

# Ab initio study of the photochemical isomerization of thiophene derivatives

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Received 20 September 2001; received in revised form 3 January 2002; accepted 10 January 2002

## Abstract

The photochemical isomerization reactions of thiophene, thiophene-2-carbonitrile, and 2-phenylthiophene were studied using ab initio methods. The results are in agreement with the previously reported data obtained through semiempirical methods. Triplet excited thiophene is a  $\pi, \sigma^*$  triplet with LSOMO at  $-9.94$  eV and HSOMO at  $-9.51$  eV and the biradical intermediate is a  $\pi, \pi^*$  species with LSOMO at  $-10.12$  eV and HSOMO at  $-4.82$  eV. In this case, the singlet excited state can evolve giving the Dewar thiophene, while the corresponding excited triplet state cannot be obtained. Furthermore, the triplet state cannot be converted into the biradical intermediate because this intermediate shows a higher energy than the triplet state, thus preventing the formation of the cyclopropenyl derivatives. Triplet excited thiophene-2-carbonitrile is a  $\pi, \pi^*$  species. It shows the LSOMO at  $-11.38$  eV and the HSOMO at  $-7.36$  eV. In this case, the direct irradiation involves the population of the excited singlet state, and then the formation of the Dewar isomer is possible. The intersystem crossing to the triplet state can occur; however, its interconversion into the corresponding biradicals cannot be efficient considering that the biradicals show a higher energy, even if for a little amount, than that of the triplet state. Triplet excited 2-phenylthiophene is a  $\pi, \pi^*$  species. It shows the LSOMO at  $-9.32$  eV and the HSOMO at  $-6.24$  eV. In this case, the direct irradiation involves the population of the excited singlet state, and then the formation of the Dewar isomer is possible. The energy of the excited singlet state was obtained from the UV absorption of the substrate. The intersystem crossing to the triplet state cannot occur; because it shows higher energy than the corresponding singlet state. Furthermore, its interconversion into the corresponding biradicals cannot be efficient considering that the biradicals show the same energy of the triplet state. The high efficiency of this reaction can be explained on the basis of low energy of the Dewar isomer. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Photochemistry; Ab initio calculations; Thiophene; Isomerization

## 1. Introduction

Recently, we reported that the photochemical isomerization of pentaatomic aromatic heterocycles [1] can be described using a unifying hypothesis [2–5]. If the first excited singlet state of a molecule is populated, the molecule can convert into the corresponding triplet state or into the corresponding Dewar isomer. The efficiency of these processes will depend on energetic factors. If the Dewar isomer is formed, the isomeric product is obtained. If the triplet state is formed, cleavage of the X–C $_{\alpha}$  bond can occur to give ring opening products, decomposition products or ring contraction products. However, if the radical formed after the X–C $_{\alpha}$  cleavage shows a higher energy than the triplet state, the triplet state will not be able to give the biradical with high efficiency, and then, it will be quenched in radiative and non-radiative processes. In this case, the Dewar isomer

could be responsible for the isomerization reaction, but the isomerized product will be probably produced in very low quantum yields. These results were obtained on the basis of both semiempirical calculations [2–4] and ab initio results on the photochemical isomerization of furan derivatives [5].

In this paper, we want to report our results on thiophene derivatives using ab initio calculations in order to test the validity of the above-described hypothesis.

