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A Theoretical Study of the Photochemical Isomerization Reactions of Furans from the Triplet State

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The mechanisms of photoisomerization reactions were investigated theoretically using a model system of 2-methylfuran with the CASSCF (10-electron/8-orbital active space) and MP2-CAS methods and the 6-311-(d,p) basis set. After 2-methylfuran molecules are produced in the T_1 state by photoexcitation at 254 nm, intersystem crossing to the S_0 surface is the most probable pathway for deactivation. Relaxing to the S_0 state, the 2-methylfuran molecules can dissociate into 3-methylcyclopropene and carbon monoxide products. Otherwise, they may revert to singlet 2-methylfuran or undergo photorearrangement to produce 3-methylfuran. These stepwise mechanisms are consistent with the available experimental observations.

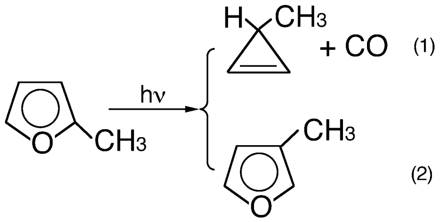
I. Introduction

Furans are one of the most important heterocyclic compounds with widespread occurrence in nature.[1] They are frequently found in natural products arising from plants and marine organisms.[2] Indeed, furans often have been employed as sources of latent functionality for the synthesis of natural products.[3] Possessing a variety of biological activities, furans are used commercially as pharmaceutical agents, fragrances, flavors, and insecticides.[4]

Besides this, the photochemistry of furans has received a considerable amount of experimental attention over the past four decades.[5−18] The phototransformations of furans have been studied independently by Srinivasan,[6−11] Hiraoka,[10−13] and van Tamelen.[14,15] These experimental observations indicate that the direct irradiation of methylfurans gives results quite different from mercury ($^3P_1$) sensitization.[12] For instance, see Scheme 1, it is found that the primary reaction in the Hg($^3P_1$) photosensitization of 2-methylfuran is the ring contraction to methyl-substituted cyclopropene and carbon monoxide. However, 3-methylfuran is also formed from 2-methylfuran. However, the vapor-phase direct irradiation mutually transforms 2-methylfuran and 3-methylfuran in low yield. Moreover, it is observed experimentally that a pressure dependence of the quantum yield for CO production observed in the Hg($^3P_1$)-senstized reaction is absent in direct photolysis. Additionally, experiments show that a triplet state is involved in such photoreactions of furans.[5−17] Because it is well-known that direct excitation from the singlet state into the excited triplet state is spin-forbidden, singlet−triplet crossing must occur during such reactions. Clearly, these key photochemical observations are intimately linked to the relative yields of the observed photoproducts.

It is these fascinating and seemingly complex experimental results that inspire this study. Theoretical investigations of furans are scarce. To the best of our knowledge, so far only one theoretical study has reported photochemical mechanisms of furans.[19] Buss and Jug have examined the photochemical isomerization of 2-methylfuran to 3-methylfuran and proposed a reaction mechanism that proceeds via a ring-contracting ring-expansion mechanism, using a semiempirical molecular orbital method. However, they did not consider the effect of the singlet−triplet crossing as well as the formation of 3-methylcyclopropene upon decarbonylation in their work. It is therefore necessary to reexamine such photochemical reactions using a more sophisticated quantum chemical theory. We feel that if we could understand the mechanisms of the photoreactions of furans this would help to design some useful systems.

SCHEME 1



In the present work, the energy hypersurfaces of the excited states of furans are investigated to obtain information about their photochemical reaction behavior. A theoretical study of the photoisomerization of 2-methylfuran was chosen because experiments on this compound were available for comparison. It will be shown below that the singlet−triplet crossing plays a crucial role in the photoisomerization of these aromatic furan systems. From these investigations, a better understanding of the thermodynamic and kinetic aspects of such furan photoreactions may shed some light on the optimal design of further related synthesis and catalytic processes.

