

Research Article

Theoretical Analysis of the Effect Provoked by Bromine-Addition on the Thermolysis and Chemiexcitation of a Model Dioxetanone

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Chemi-/bioluminescence are phenomena in which chemical energy is converted into electronically excited singlet states, which decay with light emission. Given this feature, along with high quantum yields and other beneficial characteristics, these systems have gained numerous applications in bioanalysis, in biomedicine, and in the pharmaceutical field. Singlet chemiexcitation is made possible by the formation of cyclic peroxides (as dioxetanones) as thermolysis provides a route for a ground state reaction to produce singlet excited states. However, such thermolysis can also lead to the formation of triplet states. While triplet states are not desired in the typical applications of chemi-/bioluminescence, the efficient production of such states can open the door for the use of these systems as sensitizers in photocatalysis and triplet-triplet annihilation, among other fields. Thus, the goal of this study is to assess the effect of heavy atom addition on the thermolysis and triplet chemiexcitation of a model dioxetanone. Monobromination does not affect the thermolysis reaction but can improve the efficiency of intersystem crossing, depending on the position of monobromination. Addition of bromine atoms to the triplet state reaction product has little effect on its properties, except on its electron affinity, in which monobromination can increase between 3.1 and 8.8 kcal mol⁻¹.

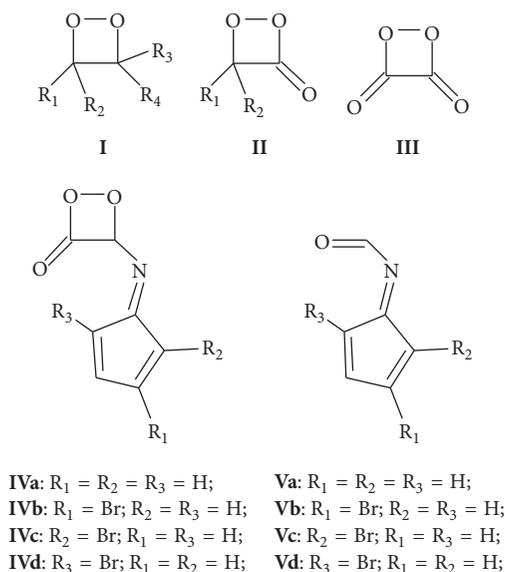
1. Introduction

Bioluminescence is a widespread natural phenomenon in which living organisms convert chemical energy into light emission via biochemical reactions [1–5]. Bioluminescence can be found in organisms as different as bacteria, dinoflagellates, fungi, crustaceans, worms, insects, and fishes. Light emission from these systems is the result of enzyme-catalyzed reactions, which can be divided into two main classes: luciferase-luciferin reactions [2, 5–8] and photoprotein systems [2, 9]. The luciferase enzyme is responsible for catalyzing the oxidation of its substrate, luciferin, which generates an electronically excited singlet state product. This product, generally termed oxyluciferin, subsequently relaxes to the

ground state by photon emission. It should be noted that luciferin, luciferase, and oxyluciferin are only generic terms, showing significant structural differences between bioluminescent species. Moreover, luciferase-luciferin reactions are the most prevalent bioluminescent systems [1–3, 5–8].

Photoprotein systems have been found to be exclusive to marine organisms and are characterized by the formation of a stable enzyme-substrate complex [2]. Such complex is formed between the apoprotein and an oxygenated marine luciferin (2-hydroxyperoxycoelenterazine). Binding of calcium ions to the photoprotein surface triggers the decomposition of the stable complex, which occurs with light emission [2].

