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Photobehavior of Crystalline 4-Styrylcoumarin Dimorphs: Structure-Reactivity Correlations

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4-Styrylcoumarin crystallizes from chloroform and hexane mixture in two morphologically different modifications. The monoclinic form (needles, $P2_1/c$) undergoes stereospecific photodimerization producing anti head-to-tail dimer across pyrone double bond, whereas the triclinic modification (prisms, $P\bar{1}$) dimerizes yielding photodimer of the same configuration, but across styrenic double bond. Single crystal X-ray analyses of the dimorphs reveal the packing differences permitting rationalization of the regio- and stereochemistry of the photoproducts. The significantly low dimer yield from the prismatic crystals is rationalized.

While several routine chemical reactions in solid state have been reported in recent years,[1—4] a great deal of research activity in solid state organic chemistry is concerned with [2+2] photocycloaddition.[5—8] The correspondence between the molecular packing in the reactant crystal and steric configuration of the product has been well-established from the pioneering work of Schmidt and co-workers.[9—11] It is well-known that the photodimer is mirror symmetric, when the precursor monomer crystals are identified by a short axis of ≤ 4.2 Å (β-packed).[9—11] However, such predictions as regards to the crystals which produce centrosymmetric photodimers still await a long term systematic investigations.

In continuation of our studies on structure-reactivity correlations and crystal engineering aspects,[12—14] we embarked upon a systematic investigation on photoreactivity of a series of 4-styrylcoumarin derivatives in the crystalline state. During the course of our study aimed at gaining more insights and deducing certain generalities with respect to α-packed crystal structures, the parent 4-styrylcoumarin (**I**) was found interestingly to crystallize, under identical experimental conditions, in two photoreactive crystalline modifications. The existence of two or more crystal forms, the so-called phenomenon of polymorphism, is wide spread.[15] Indeed, the classic experiments of Cohen and Schmidt on cinnamic acids to demonstrate the topochemical principles were based on the existence of polymorphism.[9—11] The polymorphs may differ among themselves in their properties such as melting point, density, hardness, and crystal packing. There are innumerable examples where subtle variations in the conformations of the constituent molecules are noted.[15]

The ultimate goal in studying the correlation between property and molecular packing is to be able to utilize the knowledge of crystal packing in order to design the materials with desired properties. With the molecular moiety being invariant, the polymorphs offer the unique opportunity of studying the cause and consequences of the differences in a considered property. Indeed, manifestation of the differences between the polymorphic modifications in the photoreactivity of certain reactions such as Norrish type I, type II and photodimerizations[9—11,16] have been reported. Recently, the optical purity of Norrish Type II product has been shown to depend on the crystalline modification photolyzed.[17] Herein, we report on the differences in photoreactivity of the dimophs of 4-styrylcoumarin (**I**) yielding regioisomeric stereospecific dimers as exemplified from their crystal structures.