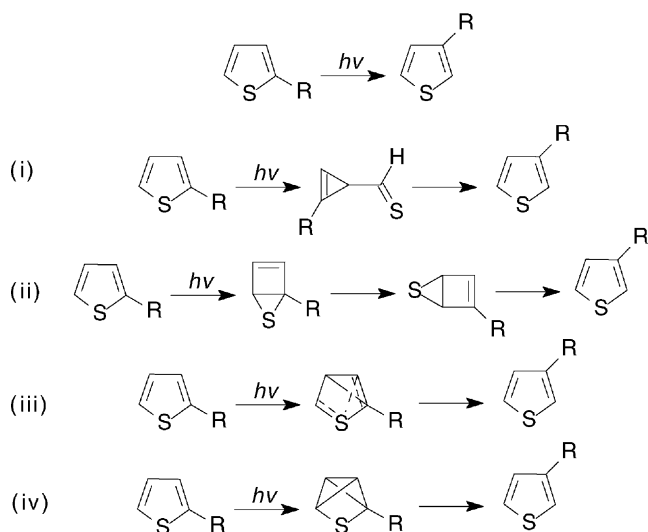
## 2. Results and discussion

The irradiation of the thiophene in gas phase yields decomposition products, while no Dewar thiophene or cyclopropene derivatives were isolated [6]. The irradiation in liquid phase gave the Dewar thiophene [7]. The Dewar thiophene and cyclopropene-3-thiocarbonyldehyde can be obtained by irradiation in argon matrices at 10 K [8].

Wynberg discovered the most interesting reaction in the photochemical reactivity of thienyl derivatives. The

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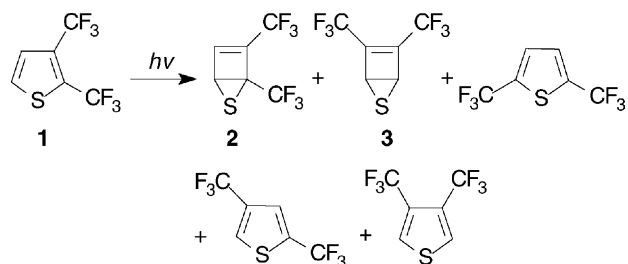


Scheme 1. Photochemical isomerization of thiophene derivatives and proposed mechanisms.

irradiation of 2-substituted thiophenes gave the corresponding 3-substituted derivatives (Scheme 1).

Several studies have been accomplished on the mechanism of this photoisomerization showing that the reaction takes place from the singlet excited state of the molecule [9,10]. Four mechanisms have been proposed (Scheme 1) and Wynberg preferred (iii) [11,12]. More recently several studies showed that mechanism (ii) is the most probable [13,14].

Alkylthiophenes reacted to give the corresponding transposition products but they showed low reactivity [15]. Better results were obtained using perfluoroalkyl derivatives. The tetrakis(trifluoromethyl) Dewar thiophene, isolated in 1970 by vapor-phase irradiation of the thiophene, was the first Dewar isomer isolated in this series [16–22]. The irradiation of 2,3-di-(trifluoromethyl)thiophene (**1**) gave a mixture of products where the authors found both isomeric thiophenes



Scheme 2. Photochemical isomerization of thiophene derivative **1**.

and a 8:1 mixture of Dewar isomers **2** and **3** (Scheme 2) [23,24].

As reported for the furan derivatives, also thiophenes, when irradiated in the presence of an amine, gave the corresponding pyrroles [25–28]. The authors proposed the formation of a cyclopropenyl intermediate, but, successively, a Dewar thiophene derivative, treated with aniline, gave the corresponding pyrrole showing that, probably, it is the true intermediate in this reaction [29].

We performed some ab initio calculations using 6–31 G\*\* basis set on Gaussian 94, using UHF method [30]. The calculations were usually done using Møller–Plesset perturbations (MP2). The Polak–Ribiere algorithm with gradient calculations was adopted for geometry optimizations. The open-shell states were treated at the same level of accuracy as the closed state states. We verified that the obtained structures were minima on the potential energy surfaces calculating the frequencies of the optimized structures. We investigated the ground state and the lowest triplet state of thiophene, the triplet biradical that results from the homolytic cleavage of the S–C $_{\alpha}$  bond (this biradical intermediate is supposed to occur in the isomerization process leading to the formation of the cyclopropenyl derivatives), and Dewar thiophene in its singlet state. The structural properties of all these compounds and/or intermediates are shown in Fig. 1.

