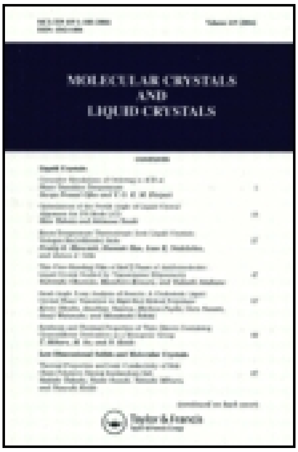

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# Synthesis and Crystal Structure of (1,2-Dimethyl -4-isopropyl-5-phenyl)-3-pyrryl-ethylidene-(isopropylidene) succinic Anhydride

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# SYNTHESIS AND CRYSTAL STRUCTURE OF (1,2-DIMETHYL -4-ISOPROPYL-5-PHENYL)-3-PYRRYL-ETHYLIDENE (ISOPROPYLIDENE) SUCCINIC ANHYDRIDE

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**Abstract** A new pyrryl fulgide, E-(α)-(1,2-dimethyl-4-isopropyl-5-phenyl)-3-pyrryl-ethylidene (isopropylidene) succinic anhydride (1), was synthesized. Molecular and crystal structures were determined. The characters of crystal structure of pyrryl fulgide (1) was discussed. It was found that the pyrryl fulgide (1) has a twisted structure between pyrrole ring and the succinic anhydride portion, the dihedral angle between these two portions is 122.86(3)°. The phenyl ring located in the 5-position of pyrrole ring is not coplanar with the pyrrole ring. The distance between two reactive sites (C1 and C22 atoms) is 3.57Å, which is favorable for the photo-induced intramolecular cyclization of pyrryl fulgide (1).

## INTRODUCTION

It is well known that fulgide is one kind of important organic photochromic compound[1]. Heller[2] suggested that fulgide compounds are useful as erasable optical memory materials. However, the photochromic properties of fulgides need to be improved, such as thermal stability, quantum yield of the photochromic reaction, absorption maximum of the colored form of fulgide, *etc*. These can be achieved by molecular design and synthesis of the fulgide compounds, as far as the molecular design is concerned, it is indispensable to know the structural information about the skeleton of fulgide molecule. The photo-chemical ring closure which results in the formation of red-absorbing 7,7a-dihydroindole-like structures have been extensively studied by Heller *et al*[3]. The molecular crystal structure and photochromic properties of (2-methyl-5-phenyl-3-thienyl) ethylidene (isopropylidene) succinic anhydride have been discussed. However, to our knowledge, little attention has been paid to synthesis and photochromic properties of fulgides [3-7] and no attempt has been made to study the crystal structure of pyrryl substituted fulgides. We have undertaken extensive studies

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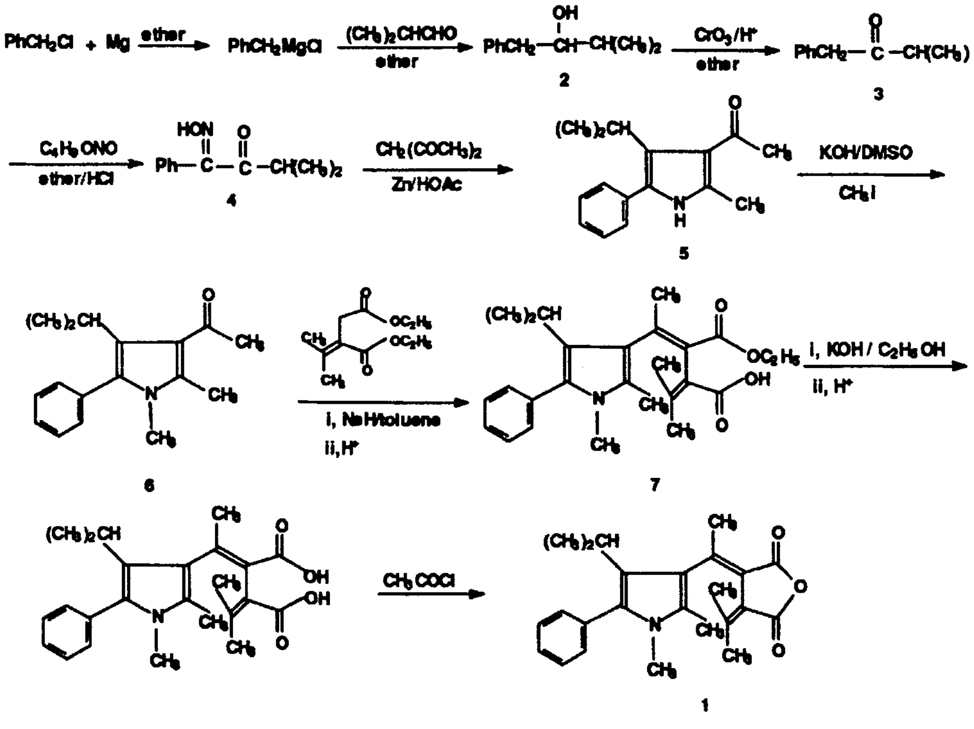
on the synthesis and photochromism of pyrryl substituted heterocyclic fulgides [8-10]. In this paper, we report the synthesis and the crystal structure of the title compound and try to elucidate the relationship between structure and photochromism of pyrryl substituted fulgides.