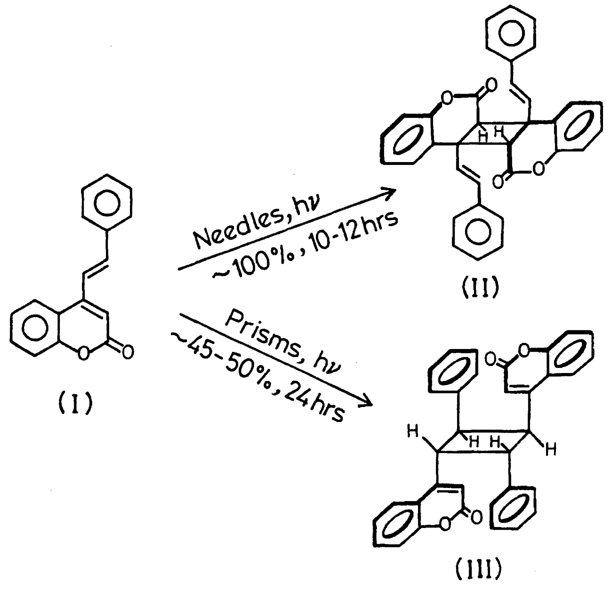
Results and Discussion

Recrystallization of **I** from chloroform and hexane (1 : 3) mixture produced a crop of needle shaped as well as prism shaped crystals of same melting point (141°). 4-Styrylcoumarin (**I**) has two potentially reactive double bonds (pyrone C(3)=C(4) and styrenic C(11)=C(12)) and, hence, may form any of eight possible dimers. The photodimers, in principle, can adopt any one of four configurations: *syn* head-to-head, *syn* head-to-tail, *anti* head-to-head, and *anti* head-to-tail. Direct ultraviolet irradiation ($\lambda \geq 320$ nm) in solid state of the dimorphs leads to regiochemically distinct and configurationally identical stereospecific *anti* head-to-tail dimers (**II** and **III**). Whereas the needles photodimerize across pyrone double bond in cent percent yield (from ^{1}H NMR integrations), the prismatic crystals undergo photodimerization across styrenic double bond in isolable ca. 45% yield (Scheme 1). The configurational assignment of the dimers was done based on the comparison of spectral characteristics of related coumarin dimers[12,18] and analogous derivatives.[19] The significantly low percent conversion (ca. 45%) of prisms when compared to that of needles was an intriguing observation. In order to provide a rationale for the lower yield in the case of prisms and the stereochemistry of the dimers in terms of crystal packing, the detailed crystallographic analyses of both the morphologically different forms (prisms and needles) were undertaken.

The two modifications correspond to two different crystal systems, namely triclinic (prisms) and monoclinic (needles). The crystallographic data are presented in Table 1 and the details of structure analyses are discussed in Experimental section. There are two molecules in the asymmetric unit cell of triclinic

Table 1. Crystal Data for the Dimorphic Prisms and Needles

Compound	Prisms	Needles
Mol. formula	$C_{17}H_{12}O_2$	$C_{17}H_{12}O_2$
M_r	248	248
Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a/Å	11.082(2)	13.418(4)
b/Å	11.215(3)	5.720(4)
c/Å	12.127(3)	17.840(3)
α/°	102.35(2)	
β/°	116.41(2)	110.79(2)
γ/° 98.62(2)		
V/Å^3	1265.9(6)	1280.1(10)
Z	4	4
D_m/Mg m^{-3}	1.299	1.290
D_x/Mg m^{-3}	1.303	1.288
Radiation used	Cu $K\alpha$	Mo $K\alpha$
λ/Å	1.5418	0.7107
μ/cm^{-1}	6.40	0.78
F(000)	520	520
Crystal size/mm	0.3×0.35×0.1	0.4×0.15×0.1
θ limit/°	65	25
Mode of data collection	$\omega/2\theta$	$\omega/2\theta$
No. of intensity controls	3	3
No. of observed reflections ($\lvert F_o\rvert \geq 3\sigma(\lvert F_o\rvert)$)	3022	1228
Final R	0.063	0.094
Final R_w	0.063	0.10
Weighting function (w)	1.00	$1.0/(\sigma^2(F)+0.000628\lvert F\rvert^2)$
Residual electron density/e Å^{-3}	0.28	0.33
No. of variables	439	439



Scheme 1.

