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# Ab Initio Study on the Photochemical Isomerization of Furan Derivatives

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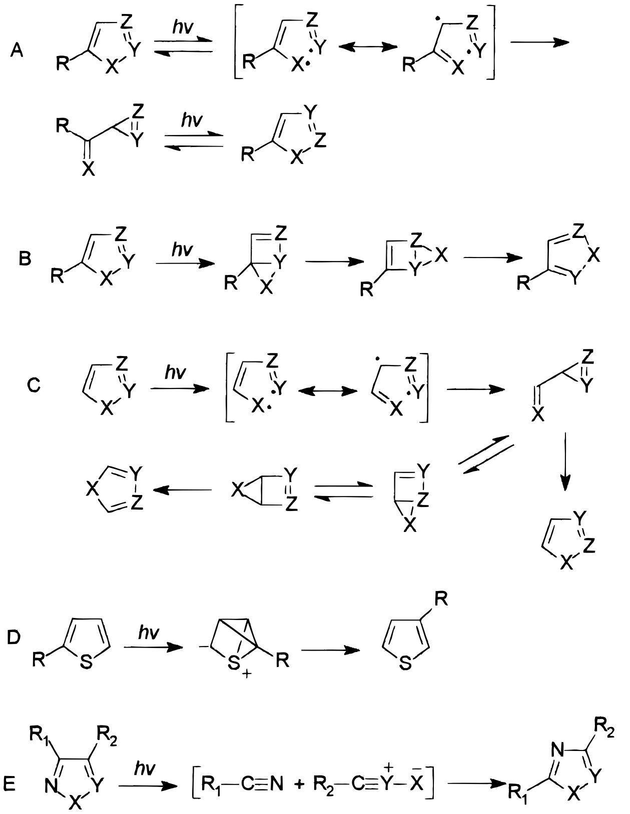
The photochemical isomerization reactions of furan, 2-methylfuran, 2-trimethylsilylfuran, and furan-2-carbonitrile were studied using ab initio methods. The results are in agreement with the previously reported data obtained through semiempirical methods. In particular, the sensitized irradiation of furan derivatives populates the first excited triplet state of the furan, and this triplet state can evolve only through O−C$_\alpha$ cleavage. The selection of the bond to be broken can depend on energetic factors (furan-2-carbonitrile) or on kinetic factors (2-methylfuran, 2-trimethylsilylfuran). The direct irradiation of furan derivatives populates the singlet excited state and leads to a conversion into the Dewar isomer or into the corresponding triplet state through the usual intersystem crossing procedure. The efficiency of these processes determines the presence or the absence of isomerized furan derivatives in the reaction mixtures.

The photochemical isomerization of pentaatomic aromatic heterocycles is a well-known reaction and there exists a comprehensive review on this subject.[1] Five mechanisms can be invoked in order to justify the observed behaviors: (1) the ring contraction−ring expansion route (RCRE) (Scheme 1, A); (2) the internal cyclization−isomerization route (ICI) (Scheme 1, B); (3) the van Tamelen−Whitesides general mechanism (VTW) (Scheme 1, C); (4) the zwitterion−tricycle route (ZT) (Scheme 1, D); (5) the fragmentation−readdition route (FR) (Scheme 1, E).

Recently we described a first attempt to give a unified description of the photochemical isomerization of these $\pi$-excessive heterocycles.[2−4] The use of semiempirical calculations allowed us to formulate a very simple unifying hypothesis. 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 not 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.

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

**Scheme 1**



## Results and Discussion

The first report on the gas-phase photolysis of furan was published in 1967.[5] The author reported that the photolysis of furan and mercury vapor at 254 nm gave carbon monoxide and a fraction containing mainly cyclopropene and a very small amount of allene (Scheme 2).

Subsequently, carrying out the reaction at a higher pressure of furan, the same author showed that three

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(1) Lablache-Combier, A. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W., Ed.; CRC Press: Boca Raton, 1995; p 1063.

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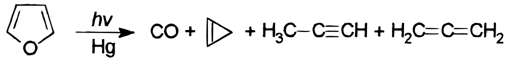
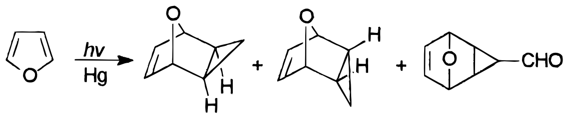
(5) Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 1758.

