

Photoisomerization of 2,3-diphenylcyclopropane-1-carboxylic acid derivatives †

J. Sivaguru,^a Steffen Jockusch,^b Nicholas J. Turro^b and V. Ramamurthy^{*a}

^a Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

^b Department of Chemistry, Columbia University, New York, NY 10027, USA

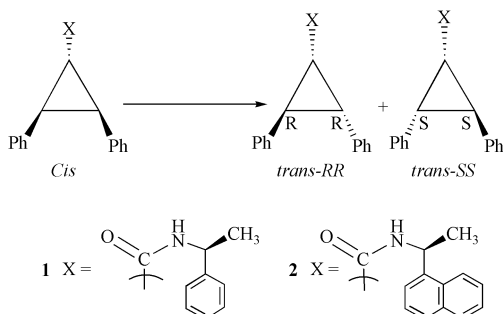
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Contrary to what is known about *cis*-1,2-diphenylcyclopropane and its derivatives, we find that they have triplet energies of *ca.* 311 kJ mol⁻¹, do not undergo intersystem crossing upon direct excitation, undergo the less common adiabatic photoisomerization to the corresponding *trans* isomers, and show emission from excited 1,3-diradical intermediates.

Introduction

Based on extensive photochemical and photophysical evidence,¹ it is believed that *cis*-1,2-diphenylcyclopropane (i) has a triplet energy of ~222 kJ mol⁻¹,² (ii) emits phosphorescence in the region 500–700 nm,² and (iii) undergoes geometric *cis*–*trans* photoisomerization upon direct excitation (at least partly) *via* a triplet state.³ The photoisomerization has been proposed to involve a fully open 1,3-diradical.³ The geometric isomerization of *cis*-1,2-diphenylcyclopropane has played a seminal role in stimulating studies of photoinduced asymmetric induction⁴ since an enantiomeric excess of *ca.* 7% was reported with (*S*)-(+)-1-[1-(*N*-acetylamino)ethyl]naphthalene as a chiral sensitizer. However, the exact function (electron transfer or singlet or triplet energy transfer) of the naphthalene chromophore is not clear.⁵ Our interest in asymmetric induction within zeolites⁶ prompted us to examine the photochemistry and photophysics of a family of 2,3-diphenylcyclopropane-1-carboxylic acid derivatives in solution. We report results on two of these derivatives: 2,3-diphenylcyclopropane-1-carboxamides of 1-phenylethylamine (**1**) and 1-naphthylethylamine (**2**) (Scheme 1). The results presented here are considered within the context of the literature results mentioned above. The following nomenclatures are used in the text to identify the structures shown in Scheme 1. The compounds are identified based on the geometrical relationship (*cis* and *trans*) between the two phenyl groups at the C₂ and C₃ carbons, and the stereochemical relationship (*R* and *S*) between them, taking the C₁ carbon into account. The first structure in Scheme 1, the *cis* isomer, is *meso* and the second and third structures, *trans* isomers, are chiral.



Scheme 1 Geometric isomerization of 2,3-diphenylcyclopropane-1-carboxylic acid derivatives: structures of the two compounds investigated.

The second and third structures in Scheme 1 are identified as *trans*-*RR* and *trans*-*SS*.

Results

The direct and triplet-sensitized solution photochemistry of the pure diastereomers *trans*-*RR*-**1** and *trans*-*SS*-**1** were examined.⁷ Since the results obtained for both isomers were identical, discussion of one of them is sufficient to illustrate the phenomenon. *trans*-*RR*-**1** did not convert to *trans*-*SS*-**1**, even after 2 h of direct irradiation (Fig. 1). The direct irradiation resulted in the conversion of *trans*-*RR*-**1** to *cis*-**1** only. This suggests that the two chiral half-open structures **3** and **4** in Scheme 2 do not interconvert under the direct excitation conditions. The results are also consistent with the formation of non-interconvertible structures **6** and **7** *via* cleavage of C₁–C₂ or C₁–C₃ bonds. In contrast, triplet sensitization with acetone resulted in interconversion of the diastereomers *trans*-*RR*-**1** and *trans*-*SS*-**1**, implying that the triplet 1,3-diradical intermediates **3** and **4** establish, prior to ring closure, an equilibrium amongst themselves *via* structure **5** (Fig. 2, Scheme 2). Thus, photochemical studies with pure diastereomers of *trans*-**1** revealed differences between the singlet and triplet processes, and established that, upon direct excitation, triplet states are not involved in the isomerization process (contrary to what might be expected from the reported results).³ We recognize that in the absence of isolation of the all-*cis* isomer, there is no need to invoke the diradical **4** in the mechanistic model. The product studies unequivocally suggest that during triplet sensitization, the

