



**Spiro-Acridyl Substituted Adamantylidene 1,2-Dioxetane
(SAAD) Chemiluminescent Mechanism: DFT Investigations Utilizing
Long Range Corrected Functionals**

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Abstract

The mechanism of chemiluminescent decomposition in Spiro-Acridyl Substituted Adamantylidene 1,2-Dioxetane (SAAD) is explored by LC-wPBE /6-31+G* method using the Gaussian 09 software. The energetics of the decomposition reaction via transition states/intermediates at the lowest singlet and triplet states are studied using complete optimisation as well as frequency analysis. According to the findings of the current study, SAAD's chemiluminescent decomposition occurs via a biradical pathway that includes the production of the triplet biradical intermediate ³BR. The findings are in accordance with earlier theoretical and experimental studies.

Keywords: Chemiluminescent, 1,2-Dioxetane, spiro-acridane, SAAD, transition state, biradical pathway, decomposition.

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Introduction

A chemiluminescent reaction occurs when light is released during the product production of a chemical process¹. In many chemiluminescent reactions, the primary source of energy comes from the cleavage of energy-rich bonds like peroxides, hydroperoxides, 1,2-dioxetanes, or dioxeytenones². Over the past few decades, 1,2-dioxetanes have gathered a lot of interest from both theorists and experimentalists due to their distinct chemiluminescent properties in biochemical and immunological aspects. In thermo-chemiluminescent immunoassays (Version, 1988)³ a variety of 1,2 - dioxetanes with bulky substitutions, such as spiro-adamantyl, spiro-acridyl, and spiro-xanthyl groups are used. These significant substitutions improve the energy transfer efficiency and stability of 1,2-dioxetanes, resulting in brighter and more persistent chemiluminescence signals.

When 1, 2-dioxetane derivatives are decomposed, two fragments are formed, one of which is electrically excited. The mechanism of the 1, 2-dioxetanes decomposition is still up for debate despite the fact that they have been known for a very long time. The first mechanism, called the synchronous or concerted process, was put up by McCapra

(McCapra, 1968)⁴, (McCapra, 1966)⁵ and Turro (Turro & Lechtken, 1973)⁶, (Arnstein et al., 1975)⁷ at the end of the 1960's. It usually involves a symmetrically barred pericyclic rearrangement. It signifies the parallel homolytic fission of the carbon (C-C) and oxygen (O-O) atom bonds.

O'Neal and Richardson (The et al., 2002)⁸, (Richardson & Neal, 1972)⁹, (Richardson et al., 1974)¹⁰ have described a stepwise method that uses a biradical intermediate. They claim that homolytic splitting of the O-O bond produces a biradical molecule, which is supported by kinetic (Richardson et al., 1974)¹⁰ and ab initio calculation (Harding & Goddard, 1977)¹¹ results.

Moreover, the **CIEEL** (Chemically Initiated Electron Exchange Luminescence) (Schuster, 1979)¹² was proposed by Schuster et al. as a new decomposition mechanism to explain this extremely effective chemiexcitation (Schuster, 1979)¹², (J. young Koo & Schuster, 1977)¹³, (J. Y. Koo et al., 1978)¹⁴, (Schmidtza, 1980)¹⁵, (Schmidt & Schuster, 1980)¹⁶, (*Chem Ilu Minescence of Organic Compounds*, 1978)¹⁷. A mono-electronic transfer from a donor molecule (D) to the dioxetane ring, which decomposes to produce a radical anion intermediate, constitutes the first step in the CIEEL mechanism. The final excited product is formed accordingly the latter's reaction using the radical cation of the donor molecule (D⁺).

Computational Methods

The Gaussian 09 program¹⁸ was used to perform all the calculations. The calculations are based mostly on optimizing the geometries, vibrational frequencies, and intrinsic reaction coordinates. The vibrational frequencies of the optimized geometries

were used to analyse them. By using LC-wPBE/6-31+G* method (Vydrov et al., 2006)¹⁹, the ground state and the transition states were optimized. ULC-wPBE/6-31+G* is used to optimize the biradical intermediate ³BR, triplet transition state ³TS1, and singlet transition state ¹TS1. (S₀) and triplet (T₁) states, the decomposition reaction of SAAD was investigated, by the elongation of C-C and O-O bonds.