II. Methodology

All geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structures showed various elements of symmetry. The CASSCF calculations were performed using the MCSCF program released in Gaussian 03.[20]

In the investigation of photochemical reaction pathways, the stationary point structures on the S_0 and T_1 surfaces were optimized at the complete active space self-consistent field (CASSCF) level of calculations using the standard 6-311G(d) basis set.[21] The active space for describing the photoisomer-

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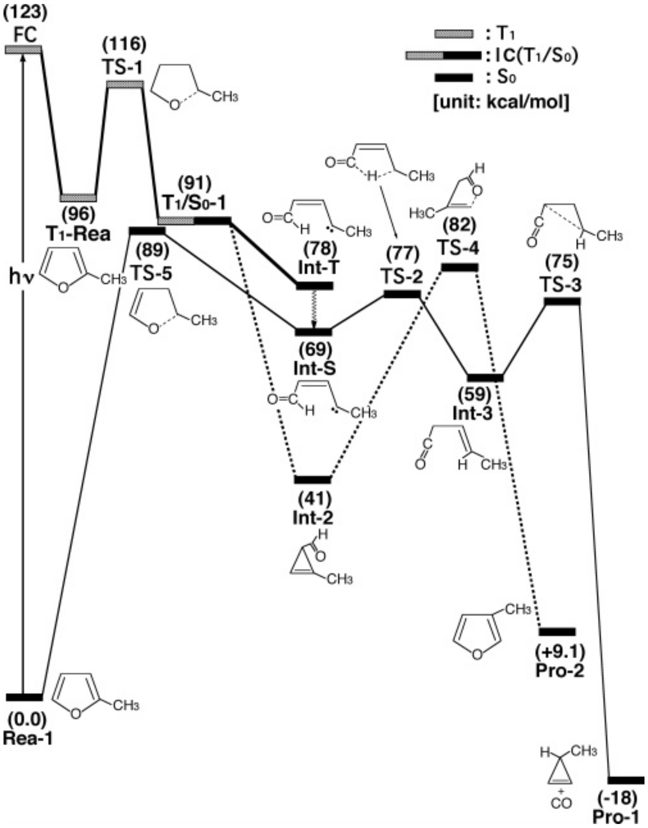

Figure 1. Energy profiles for the photoisomerization modes of 2-methylfuran (**Rea-1**). The abbreviation FC stands for Frank−Condon. The relative energies were obtained at the MP2-CAS(10,8)/6-311G-(d,p)//CAS(10,8)/6-311G(d) level of theory. All energies (in kcal/mol) are given with respect to the reactant (**Rea-1**). For the CASSCF optimized structures of the crucial points, see Figure 2. For more information see the text.

izations of 2-methylfuran comprises 10 electrons in 8 orbitals, i.e., five p π-orbitals, one lone pair orbital plus the σ(C−C) and σ*(C−C) orbitals. This active space is referred to as CASSCF(10,8). The state-averaged CASSCF(10,8) method was used to determine geometry on the intersection space.

Every stationary point was characterized by its harmonic frequencies computed analytically at the CASSCF level. The harmonic vibrational frequencies of all stationary points were computed analytically to characterize them as minima (all frequencies are real) or transition states (only one imaginary frequency). The optimization was determined when the maximum force and its root-mean-square (rms) were less than 0.00045 and 0.00005 hartree/bohr, respectively. Localization of the minima, transition states, and crossing minima have been performed in Cartesian coordinates; therefore, the results are independent of any specific choice of internal variables.

To correct the energetics for dynamic electron correlation, we have used the multireference Møller−Plesset (MP2-CAS) algorithm[22] as implemented in the program package Gaussian 03. Unless otherwise noted, the relative energies given in the text are those determined at the MP2-CAS(10,8)/6-311G(d) level using the CAS(10,8)/6-311G(d) (hereafter designed MP2-CAS and CASSCF, respectively) geometry.

III. Results and Discussion

For an understanding of the photoreaction mechanisms of 2-methylfuran (**Rea-1**), it is best to start the discussion with the reaction profiles as summarized in Figure 1, which also contains the relative energies of the crucial points with respect to the ground-state minimum **Rea-1**. Selected optimized geometrical parameters for the stationary points are collected in Figure 2, and their corresponding relative energies are given in Table 1. Cartesian coordinates and energetics calculated for the various points at the CASSCF(10,8)/6-311G(d) and MP2-CAS-(10,8)/6-311G(d) levels are available as Supporting Information.