## EXPERIMENTAL

UV-Vis absorption spectra were measured on Hitachi-557 spectrometer. NMR spectra were obtained with an FT80 (80 MHz) or a Varian XL-400 (400 MHz) instrument in $CDCl_3$ using tetramethylsilane as internal standard. Mass spectra were measured using a Finnigan 4021C mass spectrometer with an electron-impact source at 25 or 70 ev. Reagents and solvents were purified before use.

The title compound was synthesized by following steps including Stobbe condensation, which is shown in scheme 1.



Scheme 1

According to literature, 1-phenyl-3-methyl-2-butanone (3)[11], α-oximino ketone (4) [12], 2-methyl-3-acetyl-4-isopropyl-5-phenyl pyrrole (5)[13], and 1,2-dimethyl-3-acetyl-4-isopropyl-5-phenyl-pyrrole (6)[14] were obtained. Compound 6 was condensed with diethyl isopropylidene succinate *via* Stobbe condensation, gave fulgide (1).

(*E*)-(1,2-Dimethyl-4-isopropyl-5-phenyl)-3-pyrryl ethylidene (isopropylidene) succinic anhydride (1)

A mixture of 1,2-dimethyl-3-acetyl-4-isopropyl-5-phenyl pyrrole (6) (12.75 g, 0.05mol) and diethyl isopropyldiene succinate (10.7 g, 0.05 mol) in dry toluene (70 ml) was added to a stirred solution of sodium hydride (80% dispersion in oil, 3.8g, 0.125mol) suspended in dry toluene (10 ml) under nitrogen atmosphere. Few drops of absolute ethanol was added to initiate the exothermic reaction. The reaction mixture was stirred for about 40hrs at ambient until no hydrogen was formed, and finally the reaction mixture was poured into crushed ice-water (100ml). The organic layer was separated and extracted with saturated sodium carbonate solution (2x50ml). The combined aqueous layer was extracted with toluene (50ml), and then the aqueous phase was acidified slowly with 5M HCl, and extracted with toluene (3x100 ml). The toluene solution was dried with $MgSO_4$, and the solvent was removed. The half esters (7) were obtained as a gum.

The crud halt esters (7) were hydrolyzed by boiling (8 hrs) with 10% (w/v) ethanolic potassium hydroxide (100 ml). On cooling, the dipotassium salt of the diacid was filtered off and washed with a small amount of cold ethanol, most of the solvent was removed from the filtrate under reduced pressure using a rotatory evaporator and the left was cooled again, a second crop of crystal of the dipotassium salt of the succinic acid was obtained and washed with a small quantity of cold alcohol, the combined potassium salts were dissolved in water (100ml), acidified slowly with 5M HCl, the liberated acids solid (8) were filtered and dried thoroughly, compound 8 was treated with acetyl chloride (100ml), and left for 30 hrs at room temperature. without exposure to UV light. After remove of the excess acetyl chloride, the residue was chromatographed on silica gel column using chloroform-petroleum ether (60-90°C) (1:1) as eluent, the photochromic fraction was collected and the solvent were removed and crystallized from n-hexane-ether to give photochromic fulgide (1) as pale yellow crystals (0.2g, 1.06%) m.p. 158-159°C. Found: C,76.29; H,7.32; N,3.83; $C_{24}H_{27}NO_3$. Required: C,76.36; H,7.21; N,3.71. $\delta_H$ (ppm): 0.82 (d,3H, J=8.5Hz, $CH_3$); 1.06 (d,3H, J=8.5Hz, $CH_3$); 1.18 (s,3H, $CH_3$); 1.96 (s,3H, $CH_3$); 2.32 (s,3H, $CH_3$); 2.66 (hepta, 1H, J=8.5Hz); 2.68(s, 3H, $CH_3$), 3.14 (s,3H,$CH_3$); 7.22-7.50(m,5H,Ar-H). m/z: 377($M^+$,45%), 362 ($M^+$-15, 10%), 238(100%).