This long-range-corrected hybrid functional (Vydrov et al., 2006)¹⁹, here referred to as LC-wPBE, is more precise for describing a variety of molecular processes, including long-range charge transfer, thermochemistry, reaction barrier heights, and bond lengths.

Results and Discussion

1. LC-wPBE/6-31+G* optimized geometries in the equilibrium ground (S₀) state of SAAD

Figure 1 depicts the optimized geometries of SAAD ground state structures. Table 1 displays SAAD's geometrical parameters.

The dioxetane SAAD is iso-electronic with xanthylideneadamantane-1,2-dioxetane (XAD). The C1-C2 in SAAD is 1.568 Å, which is just 0.007 Å shorter than the experimental value of XAD (1.575 Å) (Brouwer et al., 1988)²⁰. The dioxetane rings of SAAD are having relatively similar geometrical properties that of XAD, with length deviations ranging from 0.001 to 0.005 and bond angle deviations of 0.6°. The dihedral angle of the dioxetane rings in SAAD is -10.06°.

In comparison to the comparable theoretical values in adamantylideneadamantane 1,2-dioxetane (AAD), the ring of dihedral angle in these

systems exhibits a significant divergence in the range of 26.2° to 30.5°.

2. Structural changes and variation in energies along the reaction path of SAAD

Figure 2 shows the variation in the relative energies of SAAD along the reaction coordinate as a function of O-O stretch and C-C stretch for ground state (S_0) and triplet state (T_1).

When the O-O bond of spiro-acridyl substituted dioxetanes in the ground state (S_0) is stretched from 1.5 to 3.0 Å, the bond length of C-C is increased from 1.560 to 2.956 Å in SAAD. The C1-O4 and C2-O3 lengths became 1.212 Å and leading to two carbonyl fragments. The total energy of the fragments at O-O = 2.3 Å is 59.2 kcal/mol. On further stretching the O-O length, the C-C length is stretched out and the dihedral angle O4-C1-C2-O3 is increased to 165.09° in SAAD. The two oxygen atoms are in nearly trans arrangement.

In the triplet state, the energy falls with increase of O-O bond length from 1.5 Å to 3.0 Å and there is a trivial change observed in C1-C2 length. In the case of C-C stretching coordinate along the S_0 state, the energy increases up to 2.2 Å. On further stretching to 2.3 Å, the energy drops to 29.23 kcal/mol.

In SAAD, the C-O bond lengths of adamantanone (AD) and 9(10-H)-acridone (AE) fragments are 1.216 and 1.215 Å respectively. The dihedral angle is altered from -0.8° to -165.1°. But the energy of the triplet state along the C1-C2 stretching path increases up to 1.9 Å. On further stretching to 1.9 Å, the energy decreases and the bond

lengths becomes C1-O4 = 1.382 Å and C2-O3 = 1.398 Å.

3. SAAD intermediates and transition states along the chemical path

Using the LC-wPBE/6-31+G* and ULC-wPBE/6-31+G* techniques, the transition states along the reaction pathways for the chemiluminescent decomposition of SAAD were examined. By structural optimization along the reaction path, the transition states ¹TS1, ¹TS3, ¹TS2, ³TS1 and a triplet biradical intermediate (³BR) were identified. ULC-wPBE/6-31+G* computation is used to characterise them, it was discovered that all of these species are open-shell systems with unpaired electrons. Table 2 includes a list of the geometrical characteristics of the transition states of ¹TS1, ³TS1, ¹TS3 and a triplet biradical intermediate (³BR), which are also shown in figure 3.

¹TS1 is created by stretching the O-O bond from the reactant's ground state. The lengths of ¹TS1's C1-C2 = 1.591 Å, O3-O4 = 2.102 Å, C1-O4 = 1.422 Å, and C2-O3 = 1.431 Å. C1-C2-O3 and C2-C1-O4 have dioxetane ring angles of 101.4° and 98.9°, respectively. The O4-C1-C2-O3's dihedral angle (-0.1°) defines the geometry of ¹TS1. 31.4 kcal/mol is the potential barrier to produce ¹TS1.