10.1021/jo991655p CCC: $19.00

**Scheme 2**



**Scheme 3**



new products were obtained. The first two compounds were the Diels−Alder adducts obtained by the coupling between furan and cyclopropene while the third was the Diels−Alder adduct obtained by the coupling between furan and cyclopropene-3-carbaldehyde (Scheme 3). None of the products reported was observed on direct irradiation of furan in solution.[6,7]

Liquid-phase photolysis of furan is in agreement with the formation of cyclopropene-3-carbaldehyde.[8] The direct flash photolysis of furan gave, on the contrary, a different behavior. Mass fragments corresponding to $C_4H^+$, $C_4H_2^+$, $C_4H_3^+$, and $C_4H_4^+$ were observed together with the formation of cyclopropene-3-carbaldehyde.[9] This behavior can be explained assuming that Dewar furan is the precursor of the cyclopropene derivative. Dewar furan also can be obtained by the photolysis of furan in argon matrixes at 10 K.[10] The direct irradiation of the furan gave carbon monoxide, methylacetylene, and allene, while cyclopropene was detected only in traces.[11]

We performed some ab initio calculations using 6-31G** basis set on Gaussian 94, using UHF method.[12] 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 reported in Table 1 the results of the frequency calculations for furan, methylfuran (see below), and all the intermediates involved. We investigated the ground state and the lowest triplet state of furan, the triplet biradical that results from the homolytic cleavage of the $O-C_\alpha$ bond (this biradical intermediate is supposed to occur in the isomerization process leading to the formation of the cyclopropenyl derivatives), and Dewar furan in its singlet state. The structural properties of all these compounds and/or intermediates are collected in Figure 1. It is noteworthy that, while in the $S_0$ state, furan is almost a diene with a $C_2-C_3$ bond that resembles a double bond and a $C_3-C_4$ bond similar to a single bond. In the triplet state we observe an inversion of this structural arrangement, with the $C_3-C_4$ bond shorter that the $C_2-C_3$ one. Furthermore, in the biradical intermediate the $O-C_5$ bond is a double bond, while the $C_4-C_5$ bond resembles a single carbon−carbon bond.

The relative energies for the four above-mentioned structures are shown in Figure 2 and Table 2. They are in agreement with the experimental results. In the case of sensititized reactions,[4−6] when the excited triplet state is populated, only the formation of the biradical intermediate is allowed. In this case, the observed decomposition products must result from this intermediate.

In the case of direct irradiation, the singlet exited state is populated and the formation of Dewar furan is energetically possible. This result is consistent with both the possible formation of Dewar furan in direct irradiation and the observed formation of isomeric furans.

Our results are in agreement with previous theoretical investigations on the photochemical isomerization of furan.[13,14] In these studies it was pointed out that the photochemical isomerization involved a $\pi,\pi^*$ triplet state that is converted into a $\sigma,\pi$ biradical through spin−orbit coupling. Our calculations show that triplet excited furan is a $\pi,\pi^*$ triplet with the LSOMO at −11.06 eV and the HSOMO at −6.23 eV. The resulting biradical intermediate is a $\sigma,\pi$ species with LSOMO at −11.03 eV and the HSOMO at −10.06 eV.

2-Methylfuran, irradiated in the presence of mercury vapor, gave carbon monoxide and a fraction containing 1,3-butadiene and 3-methylcyclopropene (45:55).[5] Later, it was found that in both, sensitized and direct photolysis of 2-methylfuran, a more complex mixture of products is obtained in which 3-methylfuran is also present (Scheme 4).[15,16]

The structural properties of all the possible intermediates involved in the photochemical isomerization of 2-methylfuran are collected in Figure 3. We can see that in this case, too, the triplet state of 2-methylfuran exhibits pronounced modifications of bond lengths. This is true in particular for the bond between $C_4$ and $C_5$. Furthermore, the molecule is not planar and the hydrogen atom on $C_5$ is out of plane with a torsion angle of −56.22°. It is noteworthy that in previous studies some authors claimed the possibility to predict the direction of the ring contraction: in their opinion, the weakest bond between $O-C_2$ and $O-C_5$ is broken during the reaction.[17,18] Our results do not confirm this hypothesis. In the triplet state of 2-methylfuran the distance between O and $C_2$ is the same as the one between O and $C_5$. We calculated the structural properties of all the possible biradicals that can be derived from the fission of a $O-C_\alpha$ bond (Figure 3). In all these cases the C−O bond is well described as a double bond while $C_4-C_5$ turns out to be a single carbon−carbon bond.