In the first step, the reactant (**Rea-1**) is excited to its lowest-lying triplet state (T_1) by a vertical excitation. After the vertical excitation process, the molecule is situated on the triplet surface but still possesses the ground-state (S_0) geometry. This point on the triplet surface is denoted as **FC** (T_1 (S_0 geom)). The computed triplet vertical excitation energy of compound **Rea-1** is 123 kcal/mol ($S_0 \rightarrow T_1$ (S_0 geom)) at the MP2-CAS(10,8)/6-311G(d) level of theory. The experimental triplet vertical excitation energy of **Rea-1** is 113 kcal/mol (= 254 nm),[6−13] which agrees reasonably well with the present computational result.[23] In any event, due to this agreement,[3] one would therefore expect that the same relative accuracy also should apply to the geometries as well as the energetics predicted for the discussion of the triplet photochemical reaction mechanisms of **Rea-1**.

From the Frank−Condon point (**FC**), the molecule may relax to a local minimum near the S_0 geometry. This local minimum of the triplet surface is denoted **T_1-Rea**, which is calculated to be about 96 kcal/mol above the ground-state minimum as illustrated in Figure 1. The optimized geometrical parameters of **T_1-Rea** are given in Figure 2. As one can see, the bond lengths of the five-membered ring of **T_1-Rea** are larger than those in its corresponding ground singlet conformation (**Rea-1**). Also, a slightly nonplanar structure with the dihedral angle $\angle O_1C_2C_3C_4$ of about 11° for **T_1-Rea** can be found. Then, from the local minimum **T_1-Rea**, a transition state search for the O−C bond breaking based on the model of the **T_1-Rea** conformation was investigated. The optimized transition state structure (**TS-1**) along with the calculated transition vector at the CASSCF level is shown in Figure 2. The arrows in **TS-1** indicate the direction in which the atoms move in the normal coordinate corresponding to the imaginary frequency (830i cm^{-1}). Our computational results indicate that this transition state (**TS-1**) lies above the **T_1-Rea** point by 20 kcal/mol.

According to the experimental observations,[6−18] it has been found that the photoisomerization of **Rea-1** is nonadiabatic. The reaction starts from the T_1 surface and proceeds ultimately along the ground-state (S_0) pathway. Thus, the crossing point of the T_1 and S_0 surfaces should play a crucial role in describing mechanistic photorearrangement reactions of **Rea-1**. Intersystem crossing from $^3(n\pi^*)$ to $^1(n\pi^*)$ states takes place in the region of the T_1/S_0 intersection **T_1/S_0-1**, as illustrated in Figure 1. Its fully optimized structure is collected in Figure 2. The gradient difference vector obtained at this point also is shown in Figure 2. As one can see, **T_1/S_0-1** is a nonplanar structure with a dihedral angle $\angle O_1C_2C_3C_4$ of about 36°. Our computational results predicted that **T_1/S_0-1** lies 91 kcal/mol above **Rea-1** and 32 kcal/mol below **FC**. According to the results outlined in Figure 2, relaxing through **T_1/S_0-1** may lead to two different reaction paths on the ground-state surface via the gradient difference vector. That is to say, once the **Rea-1** molecules decay onto the T_1 surface, there are two possible pathways, a biradical intermediate **Int-T** and a three-membered ring intermediate **Int-2**, through which reaction may proceed.

Our computations suggest that the **Int-T** point can relax onto the **Int-S** point via a short energy relief as demonstrated in Figure 1. The fully optimized structures of triplet (**Int-T**) and singlet states (**Int-S**) are given in Figure 2. As one can see, the