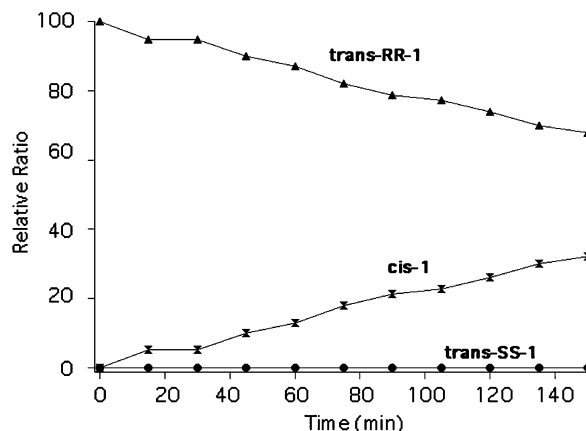
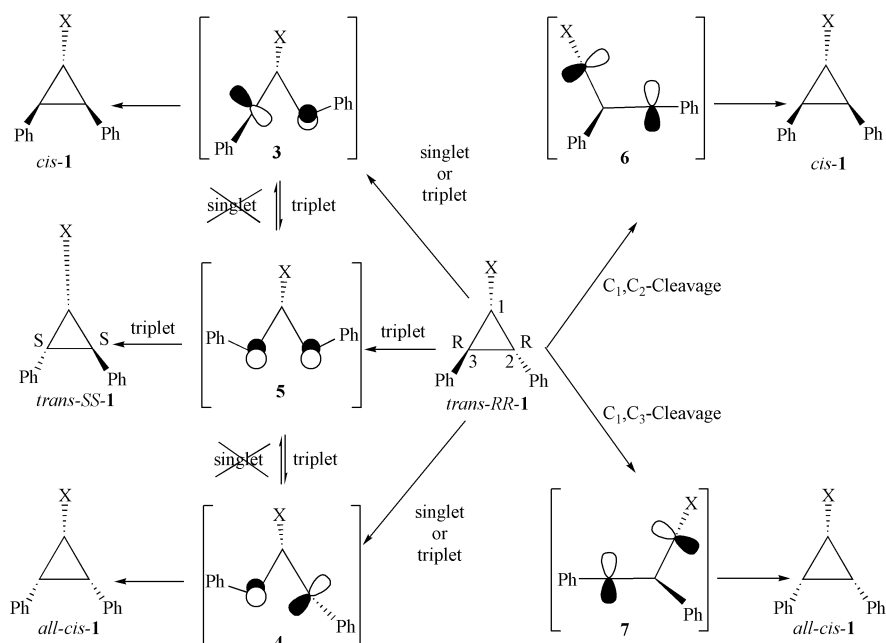


Fig. 1 Evolution of products with respect to time of irradiation: direct irradiation of *trans*-*RR*-**1**. Irradiation of the other diastereomer showed the same trend.

† This paper is dedicated to Professor Fred Lewis on the event of his 60th birthday.



Scheme 2 Mechanism of the geometric isomerization of 2,3-diphenylcyclopropane-1-carboxylic acid derivatives. The isomerization is believed to occur through breakage of the C₂-C₃ bond. The main question is whether there is an equilibrium between the diradicals 3, 4 and 5.

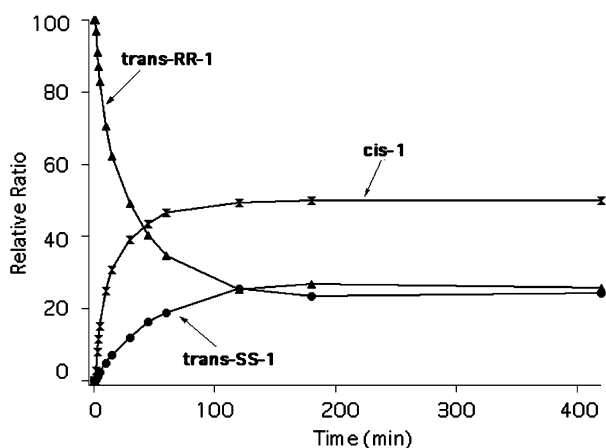


Fig. 2 Evolution of products with respect to time of irradiation: triplet sensitization of *trans*-RR-1. Triplet sensitization of the other diastereomer showed the same trend.

diradical **5** is involved, and during direct excitation, it does not play any role.

Fluorenone ($E_T = 211 \text{ kJ mol}^{-1}$) and 2-acetonaphthone ($E_T = 249 \text{ kJ mol}^{-1}$) are reported to serve as triplet sensitizers for the geometric isomerization of 1,2-diphenylcyclopropane.⁸ Consistent with these sensitization results, the emission exhibited by *cis*-1,2-diphenylcyclopropane in the region *ca.* 500–700 nm (Fig. 3) was assigned to phosphorescence.² Thus, both emission and sensitization results suggest that the triplet energy of *cis*-1,2-diphenylcyclopropane is in the region of 240 kJ mol^{-1} . However, we have found that sensitizers having triplet energies below that of acetophenone ($E_T = 311 \text{ kJ mol}^{-1}$) were inefficient in sensitizing the geometric isomerization of **1** and **2**, suggesting that the triplet energies of **1** and **2** are greater than 311 kJ mol^{-1} , which is inconsistent with the reports that fluorenone and 2-acetophenone are effective triplet sensitizers.