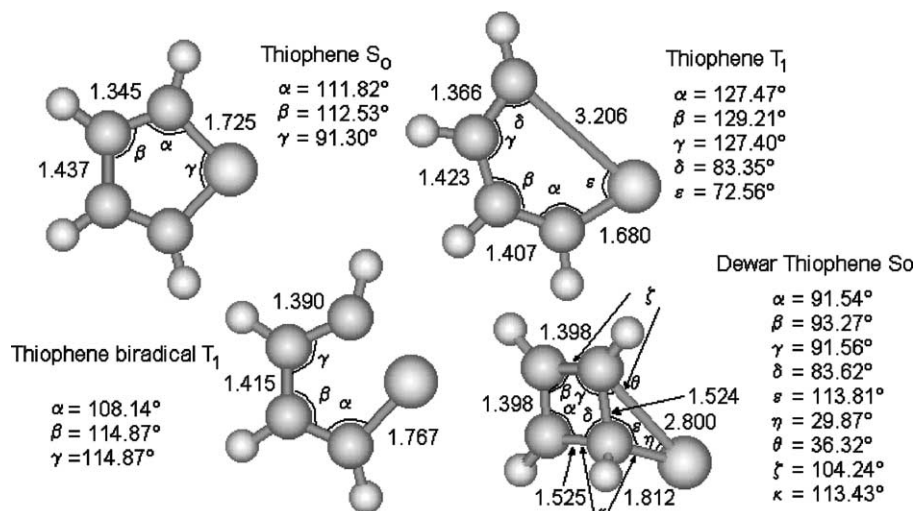


Fig. 1. Structural properties of compounds and intermediates involved in thiophene photochemical isomerization. Distances are given in angstroms.

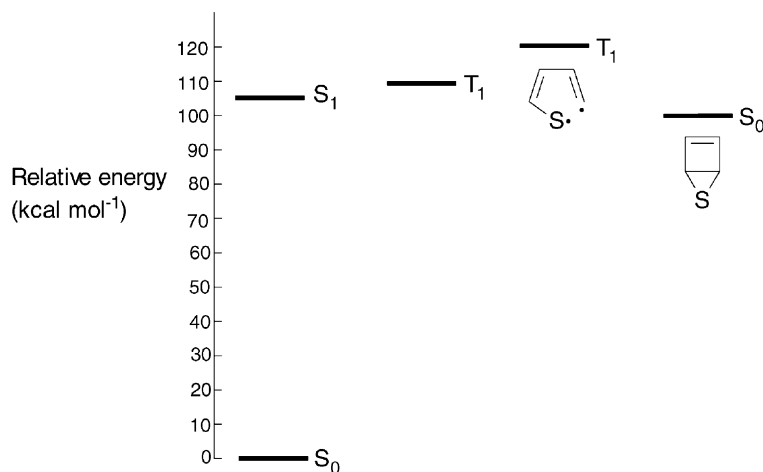
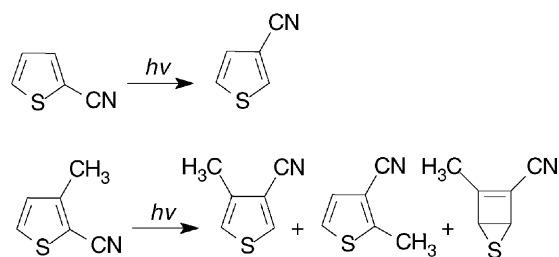


Fig. 2. Relative energy of the intermediates involved in the isomerization of thiophene.

We have to note that while thiophene in the ground state shows a partial dienic character (the C<sub>3</sub>–C<sub>4</sub> distance resembles that of a single C–C bond, while the C<sub>2</sub>–C<sub>3</sub> one is similar to a double C–C bond), the triplet state is clearly deformed until the S–C<sub>2</sub> bond can be considered as cleaved. It is interesting to note that thiophene does not show the behavior observed with furan [31]. The triplet state of furan showed that the C<sub>3</sub>–C<sub>4</sub> bond was shorter than the C<sub>2</sub>–C<sub>3</sub> one. Furthermore, in the biradical intermediate, the O–C<sub>5</sub> bond was a double bond, while the C<sub>4</sub>–C<sub>5</sub> bond resembled a single carbon–carbon bond. We do not observe the same trend in thiophene. Probably, this different behavior depends on the different nature of the electronic states involved. Triplet excited furan was a  $\pi, \pi^*$  triplet, while the resulting biradical was a  $\sigma, \pi^*$  species [5]; on the contrary, triplet excited thiophene is a  $\pi, \sigma^*$  triplet with LSOMO at  $-9.94$  eV and HSOMO at  $-9.51$  eV and the biradical intermediate is a  $\pi, \pi^*$  species with LSOMO at  $-10.12$  eV and HSOMO at  $-4.82$  eV.

