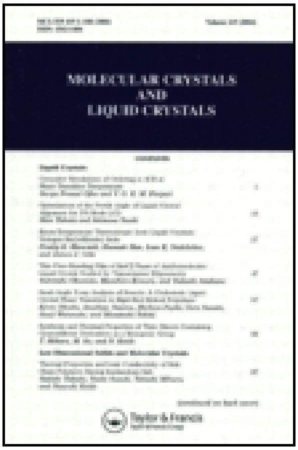

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Thermochromic and Spectral Properties of Perimidinespirocyclohexadienones: A DFT and ab initio Studies

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Thermochromic and Spectral Properties of Perimidinespirocyclohexadienones: A DFT and *ab initio* Studies

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*The ring-opening reactions of perimidinespirocyclohexadienones in the ground and first excited singlet and triplet states were studied at the DFT B3LYP/6-31G**, UB3LYP/6-31G** and CIS/3-21G** levels of theory. It has been found that the thermal isomerization is governed by the non-adiabatic mechanism involving excitation in the triplet state. The irreversible character of the ring-opening photoreaction can be explained by the absence of a local minimum corresponding to the opened form at the* S_1 *potential energy surface. According to the TD DFT calculations the low intense long-wavelength absorption band at 436 nm inherent in perimidinespirocyclohexadienones belongs to a charge-transfer electronic transition involving the frontier orbitals located at different spiroconjugated moieties.*

Keywords: absorption spectra; DFT study; perimidinecyclohexadienone; photochromism; thermochromism

INTRODUCTION

Perimidinespirocyclohexadienones is a new class of spiroheterocyclic compounds revealing photo- and thermochromic properties due to the photoinitiated and, respectively, thermal interconversion of the

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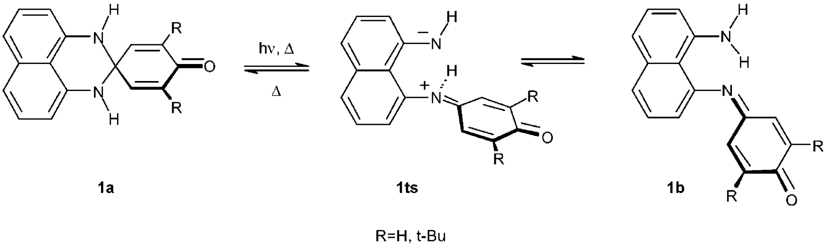
ring-closed (**1a**) and ring-opened (**1b**) forms [1].



In order to gain insight into the mechanism of the thermal- and photoinitiated reactions of spiroperimidines we have carried out quantum-chemical calculations of the corresponding reaction paths and spectral properties of their isomeric forms.

Computational Details

All stationary points on the ground and triplet potential energy surfaces (PES) were optimized at Becke's hybrid exchange functional [2] and the nonlocal correlation functional of Lee, Yang and Parr (B3LYP) [3] with 6-31G** basis set. Spin-unrestricted method UB3LYP/6-31G** has been applied for triplet state calculations. Excitation energies of the spirocyclic (**1a**) and the quinoneimine (**1b**) forms (R = t-Bu) were calculated at HF/6-31G** optimized geometries using TD B3LYP/6-31G** approach. The configuration interaction all-single-excitations with spin-restricted Hartry-Fock reference ground state CIS/3-21G** method was used to evaluate possible mechanism of the ring-opening photoreaction. All *ab initio* and DFT calculations were performed within the GAUSSIAN 98 [4] suite of programs.

RESULTS AND DISCUSSION

The calculated singlet and triplet energy profile of the perimidine-spiro-cyclohexadienone **1a** (R = H) isomerization is depicted in Figure 1, the energies of the stationary points are given in Table 1.

The spirocyclic and qiunoneimine isomers of the parent compound **1a** (R = H) are energy close, the latter being 1.3 kcal mol^{-1} energy favorable. On the other hand, according to the B3LYP/3-21G** calculations the di-(tert-butyl) derivative (R = t-Bu) is more stable in the spirocyclic form. Computed geometries of the spirocyclic isomers are in good agreement with those determined by X-ray experiments [1].