The relative energies of all possible intermediates involved in the photochemical isomerization are shown in Figure 4 and Table 2. As in the case of furan the sensitized irradiation can only lead to the formation of the biradicals. We have to note, however, that the fission

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**Table 1. Vibrational Frequencies of Suitable Structures**

| compound | electron. state | vibrational frequencies ($cm^{-1}$) |
|---|---|---|
| furan | $S_0$ | 659.21, 852.23, 955.51, 960.70, 1088.56, 1160.21, 1320.78, 1549.59, 1678.60, 1767.23, 3414.47, 3427.24, 3456.13 |
| furan | $T_1$ | 384.43, 478.33, 525.41, 801.67, 885.47, 934.61, 1070.93, 1130.55, 1168.17, 1275.31, 1361.10, 1430.76, 1500.32, 1586.97, 3401.92, 3426.37, 3447.07, 3461.91 |
| furan biradical (fission of O$-$C$_\alpha$ bond) | $T_1$ | 369.13, 514.20, 713.99, 714.36, 924.33, 948.69, 960.42, 1096.87, 1264.73, 1467.44, 1740.73, 2047.83, 2828.63, 3208.54, 3223.92, 3239.41 |
| Dewar furan | $S_0$ | 572.48, 849.45, 924.06, 945.72, 963.69, 1047.95, 1057.11, 1093.73, 1183.12, 1190.91, 1368.87, 1428.57, 1523.97, 1759.00, 3392.19, 3402.09, 3417.47 |
| 2-methylfuran | $S_0$ | 435.58, 686.76, 785.44, 914.02, 947.39, 1008.75, 1150.47, 1341.83, 1383.27, 1387.34, 1551.05, 1796.16, 1885.69, 3270.30, 3288.45, 3297.72, 3300.20 |
| 2-methylfuran | $T_1$ | 440.94, 622.14, 774.96, 797.27, 856.05, 900.59, 924.03, 1021.85, 1036.23, 1195.21, 1212.06, 1312.30, 1424.56, 1589.10, 1640.64, 3088.80, 3159.90, 3194.16, 3266.47, 3281.43, 3293.42 |
| 2-methylfuran biradical (fission of O$-$C$_5$ bond) | $T_1$ | 440.80, 622.51, 774.69, 797.31, 856.37, 900.42, 924.15, 1022.22, 1036.08, 1194.97, 1212.01, 1312.55, 1425.18, 1590.26, 1641.08, 3090.38, 3159.80, 3193.40, 3265.16, 3281.07, 3292.71 |
| 2-methylfuran biradical (fission of O$-$C$_2$ bond) | $T_1$ | 440.79, 621.91, 775.84, 797.62, 856.36, 901.60, 924.16, 1022.05, 1036.50, 1194.24, 1212.08, 1312.48, 1424.99, 1589.18, 1641.45, 3087.72, 3159.95, 3192.47, 3265.31, 3280.21, 3293.07 |
| Dewar 2-methylfuran | $S_0$ | 432.72, 505.90, 710.47, 773.08, 824.50, 932.01, 1088.34, 1151.93, 1225.30, 1310.19, 1382.20, 1800.16, 3201.34, 3257.54, 3262.55, 3283.64 |

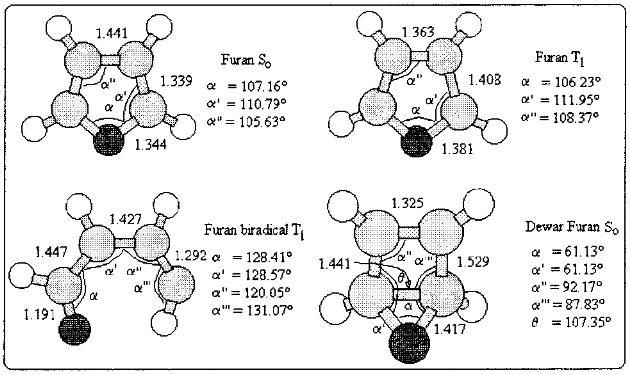


**Figure 1.** Structural properties of compounds and intermediates involved in furan photochemical isomerization. Distances are given in angstroms.