Bioluminescence can be considered a subtype of chemi-luminescence, in which light emission arises from a chemical



SCHEME 1: Schematic representation of dioxetanes (I), dioxetanones (II), dioxetanedione (III), and the model dioxetanone (IV) and its thermolysis product (V) studied here.

reaction [1, 10, 11]. The efficiency of light emission of both bioluminescent and chemiluminescent reactions is described in terms of quantum yield, which is controlled by three factors [1, 10, 11]: chemical yield of the ground state reaction, chemiexcitation yield of the singlet excited state product, and finally the fluorescent quantum yield of the emitter. Typically, bioluminescent systems present significantly higher quantum yields than chemiluminescent reactions, with some reactions reaching quantum yields of 45–61% [12]. Given this efficient production of electronically singlet excited state products, relative nontoxicity of luciferin compounds, and the relatively simple chemistry of these systems, among other beneficial characteristics (as sensitivity and sensibility), several chemi-/bioluminescent systems have gained numerous biomedical, pharmaceutical, and bioanalytical applications. More specifically, these systems are used in the analytical determination of ATP and other metabolites, in environmental monitoring, in bioimaging, and in biosensing, as a gene reporter, tested as alternative excitation sources in photodynamic therapy of cancer, and used in investigations of infectious diseases, among others [13–17].

The efficient formation of singlet excited state products, necessary for the use of these systems in the many applications referred above, is only made possible by the formation of cyclic peroxide intermediates during the different chemi- and bioluminescent reactions [18–28]. Within the large number of different chemi- and bioluminescent systems, these peroxide intermediates can take the form of dioxetanes (I), dioxetanones (II), or dioxetanedione (III) [18–28], which can be seen in Scheme 1. These cyclic peroxides are responsible for chemi- and bioluminescence as their thermolysis provides a route for a thermally activated ground state reaction to produce singlet excited state products [18–28]. This chemiexcitation process is thought to arise from crossing

points between the ground state and excited state potential energy surfaces (PES) on the reaction coordinate.

It should be noted that while chemi- and bioluminescent systems are better known for their production of singlet excited states, experimental studies have shown that more structurally simple dioxetanes and dioxetanones have the ability to produce triplet excited states [1, 10, 25–27]. While no experimental results are found for more complex chemi-/bioluminescent systems, different theoretical studies have found pathways for triplet chemiexcitation in the thermolysis of dioxetanone rings in several systems [1, 11, 18, 19, 24, 28, 29]. This production of triplet excited states can be problematic for the several practical applications based on the formation of light-emitting singlet states, as triplet states are very easily quenched, and their formation will not be detected with the luminescent and fluorescent approaches typically used to detect chemi-/bioluminescence. Moreover, triplet states are more reactive and are able to produce harmful reactive species (as singlet oxygen), which can lead to some problems when using these systems in biological samples.

While the formation of triplet state (instead of singlet ones) is not desired in the typical applications of chemi-/bioluminescence, such states can have important roles in other applications. One such example is upconversion by triplet-triplet annihilation, which typically proceeds as follows [30–32]: a sensitizer molecule is photoexcited and undergoes intersystem crossing to a triplet state. Subsequently, the sensitizer transfers its energy to an emitter molecule via fast triplet-triplet energy transfer, which stores the energy in the lowest triplet state of the emitter molecules. Then, two emitters interact and triplet-triplet annihilation occurs, which brings one emitter molecule to an excited singlet state while quenching another to its ground state. The emitter then emits light via fluorescence, at a higher energy than that of the photons initially absorbed by the sensitizer. Triplet-triplet annihilation has been already applied with success in several research fields, as in luminescence bioimaging [33], photovoltaics [34, 35], and photoinduced drug release [36].

Another useful application of triplet excited states is on the field of photocatalysis [37–39]. In this field, photosensitizers are used to mediate photochemical reactions by absorbing light and using that energy to activate ground state reactants toward some specific chemical reactions. One common method of photoactivation is via energy transfer from the longer-lived triplet state of the photosensitizer to the substrate [37–39]. Another photoactivation pathway involves an electron transfer from or to the photoexcited sensitizer [37, 38].