If the triplet energies of **1** and **2** are indeed higher than 311 kJ mol^{-1} , then the observed emission in the region 500–700 nm cannot be from the triplets of **1** or **2**. Nevertheless, we have found that *cis*-1,2-diphenylcyclopropane (as reported in the literature;² Fig. 3), as well as a number of *cis*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives, emits in the 500–700 nm range in addition to short wavelength regions where the

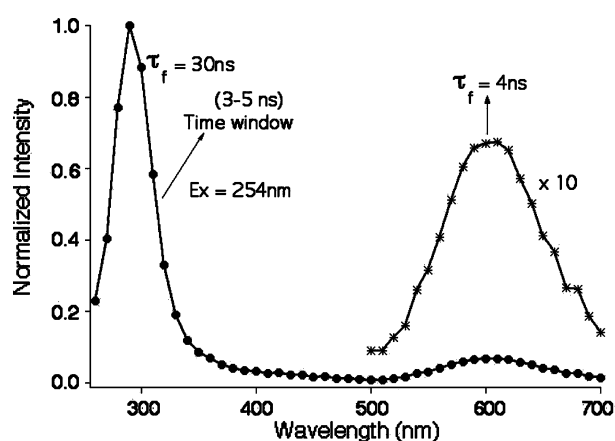


Fig. 3 Time-resolved emission spectrum of *cis*-1,2-diphenylcyclopropane.

fluorescence of benzene derivatives is expected. Examples of the long and short wavelength emissions, together with the corresponding excitation spectra in the case of *cis*-**1** at 77 K, are shown in Fig. 4. Both emissions (labeled I and II) show identical excitation spectra, indicating a common absorbing chromophore. Based on time-resolved emission spectra (Fig. 5) the lifetimes of the transients responsible for emissions I and II were determined to be ~ 35 and ~ 14 ns, respectively. Such short lifetimes are consistent with fluorescence, and not phosphorescence, for both emitting species.

To further probe the nature of the long wavelength emission, the photophysics of *cis*-**2** were examined. At 77 K, this molecule shows four emissions (Fig. 6 and 7): (i) the standard emission of a phenyl chromophore in the region 270–350 nm; (ii) the standard fluorescence of a naphthyl chromophore in the region 300–380 nm; (iii) the standard phosphorescence of a naphthyl chromophore in the region 450–630 nm; (iv) a novel emission due to an unknown species in the region 500–700 nm. The excitation spectra of the 500–700 and 450–630 nm emissions are different (Fig. 6) suggesting that different non-interacting chromophores are responsible for these emissions. Unlike *cis*-**1**, *trans*-**1** showed *only* fluorescence in the 280–350 nm range (Fig. 8). Similarly, *trans*-**2** showed mainly fluorescence and phosphorescence from the naphthyl chromophore (Fig. 9).