Also Dewar thiophene shows a distorted structure, where the S–C<sub>2</sub> bond is almost cleaved. The relative energies for the four above-mentioned structures are shown in Fig. 2 and Table 1. They are in agreement with experimental results. In



Scheme 3. Photochemical isomerization of cyanothiophene derivatives.

fact, the singlet excited state (the energy was obtained from the UV spectrum) can evolve giving the Dewar thiophene (and, then, isomeric thiophenes), while the corresponding excited-triplet state cannot be obtained. Furthermore, the triplet state cannot be converted into the biradical intermediate because this intermediate shows a higher energy than the triplet state, thus preventing the formation of the cyclopropenyl derivatives.

The irradiation of 2- and 3-cyanothiophene gave interesting results in agreement with the scheme described above (Scheme 3). The photoisomerization reaction involved only the  $\pi, \pi^*$  excited singlet state and Dewar thiophenes were

Table 1  
Relative energy of some thiophene derivatives and reactive intermediates

Compound	Electronic state	Relative energy (kcal mol <sup>-1</sup> )
Thiophene	T <sub>1</sub>	109
Thiophene biradical (fission of S–C <sub>α</sub> bond)	T <sub>1</sub>	122
Dewar thiophene	S <sub>0</sub>	98
Thiophene-2-carbonitrile	T <sub>1</sub>	94
Thiophene-2-carbonitrile biradical (fission of S–C <sub>2</sub> bond)	T <sub>1</sub>	96
Thiophene-2-carbonitrile biradical (fission of S–C <sub>5</sub> bond)	T <sub>1</sub>	96
Dewar thiophene-2-carbonitrile	S <sub>0</sub>	98
2-Phenylthiophene	T <sub>1</sub>	102
2-Phenylthiophene biradical (fission of S–C <sub>2</sub> bond)	T <sub>1</sub>	102
2-Phenylthiophene biradical (fission of S–C <sub>5</sub> bond)	T <sub>1</sub>	102
Dewar 2-phenylthiophene	S <sub>0</sub>	56

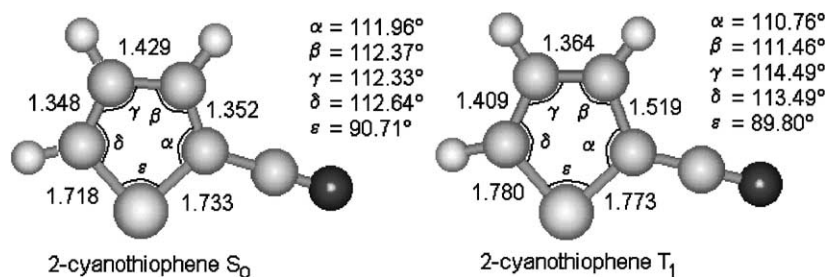


Fig. 3. Structural properties of thiophene-2-carbonitrile  $S_0$  and  $T_1$ . Distances are given in angstroms.

isolated when the reactions were carried out at  $-68^\circ\text{C}$  and shown to be intermediates in the isomerization reactions [32,33].

The structural properties of all the possible intermediates involved in the photochemical isomerization of 2-cyanothiophene are shown in Figs. 3 and 4. In Fig. 3, the structural properties of thiophene-2-carbonitrile in the ground state and in its excited triplet state are shown. In Fig. 4, the structural properties of the biradicals derived from both S-C<sub>2</sub> and S-C<sub>5</sub> bond cleavage are shown. Furthermore, Fig. 4 also shows the data relative to Dewar thiophene-2-carbonitrile.

