Studies of Relations between Molecular Structure and Photochemical Properties of Spiro[indoline-2,3′-[1,4]oxazines]

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Photochromic reactions of 17 spiro[indolineoxazine] derivatives were investigated using nanosecond laser flash photolysis techniques. The substituent in the 2′-position of the oxazine moiety plays a decisive role in the formation of photoproducts. When the 2′-substituent is hydrogen, photoexcitation of spirooxazine only yielded long-lived photomerocyanine (PMC); however, with other substituents, a short-lived charge separation twisted species (CT) was formed as the predominant product. This observation is attributed to the steric hindrance effect of the substituent in the 2′-position of the oxazine moiety and methyl groups in the 1- and 3-positions of the indoline moiety. In addition, the substituent on nitrogen atom of the indoline moiety also affects the structural characteristics of the CT intermediate. The substituents in the 5-position of the indoline moiety and 9′-position of the naphthooxazine moiety affect the system mainly through electronic effects. A substituent effect on the λ_{max} of the absorption spectra of PMC is also observed. A potential energy surface is proposed to explain these substituent effects. The structural characteristics of PMC and CT intermediates are discussed.

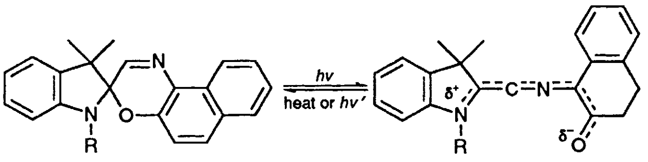
The photochromism of spirooxazines, such as those shown in Scheme 1, was first reported by Fox.[1] Although the photochromic properties of spiropyran have been extensively studied,[2] much less work on spirooxazines has been reported.[3-8] Compared with spiropyran, spirooxazines show an excellent fatigue resistance;[1,9] from a commercial point of view this is a key property which largely determines whether or not they are likely to find any practical applications: the excellent fatigue resistance has triggered considerable interest in spirooxazines.[10,11] Investigations of the photochromic mechanism and solvatochromism of spirooxazines are thus of fundamental interest.

According to the conclusions reported in refs. 3–8, the coloured ring-opened forms of spiro[indolineoxazine] can be divided into two kinds, photomerocyanines (PMC) with planar structure, and charge separation twist intermediates (CT). PMCs and CTs have significantly different lifetimes: in general, PMCs have a very long lifetime which probably reaches into seconds; actually, PMCs are so long-lived that their decay cannot be monitored by the nanosecond flash photolysis apparatus. However, CTs are short-lived species with lifetimes of only several microseconds. Some spirooxazines can produce two kinds of coloured forms, PMC and CT, whereas some of them only give PMC. (PMCs have a much lower quantum yield than CT.) The phenomenon is decided by the structure of the spiro[indolineoxazine] in question.

In the present paper, we describe the photochromism of 17 spiro[indolineoxazines] using nanosecond laser flash photolysis techniques. Photolysis of compounds **1** and **7** have been studied previously.[8]

Experimental

Materials.—Absolute ethanol was prepared by treating ethanol (Beijing Chemical Factory) with magnesium powder. Iodomethane was purified by shaking with dilute sodium thiosulfate solution and washing with water, drying (calcium chloride), then distilling fractionally. 1-Nitroso-2-naphthol was prepared by nitrosation of 2-naphthol.[12]

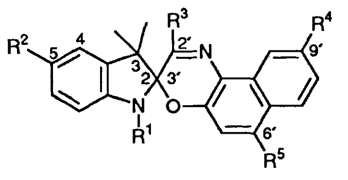


Scheme 1

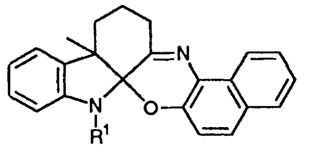
Compounds **8**–**12** were prepared according to the methods described in the following literature: **8** and **9**,[13] **10** and **11**[14] and **12**;[15] the synthesis of compounds **2**–**6** was first reported by us.[16,19] Compounds **12**–**19** are novel. Since the procedures for preparation of **13**–**17** are very similar and **18**–**19** also have very similar preparation methods, we will describe the procedures for the preparation of three compounds, **13**, **15** and **18**, in detail.