Given this, if one can shift the spin of the chemi-/bioluminescent products, from light-emitting singlet to triplet states, one can open the door for new types of applications for chemi- and bioluminescent systems, as in upconversion processes by triplet-triplet annihilation and photocatalysis. One way to facilitate intersystem crossing to triplet states is to introduce heavy atoms (as bromine and iodine) into the molecular structures, the so called “heavy atom effect” [40–42]. Thus, the objective of this work is to model theoretically the effect of bromine-substitution in a model dioxetanone (IV, Scheme 1) and, more specifically, in its thermolysis and

triplet chemiexcitation steps. To our knowledge, this is the first theoretical study trying to understand the possible role of the “heavy atom effect” in the reactions of dioxetanone molecules and in what way it affects triplet chemiexcitation. To this end, a methodology combining density functional theory- (DFT-) based and multireference methods was used.

2. Theoretical Methodology

All calculations were made with the Gaussian 09 program package [43], with no solvent effects. DFT methods (particularly long-range-corrected hybrid exchange-correlation density functionals) have been gaining traction in the study of chemi-/bioluminescent reactions, given their ability to provide quite accurate qualitative pictures for these systems [18–21, 24, 28, 44–47]. In this study was used the CAM-B3LYP long-range-corrected density functional [44], which provides good estimates for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ local excitations and charge transfer and Rydberg states [45]. Moreover, this functional was already used with success in the study of different dioxetanones [20, 21].

Geometry optimizations and frequency calculations were made with the CAM-B3LYP functional, with the 6-31G(d,p) basis set being used for all atoms except bromine, for which the LanL2DZ basis set was used. The combination of 6-31G(d,p) and LanL2DZ basis set was termed Basis Set-1 (BS-1). A restricted (R) approach was used for closed-shell species, while an unrestricted (U) species was used for open-shell structures. The U approach was used with a broken-symmetry technology, which mixes the HOMO and LUMO, making an initial guess for a biradical.

The thermolysis reaction of the model dioxetanones was studied by performing intrinsic reaction coordinates (IRC) [48], at the CAM-B3LYP/BS-1 level of theory, which assessed if the obtained transition states connected the desired reactants and products. The transition states were located by using the STQN method [49]. In this work was used the QST3 variant, which requires three molecular specifications: the reactants, the products, and an initial structure for the transition state. The Cartesian coordinates of these transition state structures, used in the IRC calculations, can be found in Tables S1 and S2 of Supplementary Material available online at <https://doi.org/10.1155/2017/1903981>.

The energies of the geometry optimizations, IRC, and QST3-obtained structures were reevaluated by single point calculations with the CAM-B3LYP density functional and the 6-31+G(d,p) basis set for all atoms, except for bromine. For this atom, the LanL2DZdp basis set was used, which includes polarization and diffuse functions. The combination of 6-31+G(d,p) and LanL2DZdp basis set was termed Basis Set-2 (BS-2). Thus, the energies of the singlet ground state (S_0) and first triplet state (T_1) were both calculated at the CAM-B3LYP/BS-2 level of theory.

The spin-orbit coupling between S_0 and T_1 states was calculated by using the CASSCF method [50]. The LanL2DZ basis set was used for all atoms. The active space consisted of two electrons on two orbitals. These were single point energy

calculations made on the DFT-computed IRC- or QST3-obtained structures.

3. Results and Discussion

We started this work by analyzing the thermolysis reaction of unsubstituted dioxetanone IVa and monobrominated species IVb, whose energetic profiles are presented in Figures 1(a) and 1(c), respectively. In Figures 1(b) and 1(d) are presented important geometric parameters: the bond lengths of O_1-O_4 and C_2-C_3 (Scheme 1). It should be noted that the iminocyclopentadienyl moiety was based on the scaffold of aza-BODIPY [40–42], which are molecules capable of producing triplet states upon photoexcitation, when they are functionalized with heavy atoms.