X-ray Structure Analysis of the Title Compound (1)

Suitable single crystal for the x-ray determination were obtained by slow evaporation of a mixture of *n*-heaptane/ether solution of fulgide (1) at room temperature.

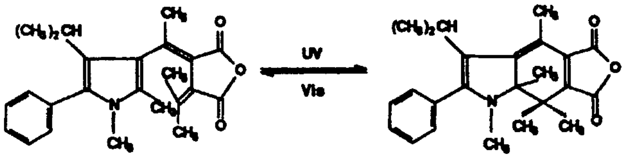
Crystal data for compound 1: $C_{24}H_{27}NO_3$, Mr=377.5, triclinic, a=10.826 (1)Å, b= 13.038(1)Å, c=8.854(1)Å, $\alpha$=109.39(1)°, $\beta$=113.65(1)°, $\gamma$=94.75 (1)°, V=1045.5 (3)$Å^3$, space group, pl, Z=2. Dx=1.151$Mgcm^{-3}$, yellow, air-stable block. Crystal dimension, 0.30x0.18x0.13 $mm^3$, $\mu$ = 5.73 $cm^{-1}$.

Data collection and processing: Enraf-Nonius CAD4 diffractometer. Scan mode $\omega/2\theta$. T=293K. Graphite monochromated CuK$\alpha$ radiation ($\lambda$=1.54178 Å) was used. 3367 reflections measured (16 <$\theta$<33°, index range, h: 0-11, k: -14-14, l:-9-9, 3079 unique (Rint=0.009), giving 2768 with I>3$\sigma$ (I).

Structure analysis and refinement: The structure was solved by direct methods using MULTAN 83 program package. Full-matrix least-squares refinement anistropically with all non-hydrogen atoms. Only coordinates of H-atoms are isotropically refined. Final R and Rw value are 0.059, 0.063. s=0.81, $(\Delta/\sigma)\max = 0.07$, $(\Delta\rho)\max=0.385$ eÅ$^{-3}$ $(\Delta\rho)\min = 0.301$ eÅ$^{-3}$. Atomic scatting factors from international tables for X-ray crystallography (1974, vol. IV).

## DISCUSSION

Black intractable oil was formed in the Stobbe condensations of 3-acetyl pyrrole with diethyl isopropylidene succinate, and the 3-pyrryl fulgide or it precursors were difficult to isolate and purify, due to the large steric hindrance of 4-isopropyl group, the yield of Stobbe condensation is fairly low. Only the *E*-form of fulgide (**1**) was obtained by column chromatography on silica gel as yellow crystal, the overall yield is much lower than for the synthesis of corresponding 3-thienyl and 3-furyl fulgides. The photochromic reaction of **1** is shown as equation (1). The colored form of **1**, 7,7a-dihydroindole derivative (**7,7a-DHI**) is thermally stable.



**(1)** **(7,7a-DHI)** (1)

The absorption $\lambda_{max}$ of **1**, and **7, 7a-DHI** in different solvents are shown in Table 1.

