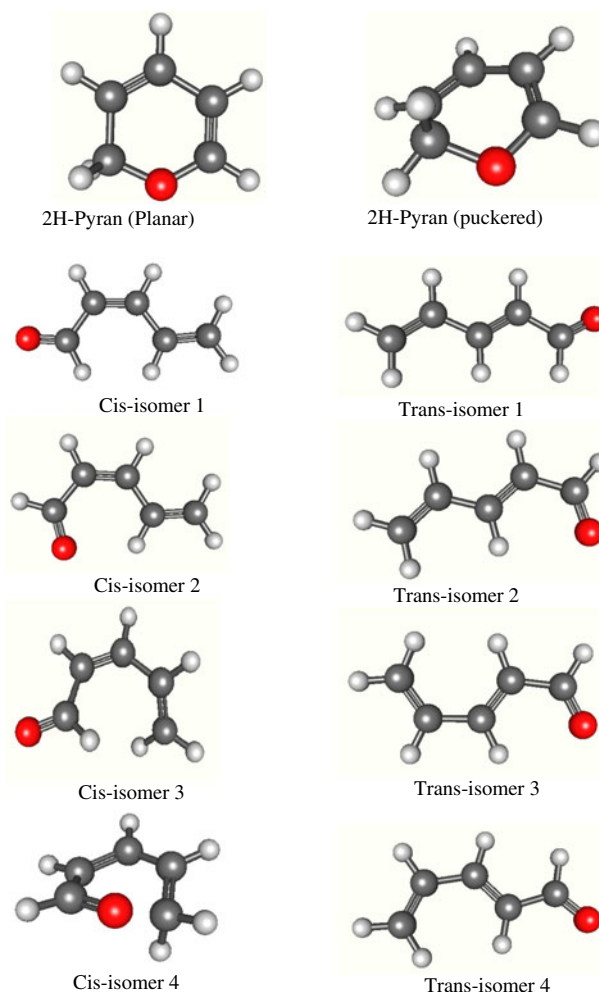

Fig. 1. 2H-pyran (top) and 2,4-pentadienal conformers. The planar pyran structure is a transition state between the two equivalent puckered forms. Isomers 1 and 2 (both cis and trans) of 2,4-pentadienal and the planar pyran structure have C_s symmetry. The remaining structures are all C_1.

cases the geometries were fully converged at the same level of theory as the reported energies.

Excited state calculations were performed using the Maximum Overlap Method (MOM) [26] on the planar 2H-pyran and cis-isomer 4 structures, as these were deemed the most likely candidates for ring opening and ring closing, respectively. MOM is a method for calculating excited state energies at the self-consistent field (SCF)

level. In this approach, an electron is manually "excited" from an occupied to a virtual orbital and this provides an initial guess for the wavefunction in a subsequent SCF calculation. In a regular SCF, the occupied orbitals on each cycle are chosen based on the aufbau principle, and this lowest-energy strategy results in the wavefunction relaxing to the ground state. In a MOM calculation, the occupied orbitals are chosen based on how well they overlap with the orbitals from the previous cycle. If the initial guess generated by exciting the electron is close to a higher energy solution of the SCF equations, then the wavefunction will relax towards this solution rather than relaxing all the way to the ground state. In this way, it is possible to obtain excited-state energies using SCF theory. It is also possible to use the resulting excited-state orbitals in post-HF methods such as MP2. Additional details about this technique can be found in the original paper [26].

The Q-Chem quantum chemistry software package [27] was used for all calculations.

3 Results and discussion

Table 1 shows the ground-state energy differences between puckered 2H-pyran and trans-isomer 1 of 2,4-pentadienal. Both HF and B3LYP consistently predict the open structure to be the most stable by $23-27$ kJ/mol whereas the post-HF methods predict very little difference in the energy of the open and closed structures for the larger basis sets. This is consistent with the uncertainty that exists in the literature about whether the closed or open form is the more stable [20]. MNDO and CNDO/2 semi-empirical studies by Böhm and Kuthan reported that the ring-opened form is lower in energy [18,19]. In 1995, Wang et al. [20] also predicted the ring-opened form to be more stable using both BLYP and MP2 studies with the 6-31G(d) basis set, but for the VWN functional the closed form was more stable.

Our results are consistent with these previous studies, but predict that the closed structure is more stable at high levels of theory. Total and relative stabilization energies with respect to 2H-pyran for all the structures considered in Figure 1 at MP2/6-31+G($2df, p$) are shown in Table 2. Although we were unable to compute CCSD results for the full range of basis sets considered, those that we could compute show good agreement with the MP2 results, from which we conclude that MP2 is a reliable method for these systems and that a basis set of at least 6-31+G($2df, p$) quality is required to correctly predict the relative stability of the open and closed structures.

Based on the ground state study, MP2/6-31+G($2df, p$) was chosen to compute the excites states using the MOM. Both singlet and triplet states were computed, however, previous experimental studies on spiropyran systems have ruled out the possibility of ring opening-closing pathway via a triplet state [11], and we also did not observe any photochemical reaction from the triplet states.