We note that in the ground state, the bond length is larger for S-C<sub>2</sub> than for S-C<sub>5</sub>, but this feature is lost in the triplet state. In the latter state, the C<sub>2</sub>-C<sub>3</sub> bond is longer than the C<sub>4</sub>-C<sub>5</sub> bond and the S-C<sub>2</sub> bond is shorter than the S-C<sub>5</sub> bond.

The biradicals that result from the fission of both the S-C<sub>2</sub> and the S-C<sub>5</sub> bond show the same structure as the triplet state: we observed the same bond lengths and the same bond angles. Furthermore, in Dewar thiophene-2-carbonitrile the S-C<sub>5</sub> bond is practically broken.

In this case, triplet excited thiophene-2-carbonitrile is a  $\pi, \pi^*$  species. It shows the LSOMO at  $-11.38\text{ eV}$  and the

HSOMO at  $-7.36\text{ eV}$ . The relative energy of the possible intermediates involved in the photochemical isomerization is shown in Fig. 5 and Table 1.

In this case, the direct irradiation involves the population of the excited singlet state (its energy was calculated on the basis of the UV absorption), and then the formation of the Dewar isomer is possible. The intersystem crossing to the triplet state can occur; however, its interconversion into the corresponding biradicals cannot be efficient considering that the biradicals show a higher energy, even if for a little amount, than that of the triplet state.

Arylthiophenes were used as substrates in the photoisomerization described in Scheme 1 [34–39]. The dithienyls gave this reaction efficiently, while 2-(2-pyridyl)thiophene and 2-(2-furyl)thiophene did not give this reaction in a reasonable yield [40,41]. Carbonyl and olefinic substituents inhibit the rearrangement [42–51].

The structural properties of all the possible intermediates involved in the photochemical isomerization of 2-phenylthiophene are shown in Figs. 6 and 7. In Fig. 6, the structural properties of 2-phenylthiophene in the ground state and in its excited triplet state are shown. In Fig. 7, the structural properties of the biradicals derived from both S-C<sub>2</sub> and S-C<sub>5</sub> bond cleavage are shown. Furthermore,

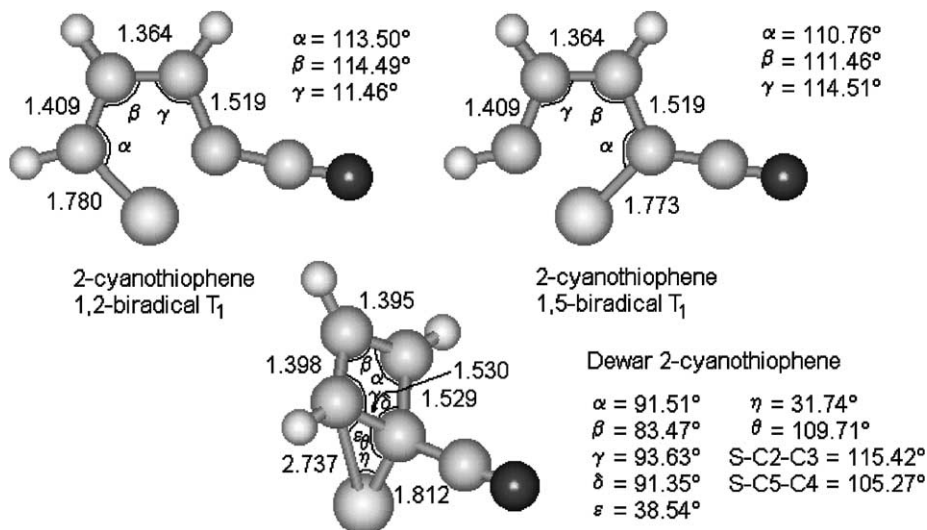


Fig. 4. Structural properties of possible intermediates involved in thiophene-2-carbonitrile photochemical isomerization. Distances are given in angstroms.