Compound **13**. 2-Benzyl-1,3,3-trimethylindole was prepared according to literature,[20] and was treated with iodomethane to give the corresponding indolium iodide. The iodide, triethylamine and 1-nitroso-2-naphthol were dissolved in absolute ethanol and refluxed for 3 h under nitrogen atmosphere. After removing solvent, the residue was separated on silica gel column [eluent dichloromethane–cyclohexane (v:v = 1:1)]. Recrystallization (acetone and water) gave a bright yellow crystal, m.p. 216–218 °C.

Compound **15**. The Grignard reagent prepared from 1-bromopropane reacted with isobutyraldehyde to give 2-methylhexan-3-ol, which was oxidized by a solution of sodium dichromate and sulfuric acid[21] to yield 2-methylhexan-3-one. The obtained ketone was transformed into the corresponding phenylhydrazone through reaction with phenylhydrazine. The phenylhydrazone was dissolved in glacial acetic acid and refluxed to produce 3,3-dimethyl-2-propylindole, which was treated with iodoethane to give the corresponding indolium iodide. A solution of the indolium iodide, triethylamine and 1-nitroso-2-naphthol in absolute ethanol was refluxed for 4 h



	R^1	R^2	R^3	R^4	R^5
1	Me	H	Me	H	H
2	Et	H	Me	H	H
3	Me	H	Me	OMe	H
4	Et	H	Me	OMe	H
5	Me	Me	Me	H	H
6	Me	Cl	Me	H	H
7	Me	H	H	H	H
8	Me	Me	H	H	H
9	Me	Cl	H	H	H
10	Me	H	H	OMe	H
11	Me	Cl	Cl	OMe	H
12	Me	H	H	H	$CH_2[CH_2]_4N$
13	Me	H	Ph	H	H
14	Me	H	Et	H	H
15	Et	H	Et	H	H
16	Me	H	Pr	H	H
17	Et	H	Pr	H	H



18 R^1 = Me
19 R^1 = Et

under nitrogen atmosphere. After evaporation of solvent, the residue was chromatographed on silica gel column [eluent dichloromethane–cyclohexane (v:v = 1:1)]. A light orange yellow crystal was obtained after recrystallization (acetone), m.p. 130–132 °C.

Compound **18**. 4a-Methyl-2,3,4,4a-tetrahydro-1*H*-carbazole was prepared from 2-methylcyclohexanone and phenylhydrazine.[22] The obtained carbazole was transformed into the corresponding carbazolium iodide by treating with iodomethane. The carbazolium iodide, triethylamine and 1-nitroso-2-naphthol were dissolved in absolute ethanol and refluxed for 3 h under nitrogen atmosphere. After solvent was removed, the residue was chromatographed on silica gel column [eluent dichloromethane–cyclohexane (v:v = 2:1)]. An orange red crystal was obtained after recrystallization (acetone), m.p. 218–220 °C.

Analysis. The structures of the seven compounds (**13**–**19**) were determined by elemental analysis, IR, ^1H NMR and MS spectra.

13. M.p. 216–218 °C (Found: C, 83.5; H, 6.0; N, 6.9. $C_{28}H_{24}N_2O$ requires: C, 83.14; H, 5.98; N, 6.93%); ν_{max}/cm^{-1} 2956, 1624, 1608, 1591 and 1487; δ_H($CDCl_3$, Me_4Si) 1.20 (s, 3 H, 3-CH_3), 1.29 (s, 3 H, 3-CH_3), 2.85 (s, 3 H, N–CH_3) and 6.58–8.74 (m, Ar–H); *m/z* 404 (100%, M^+), 389 (22, M – CH_3), 327 (9, M – Ph), 245 (26), 159 (92) and 158 (49).