Analysis of the geometric parameters shows that the thermolysis of both species occurs via a stepwise mechanism. The reaction begins by O_1-O_4 bond breaking, while the length of C_2-C_3 remains constant. Only after O_1-O_4 , does the length of C_2-C_3 increase, subsequently leading to its cleavage. Analysis of the (S^2) value for the transition state of both IVb (~ 0.57) and IVa (~ 0.55) showed that these structures have a biradical character. Given this, we can ascribe a stepwise-biradical mechanism for the thermolysis of both dioxetanone species, which is in line with previous theoretical studies of such molecules [18, 20, 21, 24, 28, 29].

While a stepwise-biradical mechanism is usually found in the decomposition of these cyclic peroxides, it can be further subdivided: the biradical is formed due to an electron transfer from an electron-rich moiety to the dioxetanone, thereby forming a radical cation and a radical anion, respectively; the biradical is formed due to the homolytic cleavage of the O_1-O_4 bond. In this case, both molecules appear to undergo thermolysis via homolysis, as the electron spin density of the transition state resides only on the O_1 and O_4 heteroatoms (Figures 2(c) and 2(d)). This finding is in line with the limited charge transfer found between the dioxetanone and iminocyclopentadiene moieties, as demonstrated in Figures 2(a) and 2(b). The atomic charges were measured within the Natural Population Analysis (NPA) scheme. The finding that these molecules undergo a homolysis-based stepwise-biradical thermolysis can be attributed to the absence of an ionizable group, as seen before in the theoretical analysis of such molecules [18, 20, 21, 24, 28, 29].

Both species have similar activation energies of $24.7 \text{ kcal mol}^{-1}$ for IVa and $24.5 \text{ kcal mol}^{-1}$ for IVb. These energies were calculated at the CAM-B3LYP/BS-2 level of theory, with thermal corrections calculated at the CAM-B3LYP/BS-1 level of theory. Considering that no solvents effects were considered and that these species are only model dioxetanones, the obtained activation parameters compare well with the experimentally obtained ones for several cyclic peroxides (within $\sim 20.0 \text{ kcal mol}^{-1}$) [51–53].

So far, the main conclusion is that the addition of a bromine atom affects slightly the decomposition of the model dioxetanone, as there are only very minor differences between the thermolysis of species IVa and IVb. In fact, both species present the same characteristics as other dioxetanone without an ionized group [18–21, 24, 28, 29].