TABLE 1 Absorption spectra data of fulgide and its colored form.

| Solvent ($E_{T(30)}$) | $\lambda_{max}$/nm<br>**1** | <br>**7,7a-DHI** |
|---|---|---|
| Acetonitrile (46.0) | 390 | 700 |
| Dioxane (36.0) | 385 | 660 |
| Toluene (33.0) | 380 | 630 |
| Cyclohexane (31.2) | 370 | 600 |

The **7,7a-DHI** is markedly solvatochromic and shows such large bathochromic shifts as to become near infrared active. The results show that fulgide **1** possesses excellent photochromic properties in organic solvents.[15]

The molecular conformation and atomic labeling structure of **1** is shown as follows. Atomic coordinates for atoms of **1** are given in Table 2. Bond distances and bond angles of **1** are reported in Table 3.

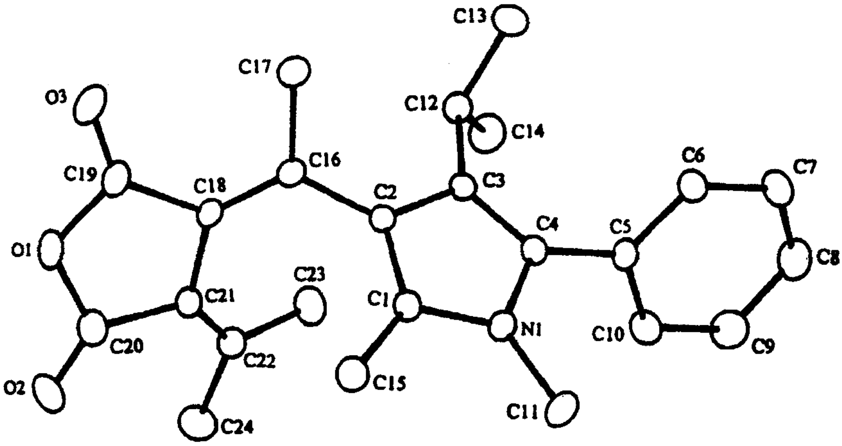


TABLE 2 Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters (Å$^2$) with e.s.d's in parentheses in an independent unit

| Atom | x | y | z | Ueq(Å$^2$) |
|---|---|---|---|---|
| O1 | 0.4088(2) | 0.1000(2) | 0.4492(3) | 4.00(5) |
| O2 | 0.3219(2) | 0.0850(2) | 0.1663(3) | 5.61(7) |
| O3 | 0.5431(2) | 0.1317(2) | 0.7367(2) | 4.45(5) |
| N1 | 0.9938(2) | 0.1408(2) | 0.4232(3) | 2.70(5) |
| C1 | 0.8765(3) | 0.1105(2) | 0.4378(3) | 2.68(6) |
| C2 | 0.8860(3) | 0.1912(2) | 0.5926(3) | 2.50(6) |
| C3 | 1.0148(3) | 0.2738(2) | 0.6761(3) | 2.54(6) |
| C4 | 1.0792(3) | 0.2408(2) | 0.5686(3) | 2.63(6) |
| C5 | 1.2106(3) | 0.2954(2) | 0.5933(3) | 2.78(7) |
| C6 | 1.3356(3) | 0.3190(3) | 0.7355(4) | 3.45(7) |
| C7 | 1.4598(3) | 0.3743(3) | 0.7551(4) | 4.14(9) |
| C8 | 1.4612(3) | 0.4028(3) | 0.6190(4) | 4.55(9) |
| C9 | 1.3387(4) | 0.3771(3) | 0.4647(4) | 4.72(9) |
| C10 | 1.2140(3) | 0.3257(3) | 0.4472(4) | 3.82(8) |
| C11 | 1.0296(3) | 0.0699(3) | 0.2878(4) | 4.06(8) |
| C12 | 1.0546(3) | 0.3842(2) | 0.8343(4) | 3.24(7) |
| C13 | 1.1678(4) | 0.3907(3) | 1.0129(4) | 4.90(1) |
| C14 | 1.0943(4) | 0.4869(3) | 0.7995(5) | 4.90(1) |
| C15 | 0.7695(3) | 0.0034(3) | 0.3056(4) | 3.96(8) |
| C16 | 0.7816(3) | 0.1882(2) | 0.6591(3) | 2.67(6) |
| C17 | 0.8346(3) | 0.1872(3) | 0.8454(3) | 3.64(8) |
| C18 | 0.6451(3) | 0.1775(2) | 0.5580(3) | 2.80(6) |
| C19 | 0.5371(3) | 0.1387(2) | 0.6031(4) | 3.48(7) |
| C20 | 0.4219(3) | 0.1169(3) | 0.3080(4) | 3.98(8) |
| C21 | 0.5672(3) | 0.1802(2) | 0.3787(3) | 3.07(7) |
| C22 | 0.6015(3) | 0.2442(3) | 0.3029(4) | 3.55(7) |
| C23 | 0.7369(4) | 0.3302(3) | 0.3959(4) | 4.54(9) |