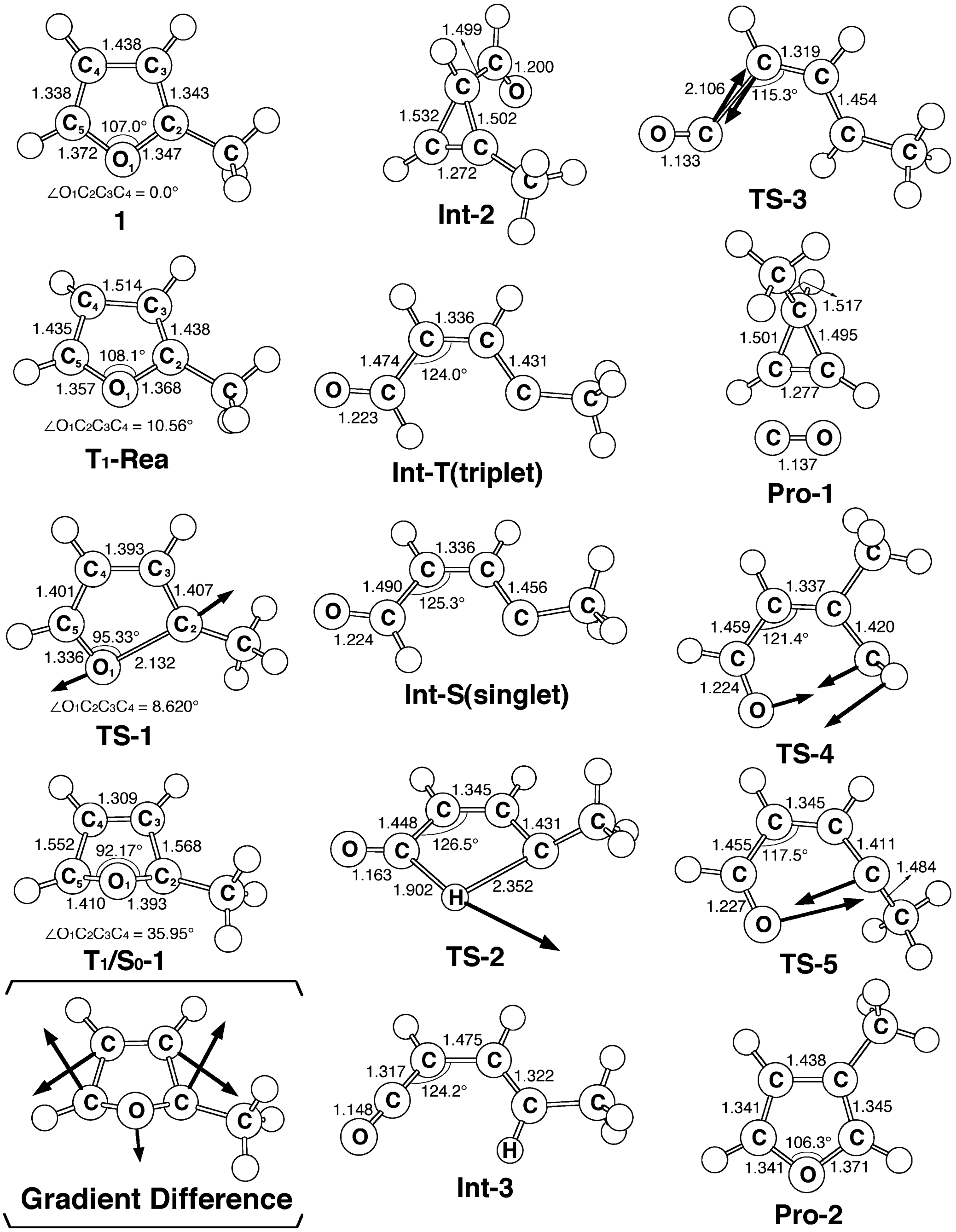

Figure 2. CAS(10,8)/6-311G(d) geometries (in Å and deg) for 2−2-methylfuran (**Rea-1**), intermediate (**Int**), transition state (**TS**), and isomer products (**Pro**). The gradient difference vectors—those which lift the degeneracy—were computed with CASSCF at the intersections **T_1/S_0-1**. The corresponding CASSCF vectors are shown in the inset. For more information, see the Supporting Information.