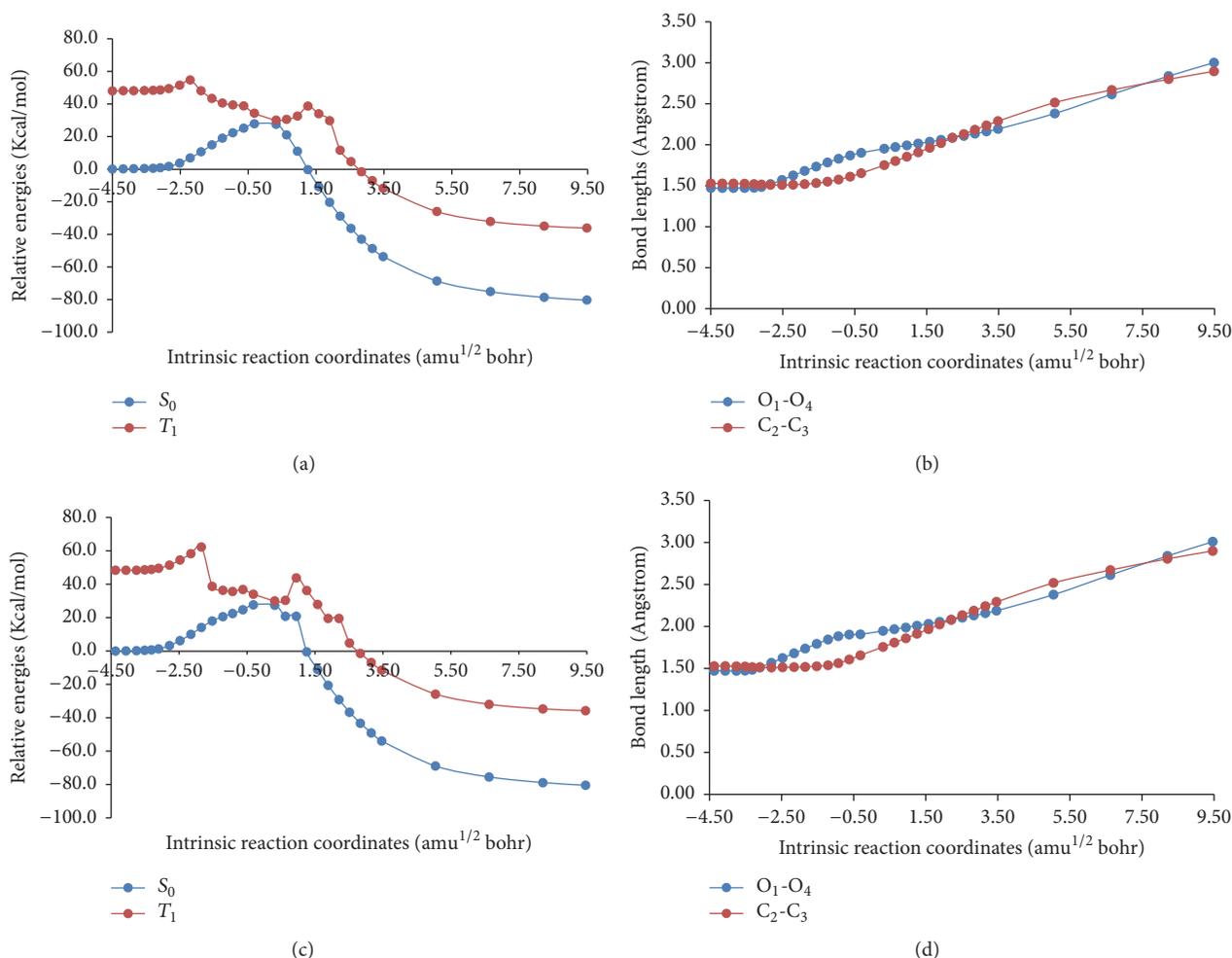


FIGURE 1: Energy profiles of the S_0 and T_1 states, determined in the S_0 -computed IRC path, for species IVa (a) and IVb (c). O_1 - O_4 and C_2 - C_3 bond length variations recorded during the IRC calculations for IVa (b) and IVb (d).

In the same vein, we have found a pathway for triplet chemiexcitation for species IVa and IVb (Figures 1(a) and 1(c), resp.), in line with other theoretical works on different dioxetanones, dioxetanes, and dioxetanedione [11, 18, 19, 24, 28, 29]. Upon starting the reaction, the energetic difference between S_0 and T_1 states was large for both molecules (about 48 kcal mol⁻¹). However, from the reactant onward, the energy of the T_1 state decreased significantly to a point in both species where the S_0 - T_1 energy gap is low enough to allow chemiexcitation: 2.5 kcal mol⁻¹ (at 0.32 amu^{1/2} bohr) for IVa and 2.6 kcal mol⁻¹ (at 0.32 amu^{1/2} bohr) for IVb. In conclusion, by analyzing the S_0 and T_1 energetic profiles, our results indicate that both IVa and IVb species are capable of triplet chemiexcitation. Moreover, the very similar S_0 - T_1 energy gap suggests a triplet chemiexcitation of similar magnitude, thereby indicating a small effect provoked by the addition of a bromine heavy atom.

It should be noted, however, that intersystem crossing is a process formally forbidden in nonrelativistic quantum theory, and, so, inferring singlet-triplet transition probabilities from energy gaps is not sufficiently accurate [40, 54].