14. M.p. 139–141 °C (Found: C, 80.9; H, 7.1; N, 7.7. $C_{24}H_{24}N_2O$, requires: C, 80.87; H, 6.79; N, 7.86%); ν_{max}/cm^{-1} 2984, 1617, 1608, 1594 and 1491; δ_H($CDCl_3$ Me_4Si) 1.20 (s, 3 H, 3-CH_3), 1.22 (s, 3 H, 3-CH_3), 1.40 (t, 3 H, CH, 2′-CH–CH_3), 2.55 (m, 2 H, 2′–CH_2–), 2.93 (s, 3 H, N–CH_3) and 6.56–8.65 (m, Ar–H); *m/z* 356 (18%, M^+), 327 (100, M – C_2H_5), 312 (22), 182 (22), 159 (33) and 158 (68).

15. M.p. 130–132 °C (Found: C, 80.7; H, 7.0; N, 7.35. $C_{25}H_{26}N_2O$, requires: C, 81.05; H, 7.07; N, 7.56%); ν_{max}/cm^{-1} 2981, 1625, 1608, 1593 and 1484; δ_H($CDCl_3$, Me_4Si) 1.20 (s, 3 H, 3-CH_3), 1.23 (s, 3 H, 3-CH_3), 1.36 (m, 6 H, N–CH_2CH_3 and 2′-CH_2CH_3), 2.46 (m, 2 H, 2′–CH_2–), 3.35 (m, 2 H, N–CH_2–) and 6.55–8.66 (m, Ar–H); *m/z* 370 (17%, M^+), 341 (100, M – C_2H_5, 326 (18), 182 (16), 172 (44) and 158 (24).

16. M.p. 144–146 °C (Found: C, 81.2; H, 7.1; N, 7.5. $C_{25}H_{26}N_2O$, requires: C, 81.05; H, 7.07; N, 7.56%); ν_{max}/cm^{-1} 2993, 1620, 1607, 1595 and 1487; δ_H($CDCl_3$, Me_4Si) 1.08 (t, 3 H, 2′-CH_2–CH_2–CH_3), 1.19 (s, 3 H, 3-CH_3), 1.23 (s, 3 H, 3-CH_3), 2–2.5 (m, 4 H, 2′-CH_2–CH_2–), 2.94 (s, 3 H, N–CH_3) and 6.56–8.62 (m, Ar–H); *m/z* 370 (21%, M^+), 327 (100, M – C_3H_7), 312 (18), 182 (15), 159 (22) and 158 (47).

17. M.p. 128–130 °C (Found: C, 81.3; H, 7.35; N, 7.2; $C_{26}H_{28}N_2O$, requires: C, 81.21; H, 7.34; N, 7.29%); ν_{max}/cm^{-1} 2966, 1618, 1593 and 1492; δ_H($CDCl_3$, Me_4Si) 1.05 (t, 3 H, 2′-$CH_2CH_2CH_3$), 1.21 (s, 6 H, 3-CH_3), 1.35 (t, 3 H, N–CH_3), 2–2.42 (t, 4 H, 2′-CH_2–CH_2), 3.4 (m, 2 H, N–CH_2–) and 6.56–8.62 (m, Ar–H); *m/z* 384 (18%, M^+), 341 (100, M – C_3H_7), 326 (13), 297 (3) and 172 (3).