molecule in both **Int-T** and **Int-S** points has a carbene-like structure with two unpaired electrons lying on the same carbon atom. Additionally, the calculated energies of the **Int-T** and **Int-S** structures are given in Table 1, from which one can see that the energy difference between them is about 9.0 kcal/mol with **Int-T** lying above the **Int-S** species. As a consequence, from the above discussion, our theoretical observations suggest that the short-lived **Int-S** intermediate can be formed via a fast **T_1/S_0-1** intersystem crossing. That is to say, relaxation of excited triplet **T_1-Rea** toward the singlet **Int-S** point occurs with considerable efficiency via the **T_1/S_0-1** crossing point. This explains why triplet furan originating from collision with Hg-($^3P_1$) atoms is a necessary precursor for the ring contraction to 3-methylcyclopropene (see below).[3−18]

Then, from the **Int-S** point, the **Rea-1** molecule can either produce 3-methylcyclopropene and carbon monoxide (**Pro-1**) via the **TS-2**, **Int-3**, and **TS-3** points (path A) or go back to the original reactant **Rea-1** via the **TS-5** state (path B). As shown in Figure 1, the energies of the **TS-2**, **Int-3**, and **TS-3** states connecting **Int-S** and **Pro-1** on the S_0 surface lie 77, 59, and 75 kcal/mol above that of the reactant, **Rea-1**. In addition, the products **Pro-1** (3-methylcyclopropene and carbon monoxide) are thermodynamically stable by 18 kcal/mol compared with 2-methylfuran **Rea-1**. Similarly, for reaction path B, the relevant transition structure (**TS-5**) lies 89 kcal/mol above 2-methylfuran **Rea-1**. It should be mentioned here that the 2-methylfuran molecule possesses an excess energy of about 27 kcal/mol arising from the relaxation to the local minimum **T_1-Rea**. This energy is greater than the energy difference between **Int-S** and **TS-2** (8.0 kcal/mol) or between **Int-S** and **TS-5** (20 kcal/mol) for reactions A and B, respectively. As a consequence of the above findings, it is evident that this system has sufficient

TABLE 1: Energies (in kcal/mol) of the Critical Points Located along the Pathways at the MP2-CAS(10,8)/6-311G(d,p) and CASSCF(10,8)/6-311G(d) (in Parentheses) Levels of Theory[a]

structure	state	$\Delta E_{\mathrm{rel}}{}^{b}$
2-methylfuran (**Rea-1**)	S_0	0.0 (0.0)
FC	S_1	123.1 (145.4)
T_1-Rea	T_1	96.31 (114.5)
TS-1	T_1	116.4 (117.2)
T_1/S_0-1	T_1/S_0	91.37 (92.07)
Int-T	T_1	78.31 (57.68)
Int-S	S_0	69.36 (50.82)
TS-2	S_0	77.47 (80.52)
Int-3	S_0	59.34 (70.34)
TS-3	S_0	75.10 (90.02)
Pro-1	S_0	−18.06 (−22.08)
Int-2	S_0	41.35 (43.78)
TS-4	S_0	81.76 (60.76)
TS-5	S_0	88.64 (49.75)
3-methylfuran (**Pro-2**)	S_0	9.068 (1.079)

[a] See Figures 1 and 2. [b] Energy relative to 2-methylfuran.

internal energy to overcome these energy barriers. That is, our model calculations are consistent with the fact that triplet 2-methylfuran can react either to produce 3-methylcyclopropene upon decarbonylation or revert to singlet **Rea-1** without any difficulty after Hg($^3P_1$) sensitization.[3−18] In short, the ring-closure mechanism of triplet photoisomerization of 2-methylfuran **Rea-1** can be represented as follows:

path A:

$$\mathbf{Rea\text{-}1(S_0)} + h\nu \rightarrow \mathbf{FC} \rightarrow \mathbf{T_1\text{-}Rea} \rightarrow \mathbf{TS\text{-}1} \rightarrow \mathbf{T_1/S_0\text{-}1} \rightarrow \mathbf{Int\text{-}T} \rightarrow \mathbf{Int\text{-}S} \rightarrow \mathbf{TS\text{-}2} \rightarrow \mathbf{Int\text{-}3} \rightarrow \mathbf{TS\text{-}3} \rightarrow \mathbf{Pro\text{-}1}$$

path B:

$$\mathbf{Rea\text{-}1(S_0)} + h\nu \rightarrow \mathbf{FC} \rightarrow \mathbf{T_1\text{-}Rea} \rightarrow \mathbf{TS\text{-}1} \rightarrow \mathbf{T_1/S_0\text{-}1} \rightarrow \mathbf{Int\text{-}T} \rightarrow \mathbf{Int\text{-}S} \rightarrow \mathbf{TS\text{-}5} \rightarrow \mathbf{Rea\text{-}1}$$