So, to assess the efficiency of intersystem crossing, we must take into account the spin-orbit coupling (SOC) between S_0 and T_1 [40, 54]. These were computed at the multireference CASSCF level of theory, and the SOC values for IVa and IVb are presented in Table 1. The CASSCF-computed S_0 - T_1 energy gaps (3.1 kcal mol⁻¹ for IVb and 2.9 kcal mol⁻¹ for IVa) are in line with the DFT-computed ones gap (2.5 kcal mol⁻¹ for IVb and 2.6 kcal mol⁻¹ for IVa). Once again, it appears that the addition of a bromine heavy atom has little effect, as the SOC values for IVa (5.3 cm⁻¹) and IVb (6.1 cm⁻¹) are very similar, despite the SOC being higher for the monobrominated species.

So far, it does appear that the addition of a bromine atom has only a limited effect on the triplet chemiexcitation of model dioxetanone IV. However, it might be possible that this lack of effect is due to the position of bromine-substitution in the cyclopentadiene moiety and not due to a general absence of the “heavy atom effect” in this molecule. To test this hypothesis, we have calculated transition state structures (with the QST3 method, at the CAM-B3LYP/SD-1 level of theory) for species IVb, IVc, and IVd. The Cartesian

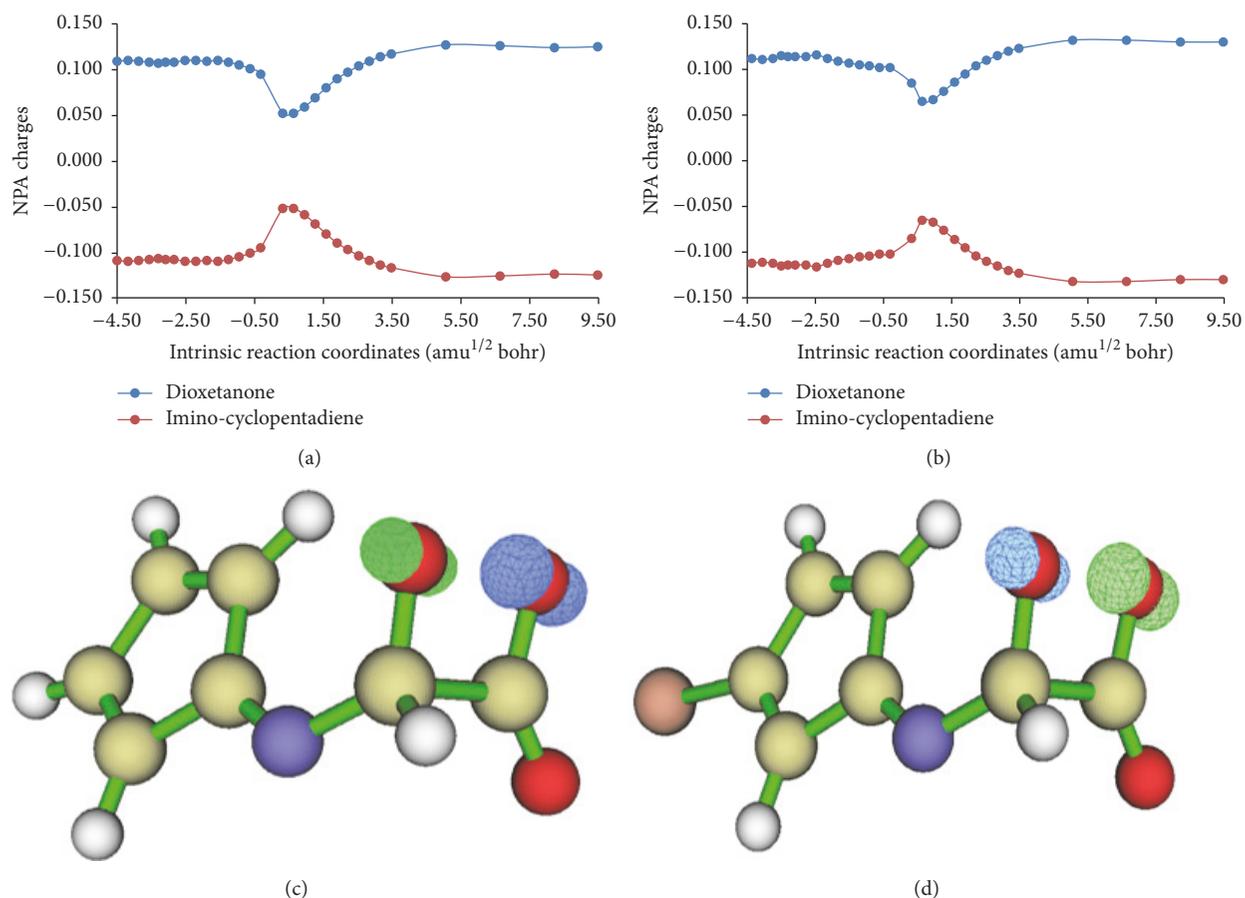


FIGURE 2: NPA charge density distribution between the dioxetanone and imino-cyclopentadiene moieties, for species IVa (a) and IVb (b). Electron spin density for the transition state structure of the thermolysis of IVa (c) and IVb (d).

TABLE 1: S_0-T_1 energy gaps ($\Delta E(S_0-T_1)$, in kcal mol $^{-1}$) and respective SOC values (SOC, in cm $^{-1}$), obtained with CASSCF(2,2)/LanL2DZ single point energy calculations on CAM-B3LYP/BS-1 structures.

| | IVa ^a | IVb ^a | IVb ^b | IVc ^b | IVd ^b |
|---------------------|------------------|------------------|------------------|------------------|------------------|