18. M.p. 218–220 °C (Found: C, 81.3; H, 7.35; N, 7.2; $C_{24}H_{22}N_2O$, requires: C, 81.33; H, 6.26; N, 7.90%); ν_{max}/cm^{-1} 2966, 1620, 1609, 1593 and 1482; δ_H($CDCl_3$, Me_4Si) 1.51 (s, 3 H, 12b-CH_3), 1.8 (m, 4 H, 13-CH_2– and 14-CH_2–), 2.54 (s, 3 H, N-CH_3), 2.9 (m, 2 H, 15-CH_2–) and 6.50–8.65 (m, Ar–H); *m/z* 354 (100%, M^+), 339 (56), 311 (15), 196 (41), 186 (26), 183 (62), 170 (36) and 158 (42).

19. M.p. 169–171 °C (Found: C, 81.45; H, 6.6; N, 7.5; $C_{25}H_{24}N_2O$, requires: C, 81.49; H, 6.56; N, 7.60%); ν_{max}/cm^{-1} 2989, 1626, 1607, 1594 and 1480; δ_H($CDCl_3$, Me_4Si) 1.00 (t, 3 H, N–CH_2CH_3), 1.49 (s, 3 H, 12b-CH_3), 1.8 (m, 4 H, 13-CH_2– and 14-CH_2–), 3.0 (m, 4 H, 15-CH_2– and N–CH_2–) and 6.54–8.67 (m, Ar–H); *m/z* 368 (100%, M^+), 353 (73), 325 (11), 196 (46), 184 (94), 172 (31) and 158 (19).

Nanosecond Laser Flash Photolysis.—The nanosecond laser flash photolysis apparatus has been described previously[16] and the excitation wavelength is 248 nm. As a control experiment, the third harmonic of YAG laser, 355 nm, was used in some experiments, the same photoproducts can also be obtained.

Acetonitrile (HPLC grade) and cyclohexane (AR) were used without further purification. The solutions were contained in 1 cm × 1 cm quartz cells. All measurements were carried out at room temperature (*ca.* 20 °C).

Results

All compounds, except **13**, show photochromic properties. Photolysis of **8**–**12** only leads to long-lived species ($\tau \gg 80$ μs), which have similar spectra and decay characteristics to that of the PMC of **7**. Therefore, these species can be assigned as planar PMCs. Compounds **3**, **4**, **6** and **14**–**19** give only CT intermediates after laser photolysis, but **2** and **5** give both CT intermediates and PMCs. Upon photolysis of **13** we did not obtain signals using our apparatus.

The λ_{max} values and the lifetimes of photoproducts of all compounds after photolysis by laser pulse are given in Table 1.

Figs. 1 and 2 show typical time-resolved transient absorption spectra: Fig. 1 shows the situation in whch a CT intermediate is the only product after photolysis; Fig. 2 shows that both the CT intermediate and PMC are involved.

Discussion

The photolysis of spiro[indolineoxazine] has been studied by Schneider *et al.*[4–6] They demonstrated that the four isomers (at least) of PMC are involved in the photoproducts.

$$\text{spiro[indolineoxazine]} \xrightarrow{h\nu} \text{PMC}$$

Table 1 λ_{max} values (nm) and the lifetimes τ (µs) of the photoproducts yielded from compounds **1**–**19** after photolysis by the excimer laser pulse (the data in parentheses are for PMC, the others are for CT)

	Acetonitrile		Cyclohexane	
Compd.	λ_{max}/nm	τ/µs	λ_{max}/nm	τ/µs
1[8]	470, 680	1.70	470, 640	0.85
	(600)	($\gg$500)	(560)	($\gg$500)
2[17]	430, 660	3.3	470, 670	0.65
			(610)	($\gg$80)
3[17,18]	460, 680	1.3	470, 640	0.5
4[17]	450, 650	5.0	480, 640	1.1
5[19]	420, 610	12	450, 640	0.8
			(600)	($\gg$80)
6	430, 670	0.6	470, 640	0.5
7[8]	(440, 600)	($\gg$500)	(560)	($\gg$500)
8[16]	(440, 630)	($\gg$80)	(440, 580)	($\gg$80)
9[16]	(440, 610)	($\gg$80)	(570)	($\gg$80)
10[16]	(470, 570)	($\gg$80)	(560)	($\gg$80)
11[16]	(600)	($\gg$80)	(560)	($\gg$80)
12	(575)	($\gg$500)	(540)	($\gg$500)
13	*a*	*a*	*a*	*a*
14	450, 700	0.12	470, 700	0.06
15	460, 720	0.08	460, 700	0.07
16	460, 700	0.15	480, 700	0.06
17	450, 720	0.17	450, 720	0.06
18	420, 710	0.15	*a*	*a*
19	420, 700	0.12	*a*	*a*