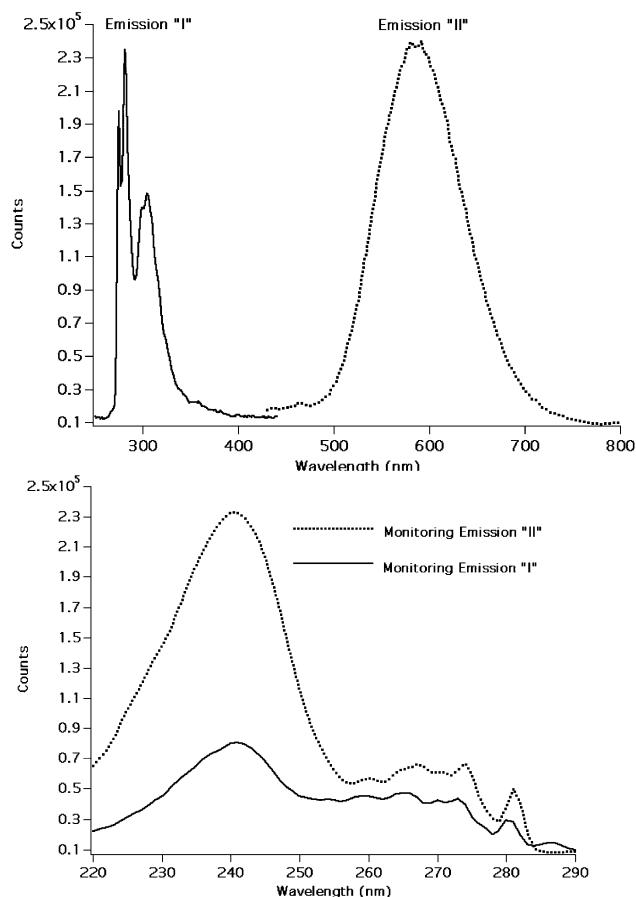


Fig. 4 (Top) Steady-state luminescence emission spectrum of *cis-1* in ethanol glass at 77 K ($\lambda_{\text{ex}} = 230$ nm). (Bottom) The corresponding excitation spectra (I: $\lambda_{\text{em}} = 290$ nm; II: $\lambda_{\text{em}} = 580$ nm).

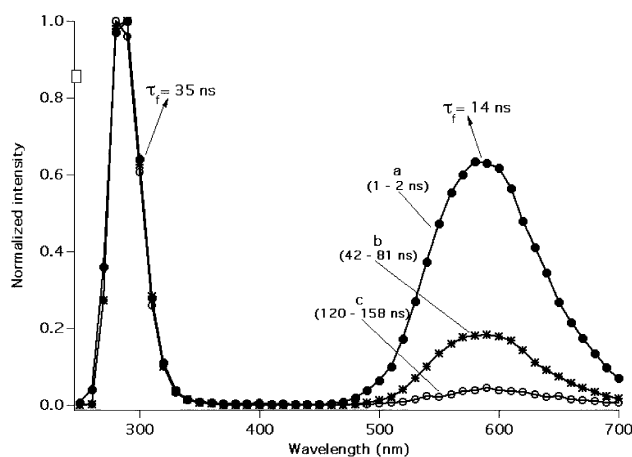


Fig. 5 Normalized time-resolved fluorescence spectra of *cis-1* in ethanol glass at 77 K at different times after excitation ($\lambda_{\text{ex}} = 230$ nm) using a pulsed H_2 lamp (~ 1 ns pulse duration).

The fact that the long wavelength emission from *cis-1* occurs at twice the wavelength of the major emission band makes light scatter a potential worry. Based on the following observations, we believe that the long wavelength emission is not an experimental artifact. (i) The *trans* isomers do not show this emission. (ii) The lifetimes of the two, short and long, wavelength emissions are not the same. For example, in the case of *cis-2*, the two emissions have widely different lifetimes (120 and 14 ns). (iii) In *cis-2*, the long wavelength emission is not exactly twice the short wavelength emission. (iv) For *cis-1*, the structures of the short and long wavelength emissions are not the same; the former is structured while the latter is broad. (v) The long wavelength emission was seen even when the short wavelength emission was blocked by placing an appropriate Corning filter on the

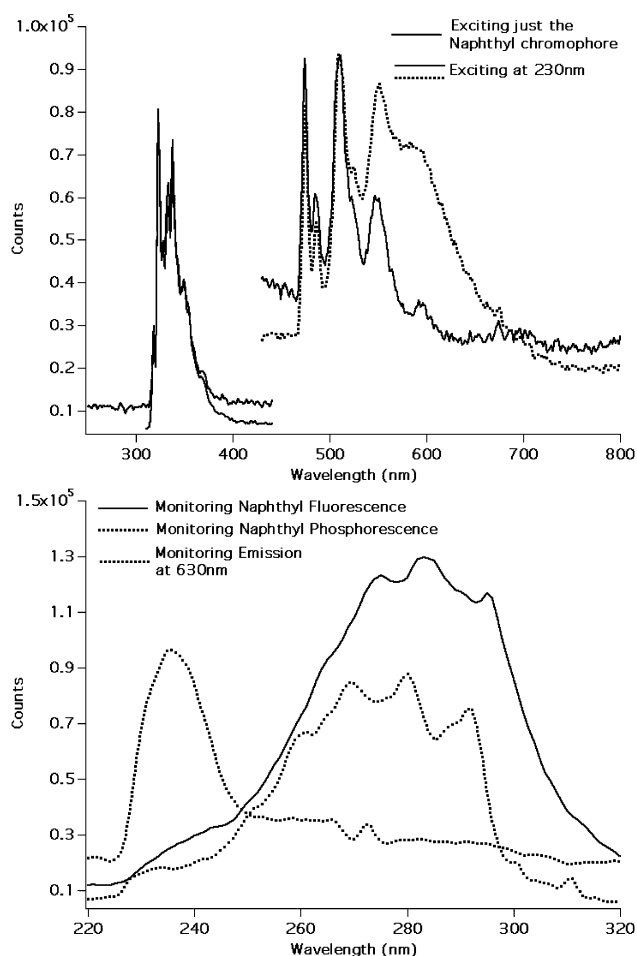


Fig. 6 (Top) Steady-state luminescence emission spectrum of *cis-2* in ethanol glass at 77 K ($\lambda_{\text{ex}} = 230$ nm). (Bottom) The corresponding excitation spectra (I: $\lambda_{\text{em}} = 290$ nm; II: $\lambda_{\text{em}} = 580$ nm).