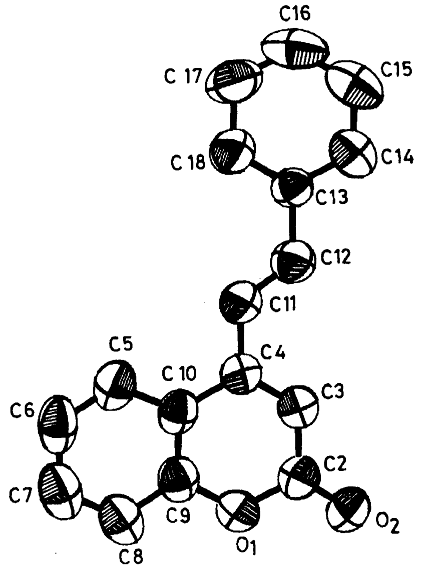


Fig. 1. A perspective view of the molecule with atomic numbering scheme and the thermal ellipsoids at 50% probability level.

modification and are designated A and B. The final positional coordinates of non-hydrogen atoms of prisms and needles are given in Tables 2 and 3, respectively. Bond lengths and bond angles are recorded in Tables 4 and 5, respectively. The perspective view with atomic numbering scheme is shown in Fig. 1. The stereoscopic packing diagrams of prisms and needles are depicted in Figs. 2 and 3, respectively.

Structure-Reactivity Correlations

Ideally, in a lattice-controlled topochemical photodimerization, overlap of the π-orbitals of the reactive partners should be favorable before the reaction

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\times 10^3$) for Non-Hydrogen Atoms of 4-Styrylcoumarin (prisms, $P\bar{1}$)
esd's are given in parentheses. The temperature factor is of the form: $U_{\text{eq}}=1/3\sum_i\sum_j U_{ij}\, a_i^*\, a_j^*\, \boldsymbol{a}_i\cdot\boldsymbol{a}_j$

Atom	x	y	z	$U_{\text{eq}}/\text{Å}^2$
Molecule A				
O(1)	2498(3)	9054(3)	2104(2)	69(1)
O(2)	679(3)	7356(3)	1123(3)	82(1)
C(2)	1412(4)	8260(4)	2091(4)	65(2)
C(3)	1271(4)	8579(4)	3228(4)	63(2)
C(4)	2157(4)	9583(3)	4285(3)	58(2)
C(5)	4245(5)	11516(4)	5255(4)	70(2)
C(6)	5282(5)	12224(4)	5153(5)	83(3)
C(7)	5388(5)	11878(5)	4056(6)	85(3)
C(8)	4443(5)	10818(5)	3043(5)	76(3)
C(9)	3398(4)	10113(4)	3160(4)	62(2)
C(10)	3260(4)	10419(3)	4251(4)	58(2)
C(11)	2072(4)	9824(4)	5470(4)	67(2)
C(12)	1207(5)	9100(4)	5677(4)	67(2)
C(13)	1150(4)	9292(3)	6890(3)	57(2)
C(14)	12(5)	8597(4)	6882(5)	73(3)
C(15)	−70(6)	8738(5)	7990(6)	91(3)
C(16)	1003(8)	9569(6)	9142(6)	100(4)
C(17)	2167(8)	10255(5)	9182(5)	106(4)
C(18)	2245(5)	10130(4)	8058(4)	82(3)
Molecule B				
O(1)	3944(2)	3167(2)	8092(2)	60(1)
O(2)	1801(3)	3249(3)	6890(2)	73(2)
C(2)	2693(4)	3340(3)	7970(3)	56(2)
C(3)	2568(4)	3584(4)	9116(3)	56(2)
C(4)	3594(3)	3637(3)	10288(3)	51(2)
C(5)	6044(4)	3422(4)	11517(4)	61(2)
C(6)	7223(4)	3191(4)	11506(4)	73(2)
C(7)	7309(4)	2971(4)	10386(4)	71(2)
C(8)	6198(4)	2967(4)	9261(4)	63(2)
C(9)	5014(4)	3188(3)	9264(3)	54(2)
C(10)	4890(3)	3412(3)	10374(3)	51(2)
C(11)	3420(4)	3867(4)	11434(4)	59(2)
C(12)	2438(4)	4292(4)	11555(4)	57(2)
C(13)	2219(3)	4526(3)	12680(3)	49(2)
C(14)	1172(4)	5063(4)	12656(4)	62(2)
C(15)	926(4)	5281(4)	13700(4)	69(2)
C(16)	1732(4)	4964(4)	14773(4)	68(2)
C(17)	2781(4)	4431(4)	14816(4)	69(2)
C(18)	3036(4)	4228(4)	13785(4)	60(2)