[a] No signal.

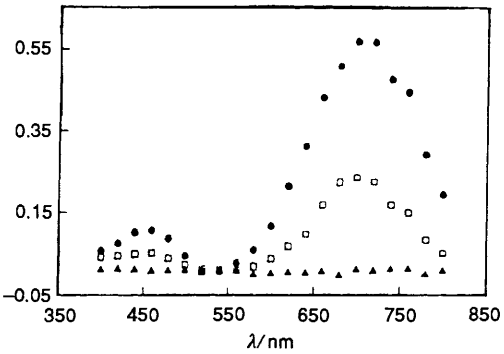


Fig. 1 Time-resolved transient absorption spectra of compound **14** in acetonitrile after a 248 nm laser pulse (only CT intermediate is observed). ●, 0.1; □, 0.3; ▲, 1.0 µs.

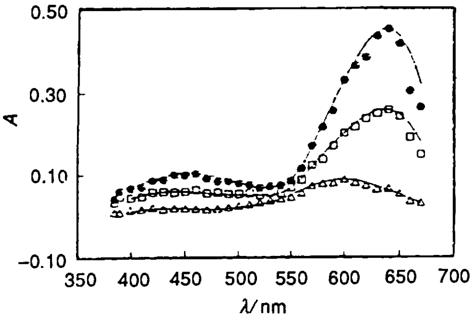


Fig. 2 Time-resolved transient absorption spectra of compound **5** in cyclohexane after a 248 nm laser flash (the solid circles represent the absorption of CT, the triangles represent mainly the absorption of PMC). ●, 0.5; □, 1.0; △, 5.0 µs.

In 1992, Fan *et al.*[8] found that when hydrogen in the 2′-position of the oxazine moiety was substituted by a methyl group (*e.g.*, **1**), a new species was observed after photolysis. This species is assigned to a CT intermediate.

Here we will discuss the relationship between molecular structure and photochromic properties of spirooxazine in detail.

First, according to the various substituents in the 2′-position, the photoproducts of spiro[indolineoxazines] are divided into two kinds. Photolysis of **8**–**12** leads to PMCs as the only products. The others give CT intermediates or CTs (the main products) and PMCs; this indicates that the substituent in the 2′-position of the oxazine moiety plays a decisive role in the formation of the photoproducts.

The photochromic reaction of spirooxazine consists of heterolytic cleavage of the C–O bond, bond rotations, especially the C(2′)–C(3′) bond, and charge redistribution.

From a molecular model, we found that when hydrogen in the 2′-position of the oxazine moiety is replaced by other groups, rotation of the C(2′)–C(3′) bond becomes very difficult because of the steric hindrance effect caused by the substituent in the 2′-position and the methyl groups in 1- and 3-positions of the indoline moiety. In this case, the molecule, after the heterolytic cleavage of the C–O bond, can only undertake moderate configurational changes and achieve a metastable state, which should be assigned to a CT intermediate.