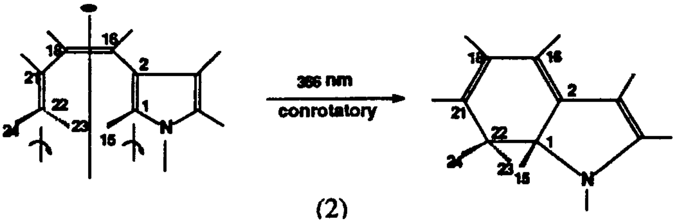
| | | | | |
|---|---|---|---|---|
| C24 | 0.5026(4) | 0.2413(3) | 0.1228(4) | 5.90(1) |

TABLE 3 Selected Bond length (Å) and angles ($^{O}$) with e.s.d's in parentheses

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|
| O1 | C19 | 1.397(3) | C5 | C10 | 1.399(5) |
| O1 | C20 | 1.397(5) | C6 | C7 | 1.388(5) |
| O2 | C20 | 1.186(3) | C7 | C8 | 1.397(7) |
| O3 | C19 | 1.193(4) | C8 | C9 | 1.380(4) |
| N1 | C1 | 1.367(4) | C9 | C10 | 1.381(5) |
| N1 | C4 | 1.394(3) | C12 | C13 | 1.533(4) |
| N1 | C11 | 1.462(4) | C12 | C14 | 1.536(5) |
| C1 | C2 | 1.381(4) | C16 | C17 | 1.520(4) |
| C1 | C15 | 1.490(3) | C16 | C18 | 1.351(4) |
| C2 | C3 | 1.431(3) | C18 | C19 | 1.481(5) |
| C2 | C16 | 1.472(5) | C18 | C21 | 1.484(4) |
| C3 | C4 | 1.374(5) | C20 | C21 | 1.484(4) |
| C3 | C12 | 1.514(3) | C21 | C22 | 1.342(5) |
| C4 | C5 | 1.473(4) | C22 | C23 | 1.494(4) |
| C5 | C6 | 1.391(5) | C22 | C24 | 1.508(5) |

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|
| C19 | O1 | C20 | 111.0(2) | C5 | C10 | C9 | 120.5(3) |
| C1 | N1 | C4 | 109.5(2) | C3 | C12 | C13 | 114.4(3) |
| C1 | N1 | C11 | 123.9(2) | C3 | C12 | C14 | 113.2(3) |
| C4 | N1 | C11 | 126.2(2) | C13 | C12 | C14 | 109.9(2) |
| N1 | C1 | C2 | 107.7(3) | C2 | C16 | C17 | 115.4(2) |
| N1 | C1 | C15 | 121.2(3) | C2 | C16 | C18 | 123.3(3) |
| C2 | C1 | C15 | 131.1(3) | C17 | C16 | C18 | 121.1(4) |
| C1 | C2 | C3 | 108.1(3) | C16 | C18 | C19 | 121.7(3) |
| C1 | C2 | C16 | 124.7(2) | C16 | C18 | C21 | 132.3(3) |
| C3 | C2 | C16 | 127.3(2) | C19 | C18 | C21 | 105.4(2) |
| C2 | C3 | C4 | 106.7(3) | O1 | C19 | O3 | 119.3(3) |
| C2 | C3 | C12 | 124.1(3) | O1 | C19 | C18 | 108.3(3) |
| C4 | C3 | C12 | 128.4(3) | O3 | C19 | C18 | 132.4(2) |
| N1 | C4 | C3 | 108.1(2) | O1 | C20 | O2 | 118.7(3) |
| N1 | C4 | C5 | 121.1(3) | O1 | C20 | C21 | 107.8(2) |
| C3 | C4 | C5 | 130.8(3) | O2 | C20 | C21 | 133.4(4) |
| C4 | C5 | C6 | 120.2(4) | C18 | C21 | C22 | 130.6(2) |
| C4 | C5 | C10 | 121.7(2) | C18 | C21 | C20 | 105.7(3) |
| C6 | C5 | C10 | 118.1(3) | C20 | C21 | C22 | 122.1(3) |
| C5 | C6 | C7 | 121.1(3) | C21 | C22 | C23 | 122.7(3) |
| C6 | C7 | C8 | 119.9(3) | C21 | C22 | C24 | 122.9(3) |
| C7 | C8 | C9 | 119.7(3) | C23 | C22 | C24 | 114.3(3) |
| C8 | C9 | C10 | 120.6(4) | | | | |