In ³BR, the length C-C bond is 1.620 Å. The bond lengths of C1-O4 = 1.372 Å and C2-O3 = 1.416 Å. C1-C2-O3 and C2-C1-O4 have dioxetane ring angles of 98.1° and 102.4°, respectively. The length of O-O is 2.113 Å, and the dihedral angle O4-C1-C2-O3 is -2.8°, which define the geometry of ³BR.

Stretching the C-C bond from the ³BR produced the triplet transition state, ³TS1.

³TS1 has lengths of 2.020 Å and 2.656 Å for its C-C and O-O, respectively. The length of C1-O4 (C2-O3) is 1.284 Å (1.281 Å). The adamantanone (AD) is in the triplet (T1) state, according to the above mentioned C-O lengths, whereas the 9(10-H)-acridone is in the singlet ground (S0) state. 13.9 kcal/mol is the possible barrier to ³TS1 formation. The C-C bond yields one imaginary vibrational frequency (149.2 i cm⁻¹).

In the current study, the thermal decomposition of SAAD was also described. Figure 4 and Table 2 both list the geometrical characteristics of the transition state, ¹TS2, which is involved in the thermal decomposition. The lengths of the O-O = 1.930 Å and C-C = 1.922 Å. 38.1 kcal/mol is the theoretical barrier to the produce of ¹TS2. One imaginary frequency (1349.2 cm⁻¹) is obtained by stretching the lengths O-O bond and C-C bond. The examination of vibrational frequencies demonstrates the coordinated process for thermal decomposition in SAAD.

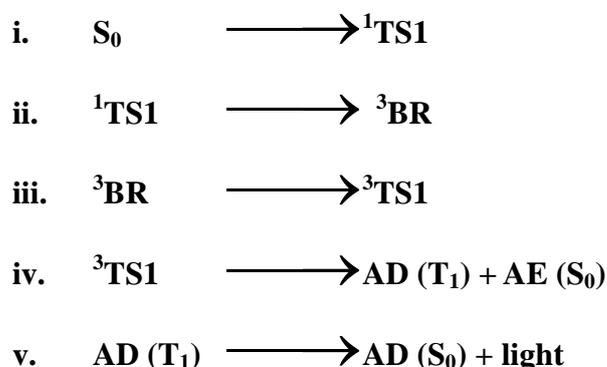
4. Products formed from the dissociation of SAAD

Table 3 provides a summary of the calculations performed on the total energy of the products generated during the thermal and chemiluminescent decomposition of the dioxetane SAAD. Figure 5 depicts the geometrical structures of adamantanone (AD) and 9(10-H)-acridone (AE). Adamantanone (AD) has a triplet excitation energy of 3.16 eV, which is 0.16 eV less than the experimental measurement (3.391 eV) (Albini & Fagnoni, n.d.)²¹. In comparison to the experimental value, the singlet excitation energy of AD is 3.57 eV, which is 0.27 eV less (3.84 eV) (Albini & Fagnoni, n.d.)²¹. In comparison to the experimental value, 9(10-H)-acridone (AE) have triplet

excitation energies 2.76 eV (2.53 eV) (Introduction, 1977)²².

5. Mechanism

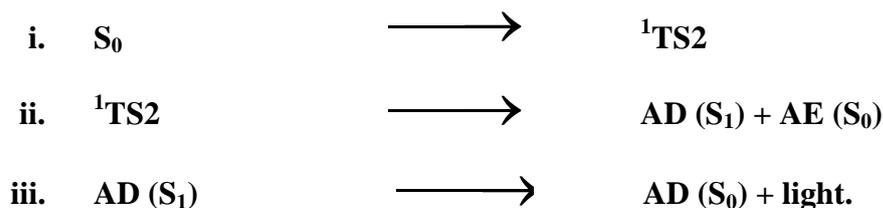
It has been noted that SAAD's chemiluminescent decomposition resembles that of Monoadamantylidene-1,2-Dioxetane (MAD) and simple dioxetanes. Only the dissociation of the triplet transition state, ³TS1, results in the creation of the products. In Scheme 1, the mechanism of SAAD's chemiluminescent decomposition is depicted.