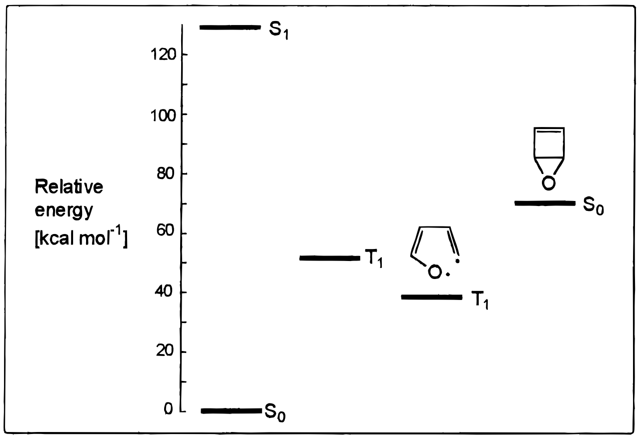


**Figure 2.** Relative energy of the intermediates involved in the isomerization of furan.

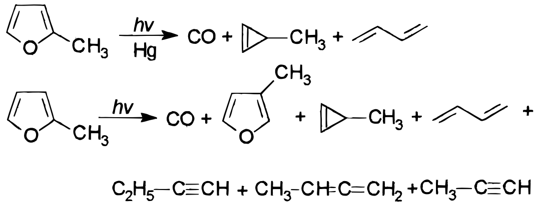
of a O$-$C$_\alpha$ bond in the triplet state is not as favored as in furan. The process should be quite inefficient. The corresponding biradicals show the same energy as the triplet state. In this case, then, the formation of a biradical should depend on the activation energy.

The photochemical isomerization of 2-methylfuran can be explained assuming the same behavior as in furan. The triplet state of 2-methylfuran is $\pi,\pi^*$ with the LSOMO at $-10.72$ eV and the HSOMO at $-6.78$ eV. The biradical derived from the cleavage of the O$-$C$_2$ bond is a $\sigma,\pi$ triplet state with LSOMO at $-10.71$ eV and the HSOMO at $-6.80$ eV. The biradical derived from the cleavage of the O$-$C$_5$ bond is the same type of triplet with LSOMO at $-10.72$ eV and HSOMO $-6.78$ eV.

**Table 2. Relative Energy of Some Furan Derivatives and Reactive Intermediates**

| compound | electron. state | relative energy (kcal mol$^{-1}$) |
|---|---|---|
| furan | $T_1$ | 52 |
| furan biradical (fission of O$-$C$_\alpha$ bond) | $T_1$ | 38 |
| Dewar furan | $S_0$ | 71 |
| 2-methylfuran | $T_1$ | 52 |
| 2-methylfuran biradical (fission of O$-$C$_5$ bond) | $T_1$ | 52 |
| 2-methylfuran biradical (fission of O$-$C$_2$ bond) | $T_1$ | 52 |
| Dewar 2-methylfuran | $S_0$ | 70 |
| 2-trimethylsilylfuran | $T_1$ | 47 |
| 2-trimethylsilylfuran biradical (fission of O$-$C$_5$ bond) | $T_1$ | 47 |
| 2-trimethylsilylfuran biradical (fission of O$-$C$_2$ bond) | $T_1$ | 47 |
| Dewar 2-trimethylsilylfuran | $S_0$ | 84 |
| furan-2-carbonitrile | $T_1$ | 47 |
| furan-2-carbonitrile biradical (fission of O$-$C$_5$ bond) | $T_1$ | 155 |
| furan-2-carbonitrile biradical (fission of O$-$C$_2$ bond) | $T_1$ | 47 |
| Dewar furan-2-carbonitrile | $S_0$ | 73 |

**Scheme 4**



The irradiation of 2-trimethylsilylfuran gave the corresponding ring opening product in 68% yield (Scheme 5).[19]

The authors, assuming the intervention of a cyclopropenyl intermediate, explained the formation of this type of product.

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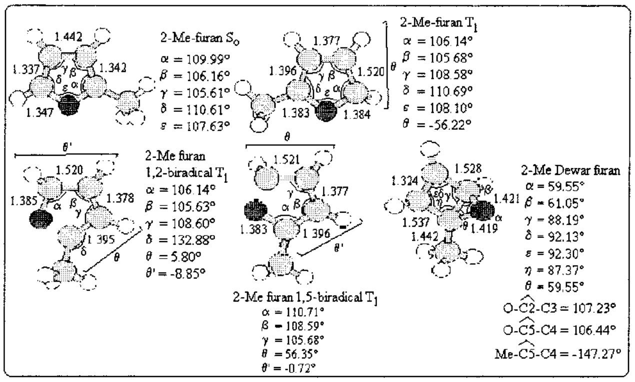


**Figure 3.** Structural properties of compounds and intermediates involved in 2-methylfuran photochemical isomerization. Distances are given in angstroms.