Excitation energies for the first few singlet states for planar 2H-pyran and the cis-isomer 4 structure of 2,4-pentadienal are given in Table 3. The structure of each

Table 2. Total (a.u.) and relative (kJ/mol) energies of the structural isomers of 2,4-pentadienal derivatives, and pyrans with respect to the lowest energy structure (puckered 2H-pyran) at MP2/6-31+G($2df, p$).

Structural isomer	Total energy/a.u.	ΔE/kJ mol^{-1}
Pyran (puckered)	-268.718467	0.0
Pyran (planar)	-268.713553	12.9
Trans-isomer 1	-268.716365	5.5
Trans-isomer 2	-268.713629	12.7
Trans-isomer 3	-268.708651	25.8
Trans-isomer 4	-268.711677	17.8
Cis-isomer 1	-268.712075	16.8
Cis-isomer 2	-268.711679	17.8
Cis-isomer 3	-268.708087	27.3
Cis-isomer 4	-268.703626	39.0

Table 3. MOM vertical excitation energies for the first five singlet states of planar 2H-pyran and the cis-isomer 4 structure of 2,4-pentadienal at MP2/6-31+G($2df, p$).

Singlet	2H-pyran (planar)		2, 4-pentadienal cis-isomer 4	
	Energy/eV	λ/nm	Energy/eV	λ/nm
1	3.69	336	4.20	296
2	5.80	216	4.43	283
3	6.30	198	6.01	206
4	6.57	189	7.31	170
5	7.65	162		

of these excited states was allowed to relax via a geometry optimization in order to search for an energy pathway between the excited state and the ground state of the target open or closed structure. Using this approach, optimization of the fourth singlet state (6.57 eV) of 2H-pyran allowed the ring to open, and optimization of the second singlet state (4.43 eV) of 2,4-pentadienal allowed the ring to close. In the case of ring closing, the reaction yielded the lowest-energy puckered structure. Figure 2 summarizes these results and shows the structures involved in the two photochemical reactions.

Figure 3 shows the energy profile for the ring opening reaction and also shows the C-O distance as a relevant reaction coordinate. This plot indicates the presence of a barrier-less pathway from the excited state at 6.57 eV of the closed ring to the ground state of the open ring structure. The pathway goes through a relatively flat region of the potential energy surface where significant changes in the bond length have little effect on the energy. This pseudo-intermediate corresponds to an open-ring structure with an energy about 3 eV higher than the lowest energy open structure.

Figure 4 shows the energy profile for the ring closing reaction and also the C-O distance. The plot indicates that
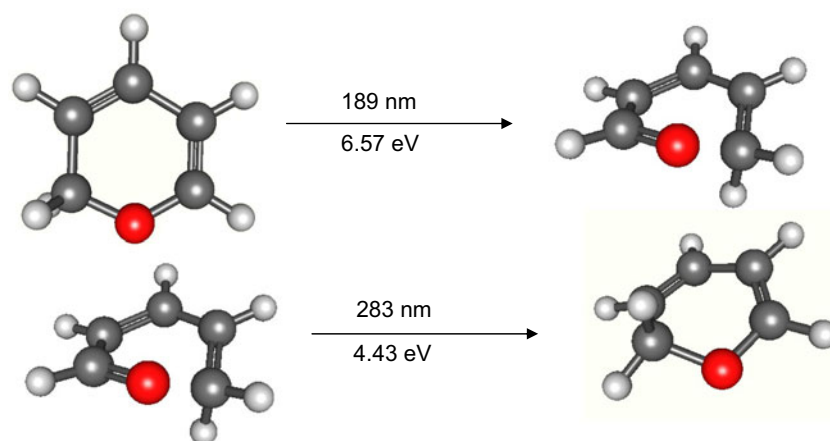
Fig. 2. The photochemically induced interchange between the ring-open and ring-closed forms of pyran. Top: Ring-opening initiates from the planar transition structure and proceeds to the cis-isomer 4 structure. Bottom: Ring closure occurs at a lower energy and proceeds to the puckered ring structure, which is more stable.
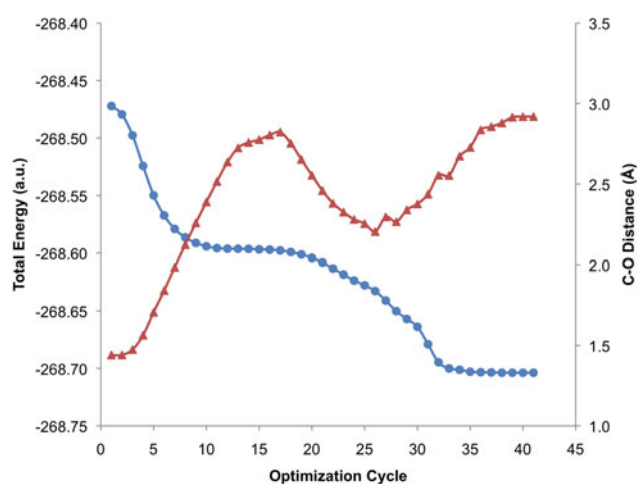