Table 3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\times 10^3$) for Non-Hydrogen Atoms of 4-Styrylcoumarin (needles, $P2_1/c$)
esd's are given in parentheses. The temperature factor is of the form: $U_{\text{eq}}=1/3\sum_i\sum_j U_{ij}\, a_i^*\, a_j^*\, \boldsymbol{a}_i\cdot\boldsymbol{a}_j$

Atom	x	y	z	$U_{\text{eq}}/\text{Å}^2$
O(1)	190(4)	413(10)	8617(3)	62(2)
O(2)	−678(4)	3396(10)	8848(3)	70(2)
C(2)	55(5)	2060(14)	9121(4)	54(3)
C(3)	831(5)	2123(15)	9930(4)	53(3)
C(4)	1638(5)	0521(13)	10201(4)	47(3)
C(5)	2476(5)	−3094(14)	9846(5)	57(3)
C(6)	2511(7)	−4679(18)	9289(6)	73(4)
C(7)	1798(7)	−4578(18)	8511(6)	78(4)
C(8)	1030(7)	−2831(17)	8298(5)	71(4)
C(9)	989(5)	−1269(14)	8869(4)	54(3)
C(10)	1724(5)	−1274(14)	9654(4)	47(3)
C(11)	2422(5)	689(15)	11023(4)	57(3)
C(12)	2540(5)	2429(15)	11513(4)	54(3)
C(13)	3304(5)	2650(13)	12333(4)	51(3)
C(14)	3232(6)	4564(16)	12784(5)	64(3)
C(15)	3921(6)	4834(17)	13562(5)	68(4)
C(16)	4694(6)	3161(15)	13907(4)	61(3)
C(17)	4772(6)	1272(16)	13471(4)	63(3)
C(18)	4103(5)	987(14)	12689(4)	53(3)

Table 4. Bond Distances Involving Non-Hydrogen Atoms of 4-Styrylcoumarin Dimorphs with esd's in Parentheses

Atoms	$P\bar{1}$, Distance/Å Molecule A	$P\bar{1}$, Distance/Å Molecule B	$P2_1/c$, Distance/Å
O(1)–C(2)	1.377(6)	1.375(5)	1.358(9)
O(1)–C(9)	1.380(5)	1.380(4)	1.391(9)
O(2)–C(2)	1.209(5)	1.210(4)	1.204(9)
C(2)–C(3)	1.432(6)	1.430(5)	1.450(10)
C(3)–C(4)	1.344(5)	1.350(5)	1.369(11)
C(4)–C(10)	1.447(6)	1.457(5)	1.449(10)
C(4)–C(11)	1.452(6)	1.461(6)	1.474(10)
C(5)–C(6)	1.364(8)	1.375(7)	1.358(13)
C(5)–C(10)	1.401(6)	1.403(5)	1.405(11)
C(6)–C(7)	1.366(8)	1.376(6)	1.379(14)
C(7)–C(8)	1.370(8)	1.371(6)	1.388(14)
C(8)–C(9)	1.381(8)	1.373(7)	1.371(12)
C(9)–C(10)	1.376(6)	1.387(5)	1.398(10)
C(11)–C(12)	1.307(7)	1.304(7)	1.297(11)
C(12)–C(13)	1.472(6)	1.466(6)	1.464(10)
C(13)–C(14)	1.374(7)	1.377(6)	1.382(11)
C(13)–C(18)	1.386(6)	1.389(5)	1.405(10)
C(14)–C(15)	1.364(9)	1.390(6)	1.376(12)
C(15)–C(16)	1.367(9)	1.370(6)	1.385(12)
C(16)–C(17)	1.374(12)	1.371(7)	1.357(12)
C(17)–C(18)	1.383(8)	1.381(6)	1.375(10)