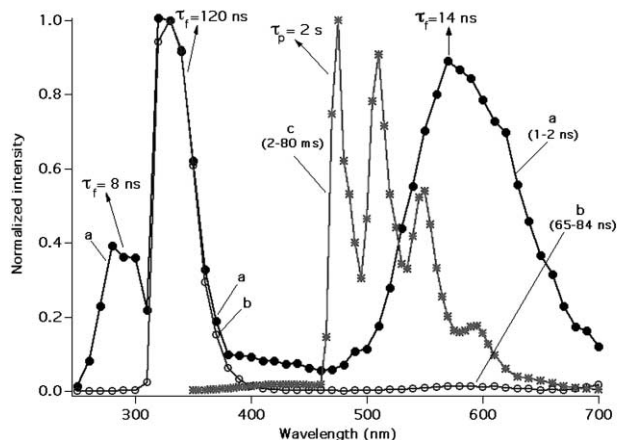


Fig. 7 Normalized time-resolved fluorescence spectra of *cis-2* in ethanol glass at 77 K at different times after excitation ($\lambda_{\text{ex}} = 230$ nm) using either a pulsed H_2 lamp [~ 1 ns pulse duration; (a) 1–2, (b) 65–84 ns] or an Xe lamp [~ 10 μs pulse duration; (c) 2–80 ms].

emission arm of the spectrofluorimeter. The emission wavelength does not depend on the nature of the glass. Identical emissions were seen in non-polar 3-methylpentane and methylcyclohexane glasses, as well as in polar ether-pentane alcohol (EPA) glass.

Discussion

Based on time-dependent product studies (Fig. 1 and 2) with pure diastereomers of *trans-1*, we can be certain that the triplet state is not involved at room temperature during the

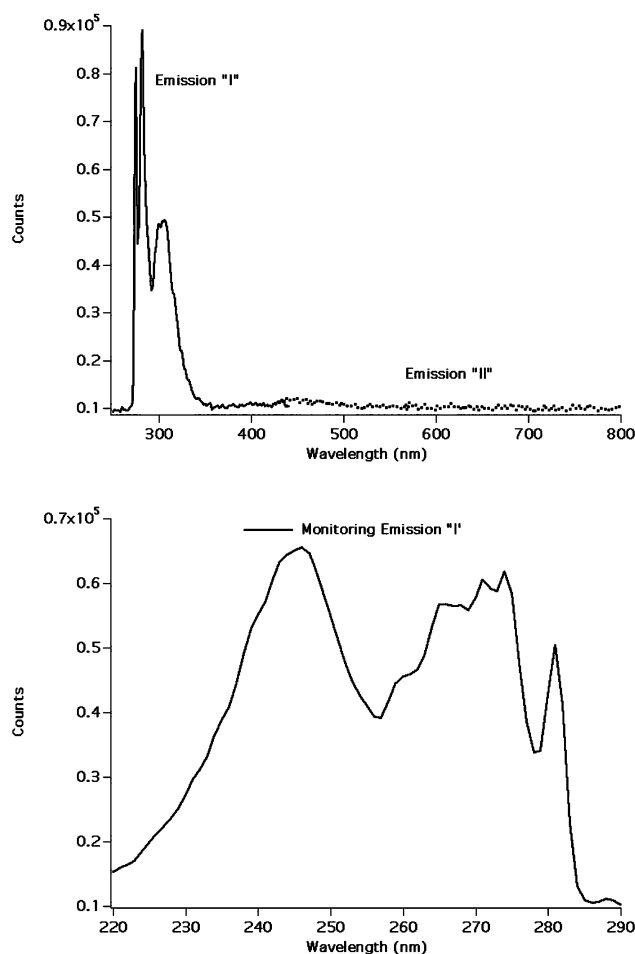


Fig. 8 Steady-state emission (top) and excitation (bottom) spectra of *trans*-1-RR. The SS isomer also showed the same photophysics.

isomerization process occurring during direct excitation. If the triplet state was involved, interconversion between the diastereomers of *trans*-1 would be expected, and this was not observed during direct excitation.