Fig. 3. Ring opening profile for 2H-pyran. The system undergoes an excitation at 6.57 eV before relaxing to the ring-opened form. The circles show the potential energy surface followed by a MP2/6-31+G($2df, p$) geometry optimization from the excited state to the open structure. The triangles show the C-O bond length associated with the ring opening.
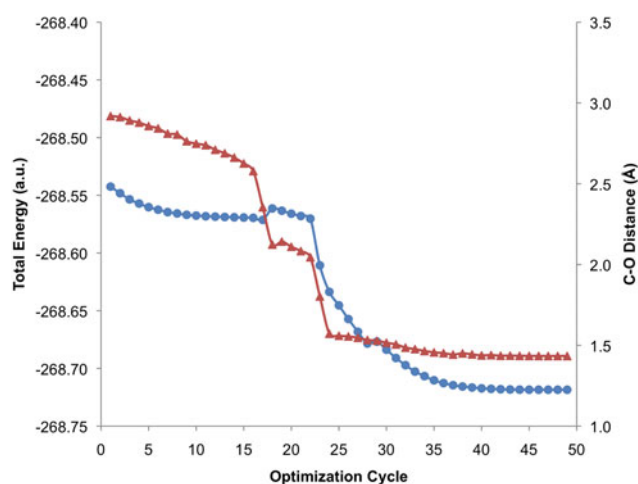
Fig. 4. Ring closing profile for 2,4-pentadienal. The system undergoes an excitation at 4.43 eV before relaxing to the ring-closed form. The circles show the potential energy surface followed by a MP2/6-31+G($2df, p$) geometry optimization from the excited state to the closed structure. The triangles show the C-O bond length associated with the ring closing.

the possible presence of a small barrier around the 17 cycle, however, given the large change in geometry that also occurs at this point, this is likely to be the optimizer overstepping the minimum pathway and landing higher up on the potential surface, and is therefore an artefact. In contrast to the ring opening, which goes through a two-phase bond-breaking process, the ring closing is concerted and proceeds rapidly once initiated.

Compared to the literature reports on excited state potential energy surfaces for ring opening by semi-empirical, TDFT, and CASSCF methods, the MOM is capable of remaining on the potential surface of photochemical ring opening process which may cross several surfaces including canonical intersections.

There is a noticeable red shift (lowering in the excitation energy) for ring closure compared to ring opening.

This is due to the conjugated π bond system of the ring opened form that has been observed in our study. CASSCF studies on benzopyran by Celani et al. [22] failed to observe a noticeable red shift. In their study, ring opening was reported at 4.7 eV (267 nm) while ring closure occurred at 4.2 eV (295 nm) [23]. Benzopyran should even show a greater red shift than 2H-pyran due to the enhanced conjugation possible in the open structure. On the other hand, experimental excitation energies of ring opening and closing of 6,8-dinitro-1′-3′-3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline], 6,8-dinitroBIPS are reported at 4.7 eV (267 nm) and 2.1 eV (560 nm), respectively showing a large red shift [11]. Enhanced red shift and direct optimization to the ground state counterpart after excitation reveals that the MOM method is a useful theoretical approach for studying the excited states of these systems.

During our calculations, we explored all ground state ring opened derivatives, 2H-pyran planer and puckered structures for possible photochemical reactions. In ring opening process, it is only the 2H-pyran planer form that showed the ring opening upon excitation. This suggests that thermal conversion from the puckered to planar form should take place before the absorption of energy corresponding to ring opening excitation. In the reverse process, only the cis-isomer 4 structure, which is also the photochemical product of 2H-pyran, resulted in ring closure upon excitation. This is because among the eight cis- and trans-2,4-pentadienal derivatives, cis-isomer 4 has the most favourable orientation to make the bond between oxygen and fifth carbon in the chain.

4 Conclusions and future work

Our study of the grounds states of 2H-pyran and 2,4-pentadienal conformers reveal that high levels of theory are required to reliably predict relative energies of the different isomers. Using MP2 theory and a basis set of at least 6-31+G$(2df, p)$ quality, the closed puckered ring structure was found to be the most stable in contrast to the findings using lower levels of theory.

Direct relaxation of the excited to the ground states for both ring opening and ring closing is the prominent observation compared to semi-empirical, TDFT, and CASSCF methods. We also observe that only the planar form of 2H-pyran undergoes photochemical ring opening reaction, and that the cis-isomer 4 structure, which has a favourable orientation between the oxygen and carbon atoms that bond. Insights gained by exploring 2H-pyran as a model compound for spiropyran will be used to understand the reversible photochemical reaction of spiropyran in future work.

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