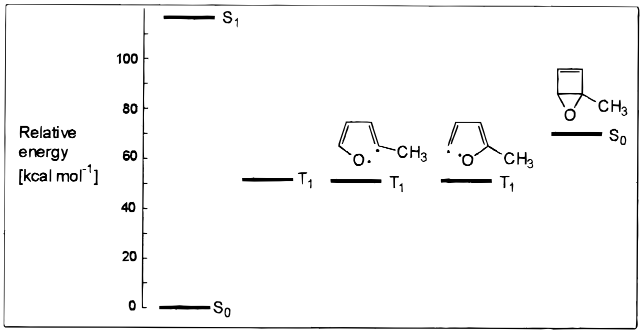
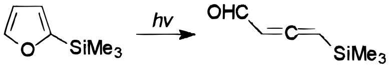


**Figure 4.** Relative energy of the intermediates involved in the isomerization of 2-methylfuran.

### Scheme 5



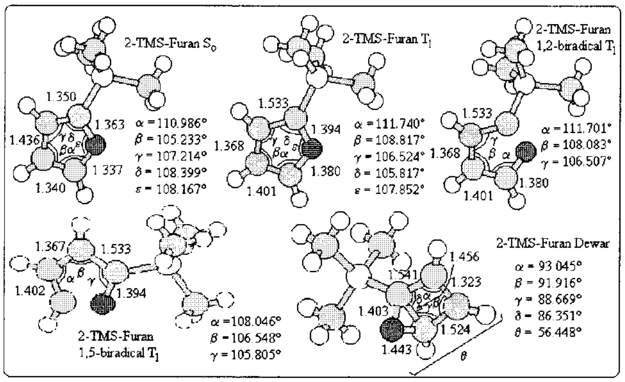


**Figure 5.** Structural properties of compounds and intermediates involved in 2-trimethylsilylfuran photochemical isomerization. Distances are given in Å.

The structural properties of all the possible intermediates involved in the photochemical isomerization of 2-trimethylsilylfuran are collected in Figure 5. We can see that in this case, too, the triplet state of 2-trimethylsilylfuran exhibits pronounced modifications of bond lengths. In contrast to the triplet state of 2-methylfuran, the triplet state of 2-trimethylsilylfuran is planar. We also calculated the properties of the possible fission products (the 1,2-biradical and the 1,5-biradical): it is interesting to note in this context that all these intermediates are planar and that they maintain bond lengths and angles of the triplet state.

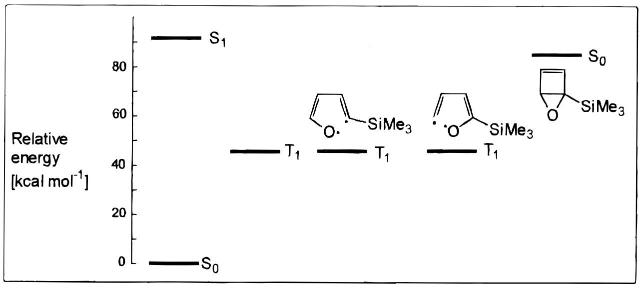
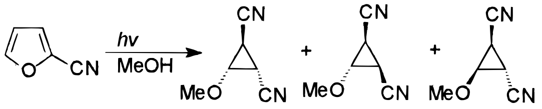


**Figure 6.** Relative energy of the intermediates involved in the isomerization of 2-trimethylsilylfuran.

### Scheme 6



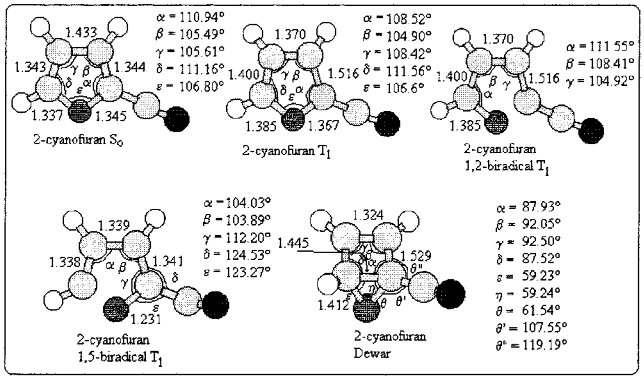


**Figure 7.** Structural properties of compounds and intermediates involved in furan-2-carbonitrile photochemical isomerization. Distances are given in angstroms.