As illustrated in Fig. 4, *cis*-1 shows two distinct emissions at 77 K. At room temperature, no emission was observed. Both emissions (I and II) have identical excitation spectra (Fig. 4, bottom). This is typical of *cis*-1,2-diphenylcyclopropane, as well as several *cis*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives. The observed short lifetimes (35 and 14 ns) suggest that the emission in the region 500–700 nm is unlikely to be due to the lowest triplet state. It should be noted that the 500–700 nm emission in the case of *cis*-1,2-diphenylcyclopropane is reported² to have a lifetime of 8.5 ± 0.5 ms, which is not consistent with our observation. The possibility that the emission is due to a singlet excimer (interaction between *cis*-phenyl groups) was ruled out on the basis that the excimers in toluene, polystyrene and diphenylalkanes emit in the region 280–380 nm.⁹

Results observed with *cis*-2 further confirm that the long wavelength emission is not due to the triplet state of the diphenylcyclopropane part of the molecule. At 77 K, this compound showed four emissions (Fig. 6 and 7) at 260–300 (fluorescence due to *cis*-2,3-diphenylcyclopropane chromophore), 300–400 (fluorescence due to naphthyl chromophore), 450–650 (phosphorescence due to naphthyl chromophore) and at 500–700 nm (emission to be characterized). If the 500–700 nm emission is due to the triplet of the *cis*-2,3-diphenylcyclopropane chromophore, one would expect it to be sensitized by the naphthyl chromophore, which has higher triplet energy. However, when the naphthyl chromophore alone was excited, only phosphorescence (450–650 nm) from the naphthyl part was observed and the 500–700 nm emission was absent. This suggests that the emission in the region 500–700 nm is unlikely to be due to the

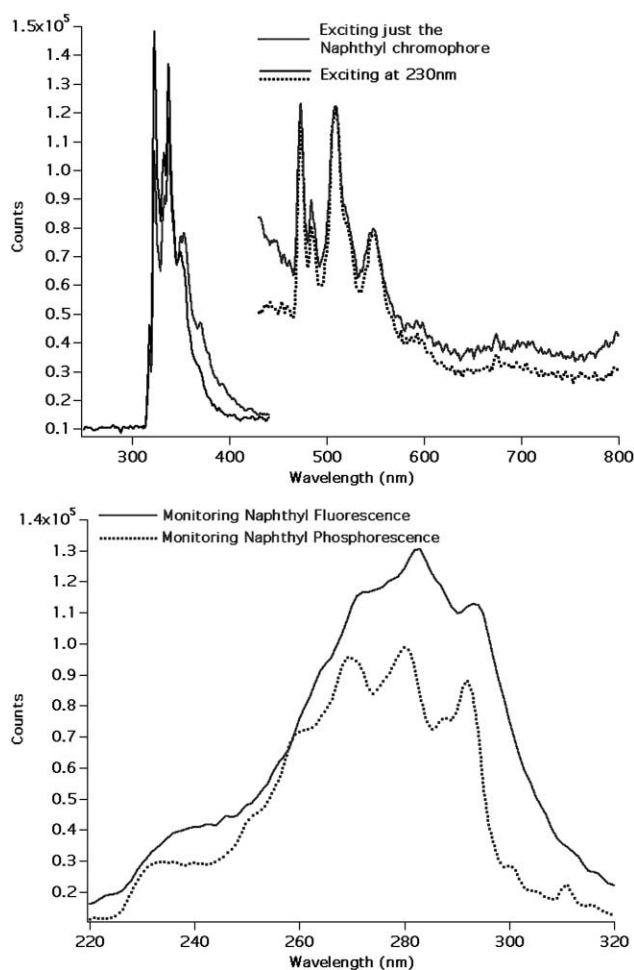


Fig. 9 Steady-state emission (top) and excitation (bottom) spectra of *trans*-2.

triplet of the *cis*-2,3-diphenylcyclopropane chromophore. The short lifetime (14 ns) is consistent with the above inference. Since the excitation spectra and lifetime of the 500–700 nm emission are identical for both *cis*-1 and *cis*-2, we believe that it must have its origin in the *cis*-2,3-diphenylcyclopropane part of the molecules and is neither due to an excimer nor the triplet of this chromophore.

Unlike *cis*-2,3-diphenylcyclopropane-1-carboxamides (**1** and **2**), the *trans* amides of 1-phenylethylamine and 1-naphthylethylamine did not show the broad emission in the region 500–700 nm. The emission spectrum of *trans*-1 consisted of only the fluorescence in the region 280–350 nm. Similarly *trans*-2 showed mainly the fluorescence and phosphorescence from the naphthyl chromophore. Of the ten *trans*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives examined, none showed the broad emission in the region 500–700 nm. But it is surprising to note that earlier studies on 1,2-diphenylcyclopropane report that *trans*-1,2-diphenylcyclopropane does not fluoresce but phosphoresces.² The origin of this discrepancy is not clear. The fact that both the *cis* and *trans* isomers do not show fluorescence at room temperature, but do so only at 77 K suggests that the isomerization from the lowest excited state of both isomers must have a small thermal barrier. Considering that the geometric isomerization in these systems is preceded by the β -cleavage process *via* mixing of the σ^* state of the PhC–CPh bond and the $\pi\pi^*$ state of the phenyl group, the presence of a barrier is expected.¹⁰