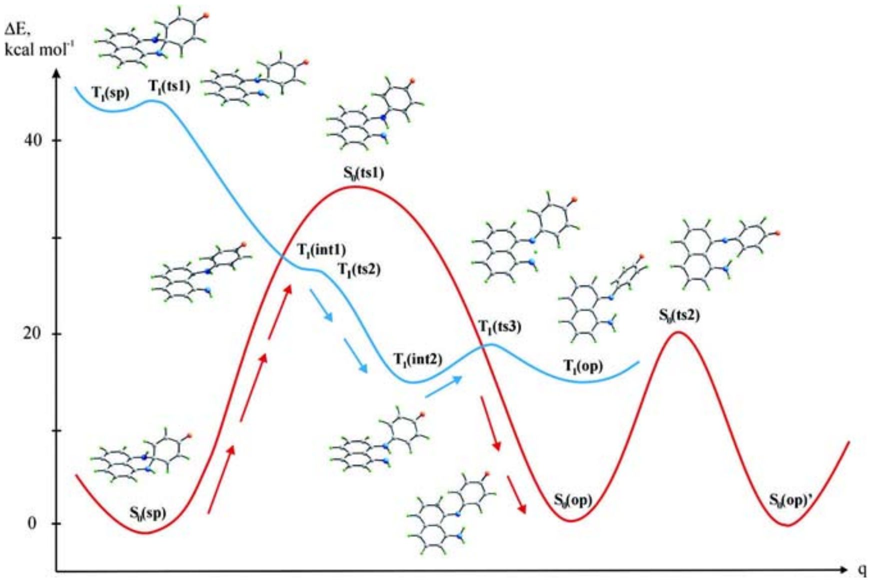


FIGURE 1 The energy profile of the perimidinespirocyclohexadienone **1a** (R = H) isomerization at the S_0 and T_1 states PES according to the B3LYP/6-31G** and UB3LYP/6-31G** calculations.

TABLE 1 Total Energies, Total Energies with Zero Point Energy (ZPE) Corrections, Imaginary Frequencies for the Transition States and Relative Energies of the Stationary Points on the S_0(B3LYP/6-31G**) and T_1(UB3LYP/6-31G**) Potential Energy Surfaces

Structure	E_{tot} (a.u.)	E_{tot} + ZPE (a.u)	ν_{im} (cm^{-1})	ΔE (kcal mol^{-1})
S_0(sp)	– 801.653309	– 801.409164	–	0
S_0(ts1)	– 801.590978	– 801.350074	55.5	37.1
S_0(op)	– 801.652931	– 801.410738	–	– 1.0
S_0(ts2)	– 801.617423	– 801.377000	207.0	20.2
T_1(sp)	– 801.574263	– 801.334594	–	46.8
T_1(ts1)	– 801.572135	– 801.333017	354.2	47.8
T_1(int1)	– 801.605157	– 801.365455	–	27.4
T_1(ts2)	– 801.605125	– 801.365760	52.4	27.2
T_1(int2)	– 801.626284	– 801.385445	–	14.9
T_1(ts3)	– 801.615841	– 801.380030	1429.5	18.3
T_1(op)	– 801.625675	– 801.386210	–	14.4

The thermal ring-opening reaction at the ground state surface that involves cleavage of a C_{spiro}-N bond and proton transfer occurs concertedly through the zwitterion-like transition state **S_0(ts1)** and requires overcoming a high energy barrier (37.1 kcal mol^{-1}). By passing through the transition state **S_0(ts1)** the molecular system relaxes down to the minimum corresponding to the quinoneimine isomer **S_0(op)** that can undergo the nitrogen inversion to convert to its enantiomeric form through the energy barrier of 21.2 kcal mol^{-1}.

A possible explanation for the substantial difference between the DFT computed and experimentally detected (15–25 kcal mol^{-1}) energy barriers for the thermal rearrangements of spiroperimidines may be associated with the nonadiabatic character of the reaction that involves singlet-triplet state crossing similar to that reported for the configurational isomerization of azobenzene [5].

At the first triplet excited state surface the ring-opening reaction, in contrast to that at the ground state is a multistep process (Fig. 1). The first reaction step that involves cleavage of a C_{spiro}-N bond occurs via transition state **T_1(ts1)** with activation barrier of 1.0 kcal mol^{-1}. The intermediate **T_1(int1)** rapidly converts to the most stable intermediate **T_1(int2)** that lies at 22.2 kcal mol^{-1} below the transition state **S_0(ts1)** on the ground state PES. The final reaction step is revealed to the proton transfer which occurs via transition state **T_1(ts3)** with activation barrier of 3.4 kcal mol^{-1}. The less stable intermediate **T_1(int1)** possessing the structure close to the transition state **S_0(ts1)** and energy lower the latter was chosen for evaluation of the activation energy barrier for nonadiabatic process (27.5 kcal mol^{-1}).

The CIS/3-21G** calculations reveal an existence only one minimum **S_1(sp)** corresponding to the spirocyclic form located at the first singlet PES. The energy gap between the ground and excited states in the vicinity of the ring-opened structure **S_1(ci)** that is not a stationary point on the S_1 PES, is very narrow (13 kcal mol^{-1}). These features are indicative of a conical intersection [6]. The absence of the minimum corresponding to the ring-opened isomer at the first singlet excited state surface explains the irreversibility of the photoreaction.

The compounds **1a** are characterized by a significant energy of spiroconjugation [7] and new 430–450 nm absorption band found in their spectra [1]. The nature of these bands associated with the charge-transfer HOMO-LUMO electronic transition has been elucidated by the performed TD B3LYP/6-31G**//HF-6–31G** calculations of **1a** (R = t-Bu). Predicted S_0-S_1excitation energy (2.508 eV) is in reasonable agreement with the experiment (2.844 eV).

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