From Figure 1, Tables 2 and 3, the following points should be addressed: the molecule of **1** contains a succinic anhydride moiety linked to a substituted pyrrole fragment through the double bond (C16=C18). The crystal structure of **1** reveals that the single crystal of this pyrryl fulgide is *E*-form. Based on the coloration theory[16], the coloration of the fulgide is a model of pericyclic reaction with some electrophilic property in accordance with Woodward-Hoffmann 4n+2 selection rule, the sequence of C1=C2-C16=C18-C21=C22 involves 6π electrons, the photochemical ring closure should be a conrotatory process. The geometrical parameters obtained from the x-ray analysis show that the distance between the reactive sites, C1 and C22 atom, is 3.57Å. Near the reactive sites, the C15 methyl group is upward, C23 methyl group is downward. This configuration provides a rationalization conrotatory ring closure reaction, as shown in equation 2. When the molecule **1** undergoes this ring closure , the two portions of the molecule rotate about the C2-C16 and C18-C21 single bonds.



(2)

The bond lengths of the double bonds C16=C18 and C21=C22 are 1.351(5)Å and 1.342(5)Å respectively, which are longer than those in the *cis*-butyldiene (1.34 Å), while the bond distances of single bonds C18-C21 and C2-C16 are 1.484(4) Å and 1.472(5) Å respectively, which are much shorter than the normal bond length of single bond (1.54 Å). These facts show that π-electrons in the 4n+2π system are partially delocalized and the bonds are hybridized between single and double bonds.

The bond angles of C2-C1-C15, C16-C18-C21 and C18-C21-C22 are 131.1(3)°, 132.3(3)° and 130.6(2)° respectively, these values are quite larger than those in the hexatriene, the reason is that, there exists a strong steric interaction (*i.e.* chemical repulsion) between the methyl group (C15) in the pyrryl moiety and the isopropylidene group (C23-C22-C24 unit) in the succinic anhydride moiety, the result is similar to that of in the 3-thienyl and 3-furyl fulgides.

The succinic anhydride moiety is not coplanar with pyrryl moiety, two planes are twisted and the dihedral angle is 128.61(2)°, the torsional angles of C1-C2-C16-C18 unit and C16-C18-C21-C22 unit are -54.13(2)° and -38.27(3)° respectively. While the torsional angle of C19-C18-C21-C20 unit is -13.80(3)°, which indicates that the succinic anhydride moiety deviates slightly from the planar structure. However, the torsional angle of the C1-C2-C3-C4 unit and C2-C3-C4-N1 unit are 0.26° and -0.14° respectively, showing that the planar structure is retained in the pyrryl moiety. The phenyl moiety linked with pyrryl fragment by C4-C5, the dihedral angle between these two planes is 122.86(3)°. In other words, the phenyl and pyrryl ring are not coplanar with each other. These results indicate that compound 1 has a twisted structure between phenyl, pyrryl and the succinic anhydride moiety.

## CONCLUSION

We have synthesized a new pyrryl substituted heterocyclic fulgides, its structure was identified. The x-ray crystal analysis of 1 shows that compound 1 has a considerable twisted configuration between phenyl, pyrryl moiety and succinic anhydride moiety. The distance between two reactive sites C1 and C22 atoms (for the forming of the σ-bond during the ring closure reaction) is 3.57Å, which is favorable for the controtatory intramolecular photocyclization. This is the reason why the title compound showing excellent photochromic properties.

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