| $\Delta E(S_0-T_1)$ | 2.9 | 3.2 | 11.4 | 11.4 | 10.8 |
| SOC | 5.3 | 6.1 | 7.5 | 8.6 | 11.5 |

^aStructures obtained during the IRC calculations, corresponding to points of lower S_0-T_1 energy gaps: 2.5 kcal mol $^{-1}$ (at 0.32 amu $^{1/2}$ bohr) for IVa and 2.6 kcal mol $^{-1}$ (at 0.32 amu $^{1/2}$ bohr) for IVb.

^bTransition state structures obtained with the QST3 method.

coordinates of these structures can be found in Tables S3–S5 of Supplementary Material. At those DFT-computed structures, CASSCF single point energy calculations were made to obtain the SOC values (Table 1). The CASSCF-computed S_0-T_1 energy gaps are similar to all species (between 10.8 and 11.4 kcal mol $^{-1}$), further indicating that the position of the bromine atom has little effect on the value of the S_0-T_1 energy gap. However, this is not true for the SOC values. These increased more significantly, from 7.5 to 11.5 cm $^{-1}$, with IVd presenting SOC values more than double the ones presented previously by IVa. Thus, these results indicate that

TABLE 2: Adiabatic S_0-T_1 energy gaps ($\Delta E(S_0-T_1)$, in kcal mol $^{-1}$) and vertical ionization energies (IE, in kcal mol $^{-1}$) and electron affinity (EA, in kcal mol $^{-1}$) for the T_1 state of species Va–d, obtained at the CAM-B3LYP/BS-2//CAM-B3LYP/BS-1 level of theory.

| | Va | Vb | Vc | Vd |
|---------------------|-------|-------|-------|-------|
| $\Delta E(S_0-T_1)$ | 25.3 | 26.0 | 21.8 | 24.4 |
| IE | 190.5 | 191.1 | 188.9 | 187.2 |
| EA | -59.1 | -67.9 | -63.9 | -62.2 |

the addition of heavy atoms can indeed increase the efficiency of intersystem crossing and, so, the formation of triplet state products, but this effect is controlled by the position in which the heavy atom is inserted.