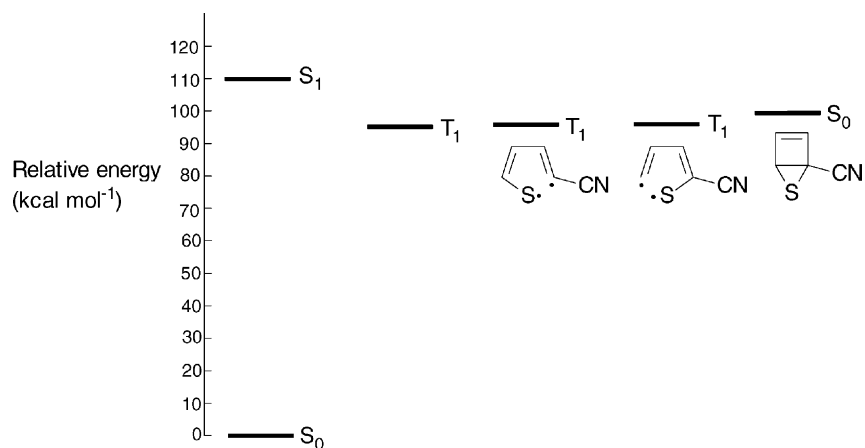


Fig. 5. Relative energy of the intermediates involved in the isomerization of thiophene-2-carbonitrile.

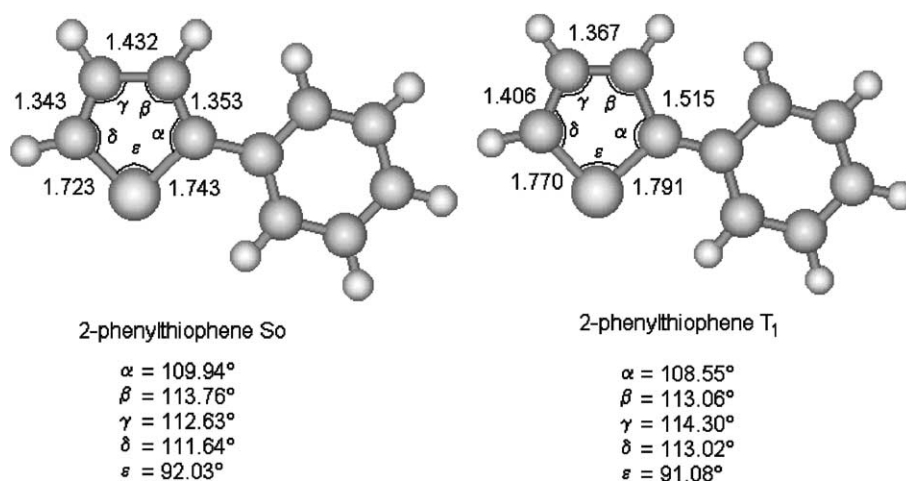


Fig. 6. Structural properties of 2-phenylthiophene S<sub>0</sub> and T<sub>1</sub>. Distances are given in angstroms.

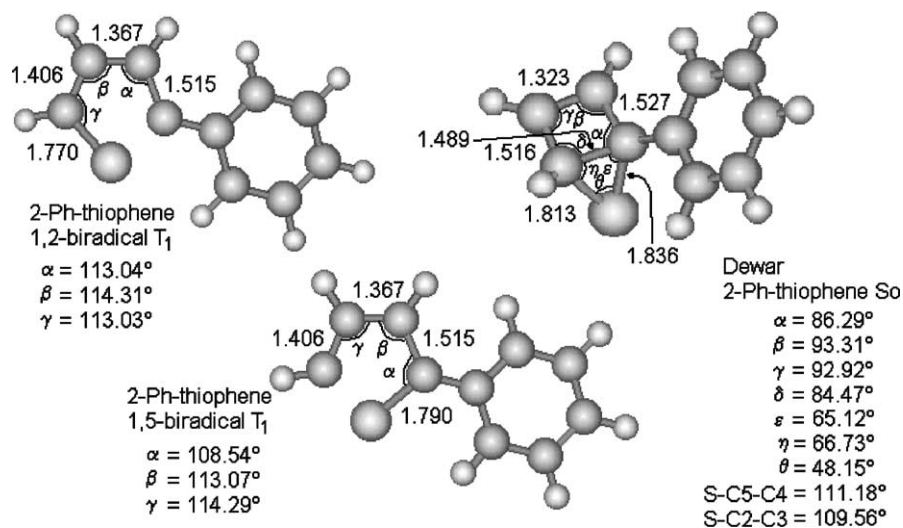


Fig. 7. Structural properties of possible intermediates involved in 2-phenylthiophene photochemical isomerization. Distances are given in angstroms.