where, ³BR is the triplet biradical state,

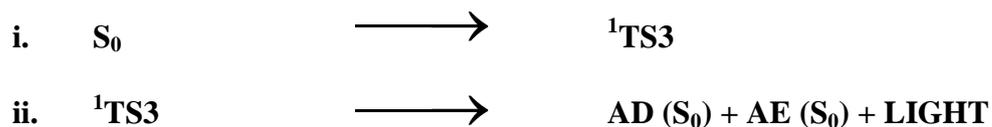
³TS1 is the triplet transition state corresponding to C-C stretching.

When both the O-O and C-C bonds are stretching in a concerted manner it leads to a transition state corresponds to ¹TS2. This transition state yields two products, one in the singlet excited state (S1) and one in the ground state (S0). 38.1 kcal/mol is the activation barrier. This mechanism of SAAD is shown in Scheme 2.



Scheme 2

When O-O and C-C bonds are stretched simultaneously, it results in a transition state that corresponds to $^1\text{TS3}$. This transition state produces two products; both are in the ground (S_0) state. The activation barrier is 28.2 kcal/mol. The mechanism behind the chemiluminescent nature of SAAD is presented in Scheme 3.



Scheme 3

Conclusions

It is claimed that the chemiluminescent decomposition of SAAD follows a biradical mechanism based on *scheme 1*. The reaction proceeds via a triplet biradical intermediate ^3BR . A triplet biradical-intermediate serves as the reaction's intermediate. Only the dissociation of the triplet transition state, $^3\text{TS1}$, produces the products. The available experimental activation energy of 27.6 kcal/mol. The above mechanism proposal is justified by the fact that the reaction uses a lower energy pathway to produce the products.

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Table 1 Bond lengths and dihedral angle in SAAD using LC-wPBE/ 6-31+G* basis set.

Parameters	SAAD	AAD ^a	XAD ^b
C1-C2	1.568	1.549	1.575
C1-O4	1.442	1.476	1.466
C2-O3	1.441	1.474	1.468
O3-O4	1.454	1.491	1.507
C1-C2-O3°	87.2	--	--
C2-C1-O4°	86.9	--	--
O3-O4/ C1-C2	0.927	--	--
O4-C1-C2-O3°	-10.06	21.3	14.8
Energy (Hartree)	-1094.734556	--	--
<p>^{a.} X-ray crystal structure of AAD – adamantylideneadamantane 1,2-dioxetane(Chemistry and Chemistry, 1977)²³</p> <p>^{b.} X-ray crystal structure of XAD²⁰</p>			

Table 2 Transition states and triplet biradical energies, selected bond lengths (Å) and angles (°) of SAAD using ULC-wPBE/6-31+G*^a. Bond length in Å, bond angle and dihedral angle in degrees, total energy in Hartree^b, and relative energy, relative energy (RE) in kcal/mol.

TS/BR	¹TS1	¹TS3	³TS1	³BR	¹TS2
C1-C2	1.594	1.687	2.020	1.620	1.922
C1-O4	1.422	1.430	1.284	1.372	1.330
C2-O3	1.431	1.425	1.281	1.416	1.380
O1-O2	2.102	2.093	2.656	2.113	1.930
C1-C2-O3	101.4	98.2	94.1	98.1	91.3
C2-C1-O4	98.9	96.5	97.9	102.4	83.6
O4-C2-C1-O3	0.1	-30.0	-64.8	-2.8	29.4
ZPE	0.421672	0.421528	0.421059	0.421226	0.421513
Frequency	312.6 i	452.6 i	149.2 i	32.1 i	1349.2 i
RE	31.4	28.2	13.9	27.6	38.1

a. For closed-shell singlet transition state, ¹TS2, LC-wPBE/6-31+G* method is used.

b. Reference energy is -1094.734556 a.u. for S0 ground state using LC-wPBE/6-31+G* method.