Having analyzed the effect of monobromination on the thermolysis and triplet chemiexcitation of model dioxetanone IV, we have studied some properties of the T_1 reaction product (species Va–d, Scheme 1). The Cartesian coordinates of these structures can be found on Tables S6–S9 of Supplementary Material. These properties are the electron affinity (EA), ionization energies (IE), and T_1-S_0 energy gaps (present in Table 2). The EA and IE were computed vertically, with single point energy calculations on the T_1 structure,

with T_1 as the reference state. All V species present very high IEs, with a limited effect provoked by monobromination, which limits the use of these species as electron donors in photocatalysis. On the contrary, the EA values are more suitable for the use of these species as electron acceptors. Moreover, the addition of bromine atoms can significantly improve the EA of V up to $8.8 \text{ kcal mol}^{-1}$, depending on the location of the substitution on the cyclopentadiene ring. As for T_1 - S_0 energy gaps, these were computed adiabatically. Our calculations have indicated that monobromination has a limited effect on the T_1 - S_0 energy gaps, except for species Vc, which decreased the gap by $3.5 \text{ kcal mol}^{-1}$.

4. Conclusion

Chemi- and bioluminescence are phenomena in which chemical energy is converted into light emission, via chemical and biochemical reactions. Given this feature, coupled to high quantum yields, relative nontoxicity of the reaction substrates, and the relatively simple chemistry, among other beneficial characteristics (as sensitivity and sensibility), several chemi-/bioluminescent systems have gained numerous biomedical, pharmaceutical, and bioanalytical applications.

The efficient formation of light-emitting singlet excited states, needed for the applications referred above, is made possible by the formation of cyclic peroxides (as dioxetanes or dioxetanones). Their thermolysis provides a route for a thermally activated ground state reaction to produce singlet excited state products. However, both experimental and theoretical studies have demonstrated that the thermolysis of these species is also able to produce triplet states. While the formation of such states is not desired in the typical applications of chemi-/bioluminescence, efficient production of triplet states might open the door for the use of chemi-/bioluminescent systems as sensitizers in the fields of photocatalysis and upconversion processes by triplet-triplet annihilation, among others.

Given this, the objective of this theoretical study was to assess the effect induced by heavy atom substitution (in this case, bromine) on the thermolysis and triplet chemiexcitation of a model dioxetanone. Our calculations indicated that monobromination has little effect on the S_0 thermolysis reaction, with little effect on the energetics of the reaction and on the variation of other parameters (as selected bond lengths and electron spin and charge density). However, the addition of bromine atoms can increase the spin-orbit coupling of the S_0 and T_1 , thereby increasing the efficiency of intersystem crossing. Nevertheless, this effect is dependent on the position of the bromine-substitution. Study of the T_1 reaction product showed a general limited effect provoked by monobromination on the ionization energies and S_0 - T_1 gaps. On the contrary, monobromination improves the electron affinity of the T_1 product, with the degree of improvement being controlled by the position of monobromination.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

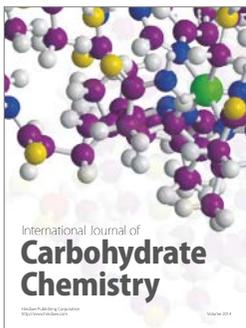
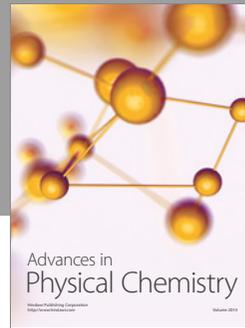
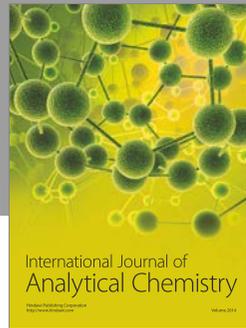
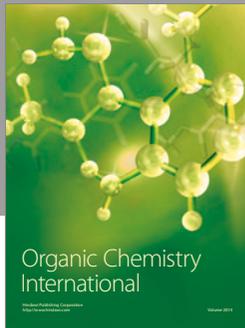
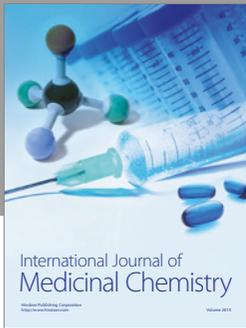
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