Two questions need to be addressed: (i) what is the origin of the 500–700 nm structureless emission and (ii) why only the *cis* isomer shows this emission. We tentatively infer that 500–700 nm structureless emission, which has an excitation spectrum identical to the absorption spectrum of *cis*-1, is the fluorescence of the singlet excited 1,3-diradicals **3** and **4**. This suggestion is

made on the basis of the resemblance between the observed emission and the known emissions from a benzyl radical and several 1,3 and 1,4-diradicals substituted with phenyl groups (450–700 nm).¹¹ While the region of the observed emission is consistent with that of benzyl radical, the lack of structure is disconcerting. Unlike typical benzyl and related radicals, singlet excited 1,3-diradicals **3** and **4** may not have corresponding minima in the ground-state surface. It is quite likely that the half-open diradicals **3** and **4** represent transition-state structures connecting *cis* and *trans* isomers of **1** in the ground state. If this is the case, a broad structureless emission would be expected (similar to excimers).

The ring-opening process of diphenylcyclopropanes as interpreted above represents an adiabatic photoprocess.¹² The qualitative state correlation diagram developed for the β -cleavage process (Fig. 10), which is also applicable to the geometric isomerization of diphenylcyclopropane in fact suggests that, if thermodynamics permit, the reaction could be adiabatic.¹⁰ The S_1 states of *cis*-2,3-diphenylcyclopropane derivatives possess sufficient energy (ca. 418 kJ mol⁻¹) to produce the excited states of diradicals **3**–**7**.¹³ At this stage, a brief discussion of the correlation diagram is appropriate. In the case of diphenylcyclopropane, the $\pi\pi^*$ and $\sigma\sigma^*$ states are localized on the phenyl and cyclopropane rings. While the $\sigma\sigma^*$ state correlates with the 1,3-zwitterionic state, the $\pi\pi^*$ state correlates with the excited state of the 1,3-diradical where the energy is localized on the phenyl ring. For the cleavage to occur from the $\pi\pi^*$ state, mixing of the $\pi\pi^*$ and the $\sigma\sigma^*$ states is necessary. Of the two lowest $\pi\pi^*$ states of the phenyl ring, due to symmetry considerations, only the second excited $\pi\pi^*$ (S_2 , L_a) state would be able to mix with the $\sigma\sigma^*$ state. Because of this, cleavage to the zwitterionic intermediate is more likely from S_2 than from S_1 . On the other hand, if energetic considerations permit, S_1 would yield the excited diradical, in which case the excess energy would be localized on the phenyl ring. Because of the intended crossing, cleavage from S_2 and S_1 would have a thermal barrier. This is consistent with the observed emission behavior. The fact that both *trans* and *cis*-2,3-diphenylcyclopropane derivatives show fluorescence at 77 K from their spectroscopic minima suggests that the cleavage process leading to the 1,3-zwitterionic state (the first step in the isomerization pathway) has a barrier. Apparently, the barrier for cleavage cannot be surmounted at 77 K and excited molecules instead follow the radiative pathway.

The final point concerns with why only the *cis*-**1** and *cis*-**2**, but not the corresponding *trans* isomers, show the adiabatic

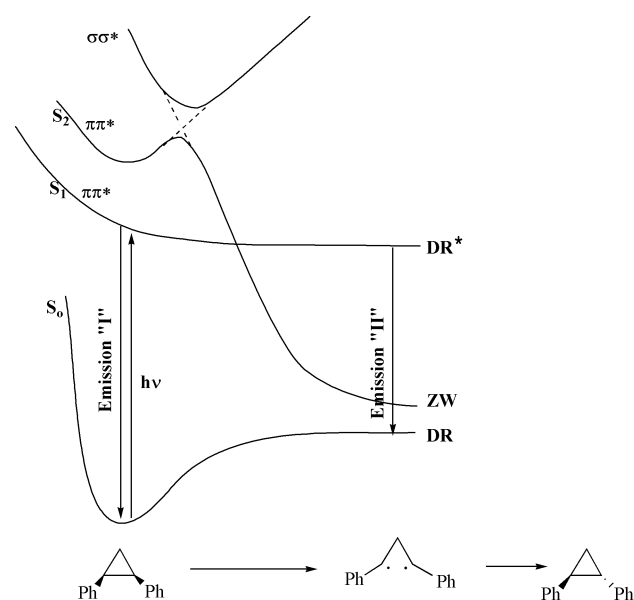


Fig. 10 Qualitative state correlation diagram for photochemical β -cleavage of the central C–C bond in diphenylcyclopropane. Breakage of this bond leads to geometric isomerization.

photochemistry. The fact that both isomers show fluorescence at 77 K from their spectroscopic minima suggests that the cleavage process leading to the 1,3-zwitterionic state (the first step in the isomerization pathway) has a barrier from both isomers. However, the barrier to generation of the excited diradical (adiabatic cleavage) seems to be higher in the case of *trans*-**1** than for *cis*-**1**. We believe that this has to do with the difference in orbital overlap between the phenyl π and C–C σ orbitals in the two systems. Ideally, the angle between the two should be 0°. The dihedral angles calculated for the geometry-optimized (HF/3-21G level) structures of *trans*-**1** and *cis*-**1** are 36 and 26°. We speculate that this difference might be responsible for the lower barrier for the adiabatic process from *cis*-**1**. Further study is needed to fully understand this phenomenon.