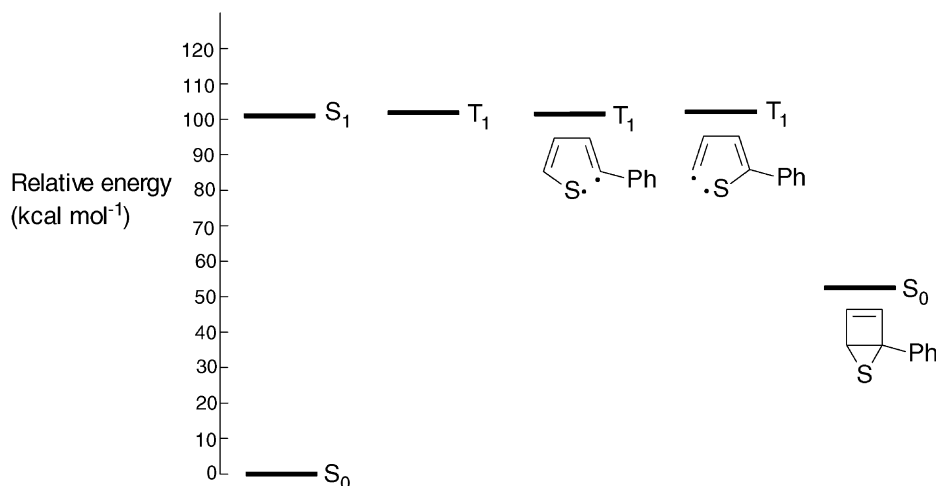


Fig. 8. Relative energy of the intermediates involved in the isomerization of 2-phenylthiophene.

Fig. 7 also shows the data relative to Dewar 2-phenylthiophene.

We note that in both the ground and triplet state, the bond length is larger for S–C<sub>2</sub> than for S–C<sub>5</sub>. In the latter state, the C<sub>2</sub>–C<sub>3</sub> bond is longer than the C<sub>4</sub>–C<sub>5</sub> bond. The biradicals that result from the fission of both the S–C<sub>2</sub> and the S–C<sub>5</sub> bond show the same structure as the triplet state: we observed the same bond lengths and the same bond angles. Furthermore, in Dewar 2-phenylthiophene both S–C<sub>2</sub> and S–C<sub>5</sub> bond have comparable lengths, showing a different behavior from thiophene-2-carbonitrile. In this case, triplet excited 2-phenylthiophene is a  $\pi, \pi^*$  species. It shows the LSOMO at  $-9.32$  eV and the HSOMO at  $-6.24$  eV. The relative energy of the possible intermediates involved in the photochemical isomerization is shown in Fig. 8 and Table 1.

In this case, the direct irradiation involves the population of the excited singlet state, and then the formation of the Dewar isomer is possible. The energy of the excited singlet state was obtained from the UV absorption of the substrate. The intersystem crossing to the triplet state cannot occur; because it shows higher energy than the corresponding singlet state. Furthermore, its interconversion into the corresponding biradicals cannot be efficient considering that the biradicals show the same energy of the triplet state. The high efficiency of this reaction can be explained on the basis of low energy of the Dewar isomer.

### 3. Conclusion

In conclusion, the results of the above-described *ab initio* study of the photochemical isomerization of thiophene derivatives are in agreement with experimental results and with previous reported data obtained from semiempirical methods. In this case, the photochemical isomerization involves the formation of the Dewar isomer. The triplet state can be obtained, and, when it can be obtained, it is not able

to convert into the corresponding biradicals via S–C <sub>$\alpha$</sub>  bond cleavage.

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