However, once decay through the **T_1/S_0-1** intersystem crossing has occurred, there is another different reaction path available on the ground-state surface: a photorearrangement to produce the 3-methylfuran product, **Pro-2** (denoted path C). Namely, from the intersystem crossing point **T_1/S_0-1**, 2-methylfuran can reach a singlet intermediate **Int-2**, from which the molecule can produce 3-methylfuran (**Pro-2**) via a transition state **TS-4**. The optimized geometrical parameters of the related stationary points can be found in Figure 2. As a result, the mechanism of path C for triplet photoisomerizations of 2-methylfuran (**Rea-1**) is represented below. This route is also likely to be accessible, as the molecule will have a great deal of excess energy once it has decayed through an intersystem crossing point.

path C:

$$\mathbf{Rea\text{-}1(S_0)} + h\nu \rightarrow \mathbf{FC} \rightarrow \mathbf{T_1\text{-}Rea} \rightarrow \mathbf{TS\text{-}1} \rightarrow \mathbf{T_1/S_0\text{-}1} \rightarrow \mathbf{Int\text{-}2} \rightarrow \mathbf{TS\text{-}4} \rightarrow \mathbf{Pro\text{-}2}$$

As seen in Figure 1 and Table 1, the activation barrier of **TS-4** (via path C) is apparently larger than that of **TS-2** (via path A) and **TS-5** (via path B). That is, our MP2-SCF calculations indicate that the barrier height decreases in the order **TS-4** (41 kcal/mol) > **TS-5** (20 kcal/mol) > **TS-2** (8.0 kcal/mol). Thus, our theoretical findings strongly suggest that paths A and path B are preferred over path C. Accordingly, on the basis of the above computational results, one may then anticipate that 3-methylcyclopropene and carbon monoxide (**Pro-1)** should be the main photoproducts in the triplet photoisomerization of **Rea-1**. The quantum yields of the photoproducts will decrease in the order **Pro-1** > **Rea-1** > **Pro-2**. Our theoretical findings are in good accordance with the available experimental observations.[6−18]

IV. Conclusions

In the present paper, CASSCF(10,8) and MP2-CAS(10,8) ab initio studies have been performed to obtain a better understanding of 2-methylfuran photoisomerization. The most probable mechanism leading to the different products is characterized on the basis of the computed potential energy surface profiles and the surface intersections, schematically illustrated in Figure 1. At the MP2-CAS(10,8) level, the triplet minimum **T_1-Rea**, the transition state **TS-1**, and the **T_1/S_0-1** point are located 27, 6.7, and 32 kcal/mol below the **FC** point, respectively. Thus, for the molecules populating the T_1 state, the intersystem crossing to the S_0 surface is energetically the most probable decay pathway. This conclusion is consistent with the experimental proposal that the photoisomerization of 2-methylfuran occurs on the S_0 surface. After relaxation to the S_0 surface, 2-methylfuran (S_0) is left with sufficient internal energy to overcome all energy barriers on the S_0 surface, producing 3-methylcyclopropene, carbon monoxide, and 3-methylfuran photoproducts or reverting to the reactant, 2-methylfuran.

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Supporting Information Available: Cartesian coordinates and energetics calculated for the various points at the CASSCF-(10,8)/6-311G(d) and MP2-CAS(10,8)/6-311G(d) levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) As pointed out by one referee, the furan molecule being vertically excited from the electronic ground state directly to its lowest triplet state (T_1) is unrealistic due to the small radiative singlet−triplet transition moment. It is thus showed that the T_1 state is excited by spin and energy transfer from a photosenitizer. Indeed, as already mentioned in the Introduction, this is consistent with the available experimental observations; see refs 6−13.