The calculated relative energies are shown in Figure 6 and Table 2. In this case the direct irradiation involves the population of the excited singlet state, and then the formation of the Dewar isomer is possible. As in 2-methylfuran, the fission of a O$-$C$_\alpha$ bond in the triplet state is not so favored as in furan. The corresponding biradicals show the same energy as the triplet state. The formation of a biradical should again depend on the activation energy.

The reaction of furan-2-carbonitrile in methanol allowed the authors to isolate a possible cyclopropenyl intermediate. In this case, the reaction gives a mixture of isomeric products containing methoxy substituents. These products clearly arise from a cyclopropenyl intermediate through a Michael addition of methanol (Scheme 6).[20,21]

The calculation of the structural properties of the possible intermediates gave the results reported in Figure 7. We note that in the ground state the bond length is larger for O$-$C$_2$ than for O$-$C$_5$, but that this feature is lost in the triplet state. In the latter state the molecule is distorted and the C$_2-$C$_3$ bond is longer than the C$_4-$C$_5$ bond and the O$-$C$_2$ bond shorter than the O$-$C$_5$ bond.

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(20) Hiraoka, H. *J. Chem. Soc., Chem. Commun.* **1971**, 1610.
(21) Hiraoka, H. *Tetrahedron* **1973**, *29*, 2955.

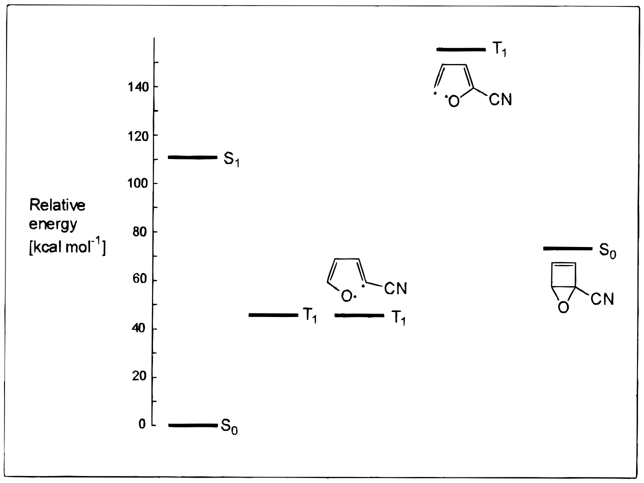

**Figure 8.** Relative energy of the intermediates involved in the isomerization of furan-2-carbonitrile.

The biradical that results from the fission of the O$-$C$_2$ bond shows the same structure as the triplet state: we observed the same bond lengths and the same bond angles. This feature is not observed when the O$-$C$_5$ bond is broken.

The relative energy of the possible intermediates involved in the photochemical isomerization is collected in Figure 8 and Table 2. In this case the direct irradiation involves the population the excited singlet state, and then the formation of the Dewar isomer is possible. We have to note that, as in furan, the fission of a O$-$C$_\alpha$ bond in the triplet state is favored if the O$-$C$_2$ bond is broken. The fission of the O$-$C$_5$ bond leads to the formation of a high energy species.

The triplet state of furan-2-carbonitrile is $\pi,\pi^*$ with the LSOMO at $-11.52$ eV and the HSOMO at $-7.41$ eV. The biradical derived from the cleavage of the O$-$C$_2$ bond is a $\pi,\pi^*$ triplet with the LSOMO at $-11.52$ eV and the HSOMO at $-7.41$ eV. In this case we do not need a crossing from a $\pi,\pi^*$ state to a $\sigma,\pi^*$ triplet state.

In conclusion, the results of the above-described ab initio study of the photochemical isomerization of furan derivatives are in agreement with the previous reported data obtained from semiempirical methods. In particular, the sensitized irradiation of furan derivatives populates the first excited triplet state of the furan, and this triplet state can evolve only through O$-$C$_\alpha$ cleavage. The selection of the bond to be broken can depend on energetic factors (furan-2-carbonitrile) or on kinetic factors (2-methylfuran, 2-trimethylsilylfuran). The direct irradiation of furan derivatives populates the singlet excited state which can be converted into the Dewar isomer or into the corresponding triplet state through the usual intersystem crossing procedure. The efficiency of these processes determines the presence or the absence of isomerized furan derivatives in the reaction mixtures.

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