In a spirooxazine molecule, the indoline and naphthoxazine moieties are almost perpendicular, and thus, there is no conjugation between the two moieties. After the C–O bond cleavage of the oxazine ring, the molecular configuration becomes flexible; thus, the two moieties of the molecule no longer remain perpendicular, and conjugation can occur between the two moieties to a certain degree. In a CT intermediate, the two moieties are unable to become co-planar because of the steric hindrance effect caused by the substitution in the 2′-position. Obviously, the conjugation depends on the dihedral angle between indoline and naphthalene moieties. But the dihedral angle is strongly dependent on the steric hindrance effect. The larger the substituent in 2′-position of oxazine moiety or on the nitrogen atom of the indoline moiety is, the larger the dihedral angle is, and thus, the less the conjugation is.

After heterolytic cleavage of the C–O bond, the charges are separated. The positive and negative charge will locate at the nitrogen atom of the indoline moiety and the oxygen atom of naphthoxazine moiety respectively. Moreover, these separated charges will be delocalized within the whole molecule. When the charges were greatly delocalized, the molecules will be weak polar and show quinoidal structural characteristics. Conversely, they may be zwitterionic.

All ring-opened forms of spirooxazines, including PMC and CT intermediates, are essentially a resonance hybrid of quinoidal and zwitterionic structures. The two structures can be distinguished easily according to solvatochromism of the ring-opened species, because the quinoidal structure will show positive solvatochromism and the zwitterionic one negative.

Second, we now discuss the results of those compounds whose predominant photoproducts are CT intermediates. The larger substituent in 2′-position of the oxazine moiety leads to a shorter lifetime of the CT intermediate. The compounds **1**–**6**, which have methyl groups in the 2′-position, exhibit longer lived CT intermediates (> 500 ns), whereas the CT intermediates of **14**–**17** show shorter lifetimes (< 200 ns). The lifetime is much shorter in cyclohexane than in acetonitrile. The phenomenon is explained as follows: the larger substituent in 2′-position leads to a larger dihedral angle and a smaller charge delocalization. This will decrease the lifetime of CT intermediates.

Concerning **13**, we did not obtain any detectable signals after photolysis; this is probably due to the strong steric hindrance effect of the phenyl group and too short a lifetime of the ring-opened oxazine species.

In the case of **18** and **19**, the indoline and naphthoxazine moieties are linked by a bridged chain, the configuration is relatively rigid even after the C–O cleavage of oxazine ring. The ring-opened species is able to be observed in acetonitrile, but not in cyclohexane using our apparatus.

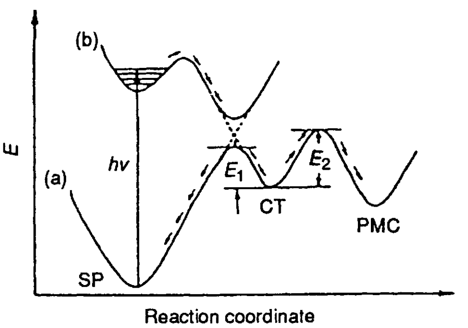


Fig. 3 Proposed potential energy surface for the photochromic reactions of spiro[indolineoxazine]. (*a*) Ground state of spirocompound, CT and PMC; (*b*) excited state of spirocompound.

Kholmanskii *et al.*,[23] discussed photochromism of spiropyrans by the potential energy surface. According to their conclusion, our results could not be explained very well. In order to understand the photochromic processes of spirooxazine, a new scheme of potential energy surface has been proposed as follows (Fig. 3); where (*a*) is the ground state potential energy curve of SP, CT and PMC and (*b*) is the excited state potential energy curve of the spiro[indolineoxazine].

CT can return to spiro[indolineoxazine] through the ring-closure reaction, or transform into PMC through the further rotation of the bonds. The predominant process depends on the ratio of E_1/E_2. The compounds without a substituent in the 2′-position (*i.e.*, **7**–**12**), may have a small E_2, so that the CT intermediates can easily transform into PMCs. In other words, only PMC can be observed. However, compounds with a substituent in the 2′-position may have a greater E_2. Therefore the quantum yield of PMC is much lower than that of a CT intermediate. The larger the substituent in the 2′-position is, the greater E_2 is, and thus, the lower the quantum yield of PMC is. That is why CT intermediates can be detected only in the compounds **14**–**19**.