Table 3 Total Energies of adamantanone (AD) and 9(10-H) - acridone (AE);

LC-wPBE/6-31+G* for S0 and ULC-wPBE/6-31+G* for T1 states.

Products	Energy (Hartree)	Relative Energy (kcal/mol)
AD(S0) + AE (S0)	-1094.6035620	-82.2
AD*(T1) + AE (S0)	-1094.7187793	-9.9
AD (S0) + AE*(T1)	-1094.7045963	-18.8
AD* (S ₁) ^a + AE (S ₀)	-1094.7460299	7.2
a. TD- LC-wPBE/6-31+G*		
*: Excited state		

Figure Captions

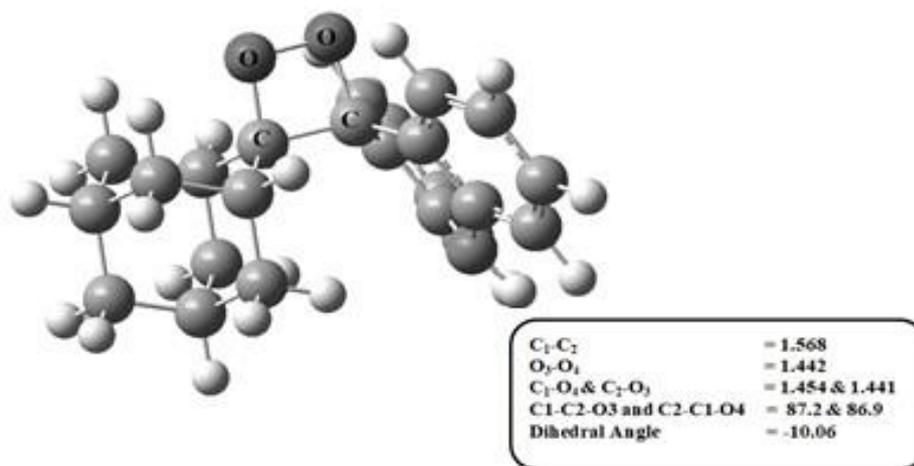


Fig. 1 Optimized geometrical parameters of the SAAD using LC-wPBE/ 6-31+G*.

Bond length in Å, bond angle and dihedral angle in degrees.

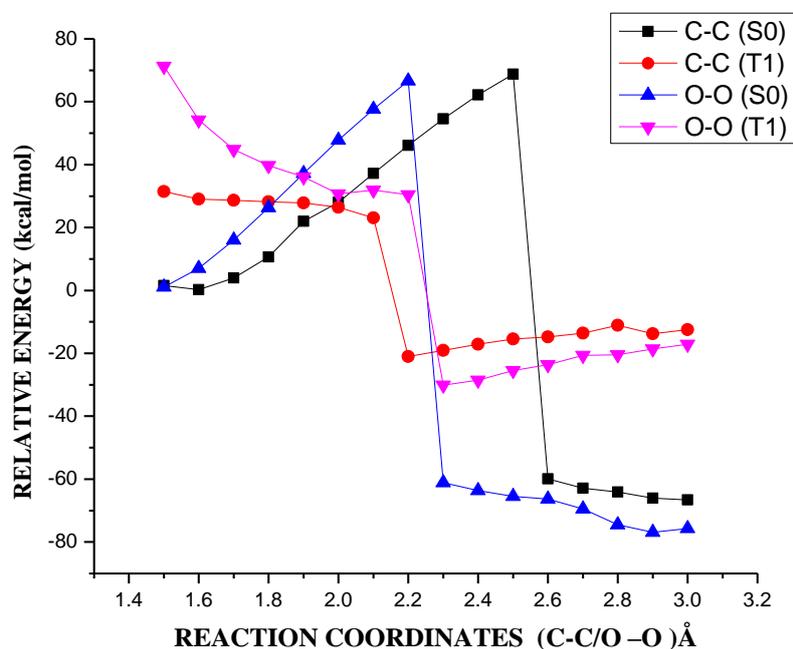


Fig. 2 Relative energy variation along the reaction path for the decomposition of SAAD into two fragments in the closed shell singlet (S_0) and triplet (T_1) states along the O-O and C-C stretching coordinates.