Our results suggest that an earlier conclusion that 2,3-diphenylcyclopropane has an unusually low triplet energy is incorrect. Furthermore, the observed broad emission in the region 500–700 nm is not due to phosphorescence from 2,3-diphenylcyclopropane. While we are confident of the above reinterpretation of the literature results based on the experiments described above, although, admittedly, we are less certain about the origin of the long wavelength emission. Further studies are required to unequivocally assign the nature of the emission.

Summary

We have shown that *cis*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives undergo an adiabatic photoprocess from their excited singlet states. In contrast to what has been reported in the literature concerning the excited-state chemistry of 1,2-diphenylcyclopropanes,^{1–4,8} we report here that these systems have inefficient intersystem crossing yields from S_1 to T_1 , have high triplet energies (~ 311 kJ mol⁻¹, and not 222 kJ mol⁻¹), and isomerize *via* non-interconverting 1,3-singlet diradicals upon direct excitation in solution.

Experimental

Materials

Dichloromethane (Fisher), hexanes (Aldrich) and acetone (Aldrich) were used as supplied for photochemical studies. HPLC grade 2-propanol (Aldrich) and hexane (Aldrich) was used for HPLC analysis. Spectroscopic grade solvents (3-methylpentane, methylcyclohexane, methanol and ethanol) from Aldrich were used for emission studies.

Photochemical studies in isotropic media

Direct irradiation. Compounds **1** or **2** (2–3 mg) were dissolved in 0.5 mL of dichloromethane in a test-tube tube (**1**: quartz test-tube; **2**: Pyrex test-tube) and 15 mL of hexanes was added. The tube was stoppered with a rubber septum and wrapped in Parafilm. The solution was then irradiated (unfiltered output from a 450 W medium pressure mercury lamp). The reactant and the photoproducts were concentrated and analyzed using a GC/HPLC.

Sensitized irradiation. Compounds **1** or **2** (2–3 mg) were dissolved in 10–12 mL of acetone in a test-tube (Pyrex), which was then stoppered with a rubber septum and wrapped with Parafilm. The solution was degassed with N_2 for 30 min and then irradiated (unfiltered output from a 450 W medium pressure mercury lamp) under positive N_2 pressure. The reactant and the photoproducts were concentrated and analyzed on a GC/HPLC.

Verification of the photoproducts

Authentic samples (*trans* and *cis* isomers independently synthesized) were injected into the GC/HPLC and their retention times used to verify those of the photoproducts.

Analysis conditions

1-Phenylethyl amide of *cis*-2,3-diphenylcyclopropane-1-carboxylic acid (1). HPLC: Rainin HPLC with Chiralpak-AD-RH as stationary phase and a mobile phase of hexane–2-propanol (95 : 5); flow rate = 1.0 ml min⁻¹, absorbance = 230 nm; retention times: *cis*-1 ~24.8 min, *trans*-SS-1 ~33.4 min, *trans*-RR-1 ~73.0 min. GC: Shimadzu GC-17A with CR-501 Chromatopac integrator and SE-30 column; program: 100 °C—1 min—7 °C min⁻¹—240 °C—10 min—1 °C min⁻¹—270 °C—1 min; retention times: *cis*-1 ~49.4 min, *trans*-RR-1 ~50.8 min, *trans*-SS-1: ~51.9 min.

1-Naphthylethyl amide of *cis*-2,3-diphenylcyclopropane-1-carboxylic acid (2). HPLC: Rainin HPLC with Chiralpak-AD-RH as stationary phase and a mobile phase of hexane–2-propanol (95 : 5); flow rate = 0.7 ml min⁻¹, absorbance = 282 nm; retention times: *cis*-2 ~43.3 min, *trans*-RR-2 ~52.5 min, *trans*-SS-2 ~68.0 min.

Instrumentation

Steady-state and time-resolved emission spectra were recorded using an Edinburgh Analytical Instruments spectrometer for samples in methanol–ethanol glasses at 77 K using an Xe lamp. Time-resolved fluorescence and phosphorescence spectra were recorded using H₂ and Xe lamps, respectively.

Acknowledgements

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