Third, we discuss the substituent effect of R^2 and R^4. Since R^2 and R^4 are far from the reaction centre, they affect the properties of photoproducts mainly by electronic effects.

Comparing the results of **3** with **1**, it is found that the photolysis of **3** only produces a CT intermediate, whereas photolysis of **1** leads to both a CT intermediate and PMC. Because the methoxy group is a strong electron-donating group, it increases the electron density of the oxygen atom and the ring-closure rate of the CT intermediate. A methoxy group can also decrease the quantum yield of PMC. Therefore, after photolysis of **3**, PMC was not detected by our apparatus.

Photolysis of **4** leads to a CT intermediate as the only measurable product as well.

The substituent effect of R^1 is mainly attributed to the steric hindrance. A large R^1 group shows a strong steric hindrance effect and leads to more zwitterionic characteristics of photoproducts.

If PMC is regarded as an intramolecular charge-transfer state in the excited state, the effect of substituents R^2, R^4 and R^5 on the absorption band of PMC can be explained.

Finally, the effect of solvent on the photoproducts is discussed. As a general rule, a CT intermediate is a resonance hybrid of quinoidal and zwitterionic structure; quinoidal structure shows positive solvatochromism and the latter negative.

In comparison of **5** with **1**, the intermediate of **1** shows strong positive solvatochromism, it has predominant quinoidal structure characteristics. The CT intermediate of **5** does not show solvatochromism, therefore it has more zwitterionic character than that of **1**. This may be attributed to the methyl group in the 5-position of the indoline moiety in **5**, the positively charged nitrogen atom may be stabilized by the methyl group.

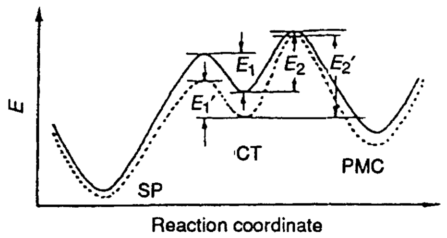


Fig. 4 Proposed potential energy surface for the photochromic reactions of compound **2** and **5** in cyclohexane (solid line) and in acetonitrile (dashed line)

The solvatochromism of the photoproduct derived from **6** is similar to that from **1**. This indicates that the chlorine atom does show an electron-donating effect.

Zwitterionic species have higher polarity and will be more stable in polar solvents. The quinoidal structure has lower polarity in comparison with zwitterions and will be unstable in acetonitrile. In photolysis of **2** and **5** in acetonitrile, both PMC and CT intermediates can be detected. However, in cyclohexane only PMC was detected. It is indicated that PMC has more quinoidal character and the CT intermediate has more zwitterionic character.

From the potential energy surface of view, the solvent effect can be explained also. The results of **2** and **5** are shown in Fig. 4. The energy surface in cyclohexane is different from that in acetonitrile, the ratio of potential energy barriers, E_1/E_2 in cyclohexane is larger than that of E_1'/E_2' in acetonitrile. In this case, the transformation of CT into PMC in acetonitrile is more difficult than that in cyclohexane. Therefore PMC can only be detected in cyclohexane.

Conclusions

The effects of substituent in spiro[indolineoxazine] molecules on the structure of the photoproducts, especially on the structural characteristics of CT intermediates, were investigated by laser flash photolysis of 17 spirooxazines. The substituent at the 2′-position of the oxazine ring is the most important, and plays a decisive role in the structure of photoproducts. R^1 influences the structural character of CT intermediates mainly through the steric hindrance effect, whereas R^2, R^4 and R^5 do so mainly through the electronic effect. Based on the experimental results, a potential energy surface is proposed to explain the substituent effects on the structure of the photoproduct. Moreover, the nature of the CT intermediate is discussed in more detail.

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