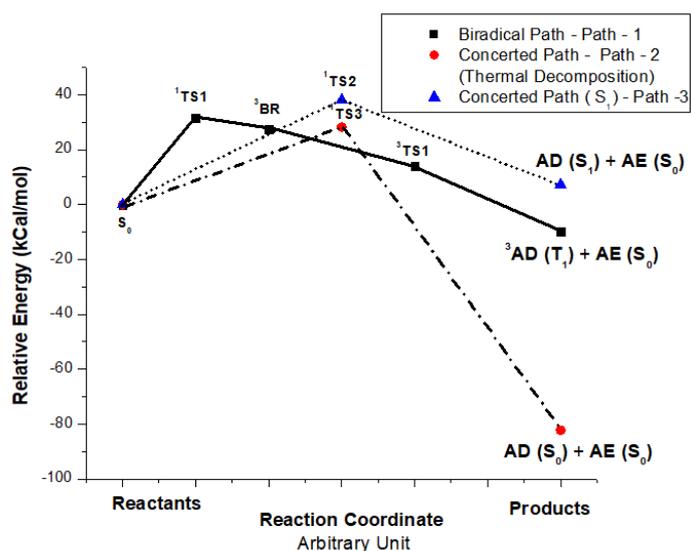
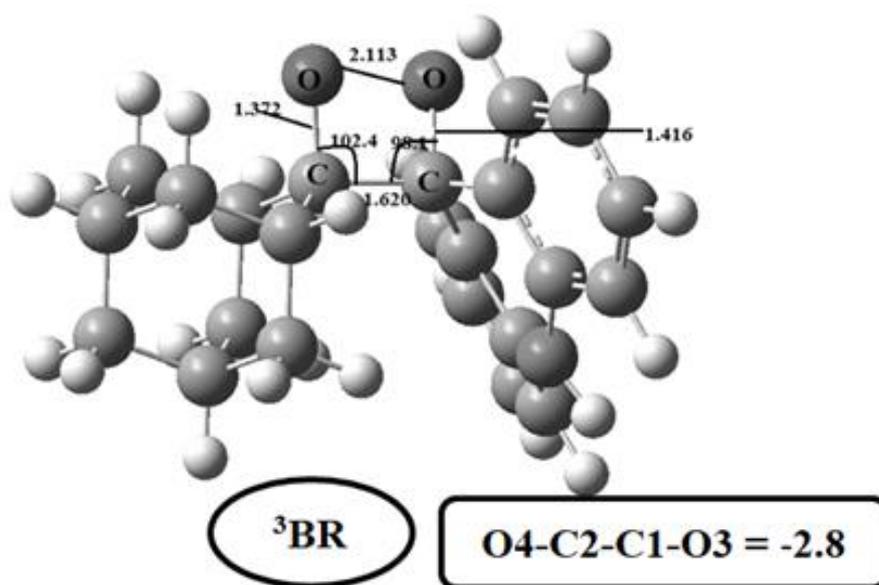
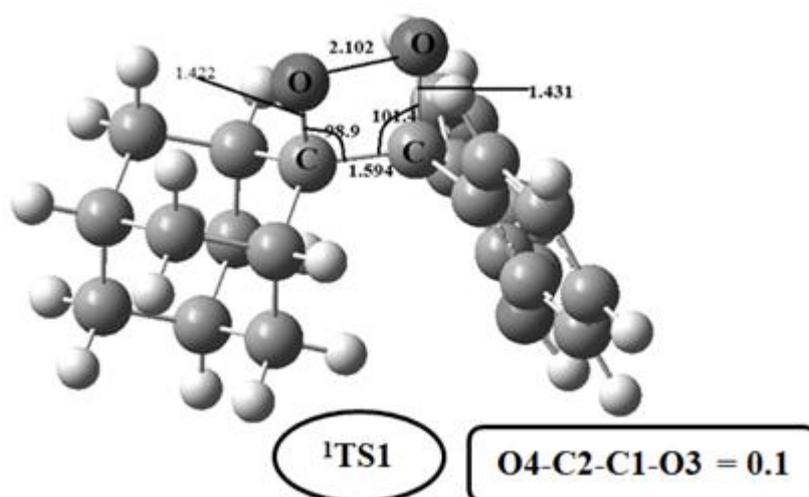


Fig. 3 Potential Energy Diagram for the decomposition of SAAD into products



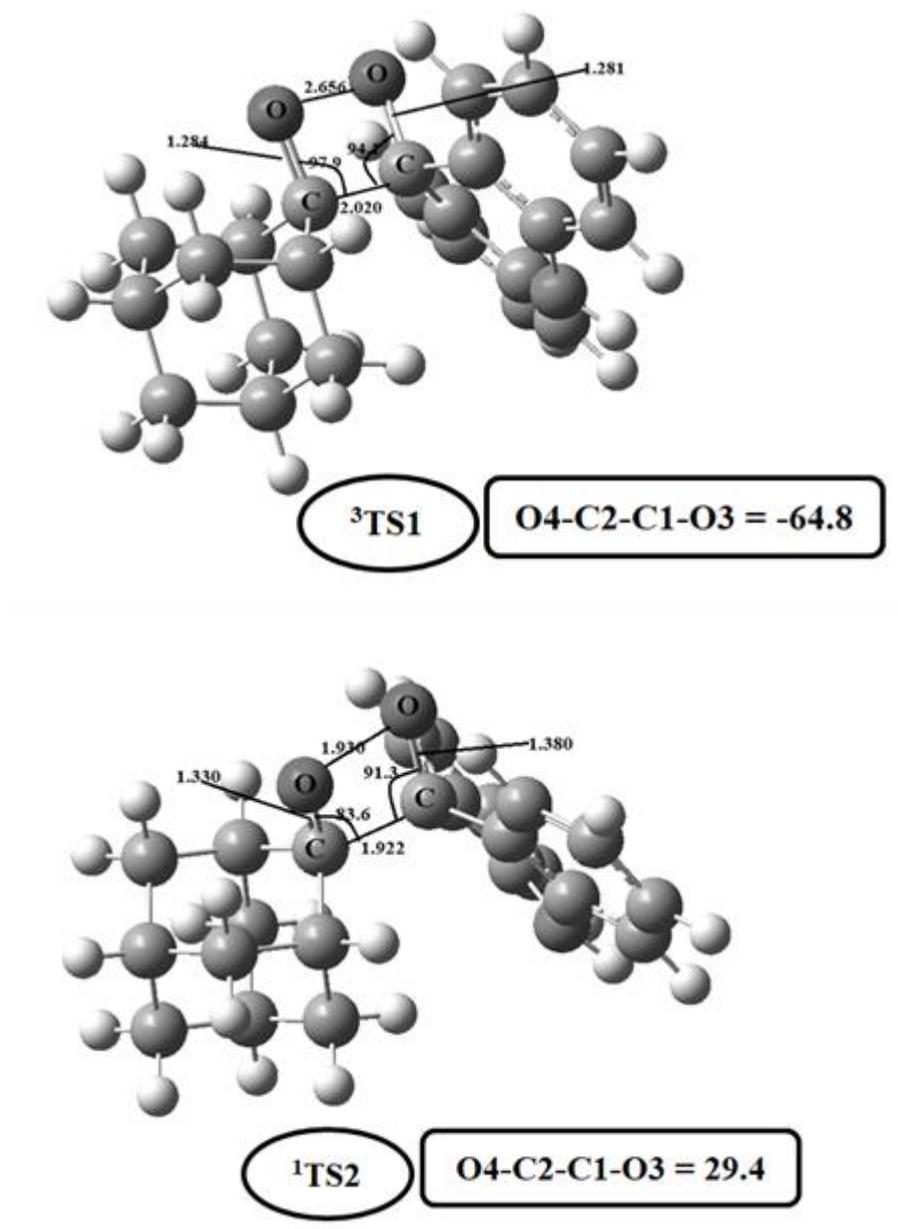


Fig. 4 SAAD's ¹TS1, ³BR, ³TS1 and ¹TS2 optimized geometrical parameters.

Bond length in Å, bond angle and dihedral angle in degrees.

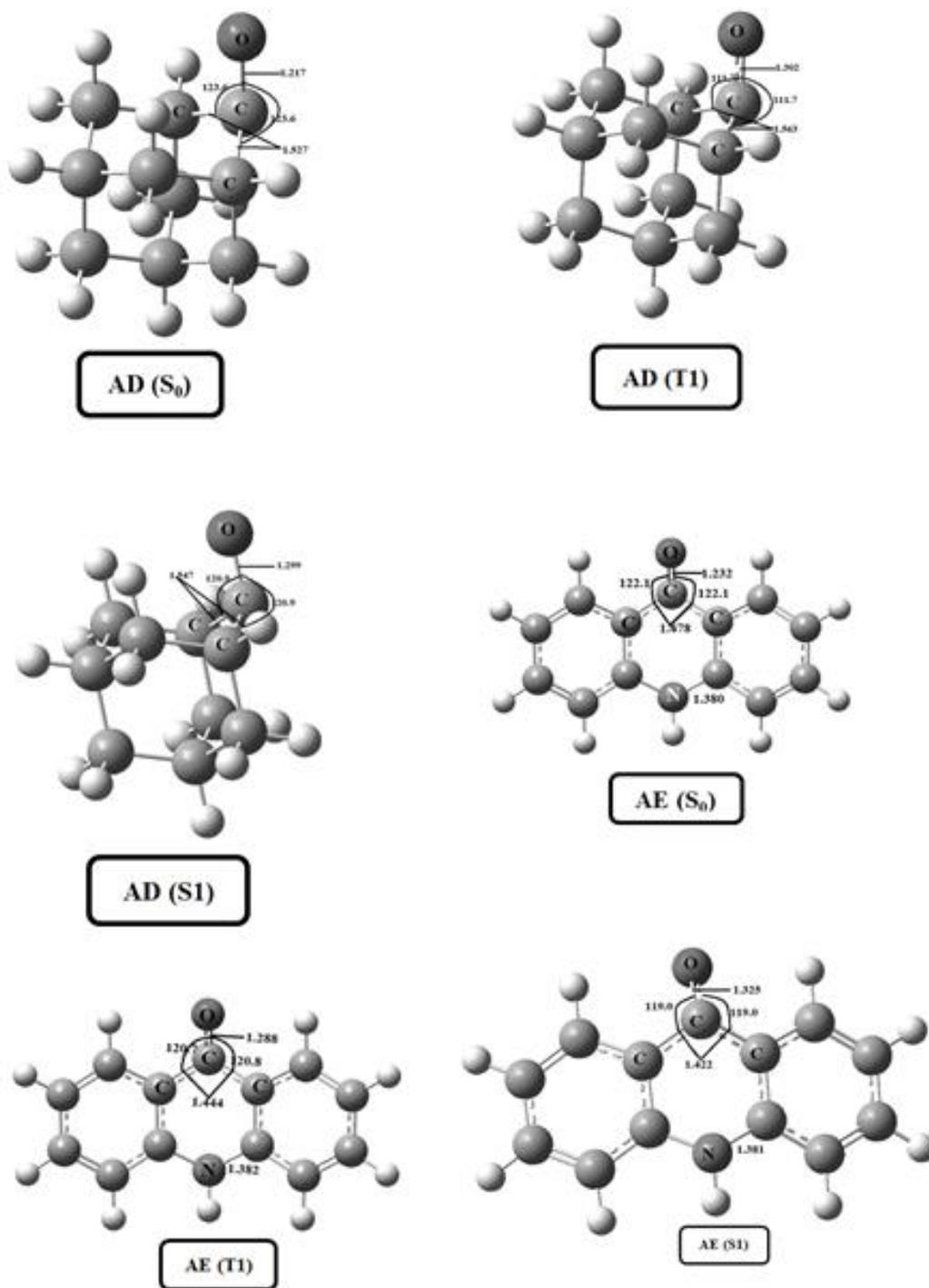


Fig. 5 Geometrical structures of the products AD and AE in S₀, T₁ and S₁ states.