occurs. If we define θ_1 as the rotation of one of the double bonds with respect to the other, θ_2 as the angle of parallelogram formed by the atoms of the double bonds C(3), C(4), C(4′), and C(3′) and θ_3 as a measure of the angle between the least-squares planes through the atoms C(2), C(3), C(4), and C(10) and C(3), C(4), C(4′) and C(3′), their ideal values should be 0, 90, and 90°, respectively (Fig. 4). The displacement of the reactive partners, d, should be 0 Å. These geometric parameters θ_1, θ_2, θ_3, and d quantitatively speak of relative orientation and hence the mutual overlap of π-orbitals of the reactive double bonds. In prisms belonging to triclinic modification, the distance of separation between the styrenic double bonds (C11=C12) of molecule B and its centrosymmetric partner B′ is 3.74 Å with θ_1=0°, θ_2=74°, θ_3=87° and d=0.2 Å being close

Table 5. Bond Angles Involving Non-Hydrogen Atoms of 4-Styrylcoumarin Dimorphs with esd's in Parentheses

Atoms	$P\bar{1}$, Angle/° Molecule A	Molecule B	$P2_1/c$, Angle/°
C(2)-O(1)-C(9)	121.4(3)	121.2(3)	122.3(6)
O(1)-C(2)-C(2)	116.6(4)	116.0(3)	117.0(7)
O(1)-C(2)-C(3)	116.9(4)	117.2(3)	117.3(6)
O(2)-C(2)-C(3)	126.5(4)	126.8(4)	125.6(7)
C(2)-C(3)-C(4)	123.0(4)	123.7(4)	122.2(7)
C(3)-C(4)-C(10)	118.7(4)	117.6(3)	118.6(7)
C(3)-C(4)-C(11)	122.1(4)	122.2(4)	120.2(7)
C(10)-C(4)-C(11)	119.2(4)	120.1(3)	121.1(6)
C(6)-C(5)-C(10)	121.6(5)	120.4(4)	121.6(8)
C(5)-C(6)-C(7)	120.5(5)	120.9(4)	121.1(9)
C(6)-C(7)-C(8)	120.0(6)	119.6(4)	119.2(9)
C(7)-C(8)-C(9)	118.7(5)	119.7(4)	119.2(8)
O(1)-C(9)-C(8)	115.2(4)	116.1(3)	116.1(7)
O(1)-C(9)-C(10)	121.6(4)	121.7(3)	120.9(6)
C(8)-C(9)-C(10)	123.2(4)	122.2(4)	122.9(7)
C(4)-C(10)-C(5)	125.7(4)	124.4(3)	125.6(7)
C(4)-C(10)-C(9)	118.4(4)	118.5(3)	118.5(7)
C(5)-C(10)-C(9)	115.9(4)	117.1(3)	115.9(7)
C(4)-C(11)-C(12)	126.0(4)	126.3(4)	126.5(7)
C(11)-C(12)-C(13)	126.9(4)	128.0(4)	127.9(7)
C(12)-C(13)-C(14)	119.7(4)	119.5(4)	118.8(7)
C(12)-C(13)-C(18)	121.4(4)	122.4(4)	123.0(7)
C(14)-C(13)-C(18)	118.9(4)	118.1(4)	118.2(7)
C(13)-C(14)-C(15)	121.3(5)	120.9(4)	121.0(8)
C(14)-C(15)-C(16)	120.0(6)	120.0(4)	120.0(8)
C(15)-C(16)-C(17)	119.8(7)	120.0(4)	119.6(8)
C(16)-C(17)-C(18)	120.4(6)	120.0(4)	121.4(7)
C(13)-C(18)-C(17)	119.6(5)	121.0(4)	119.8(7)

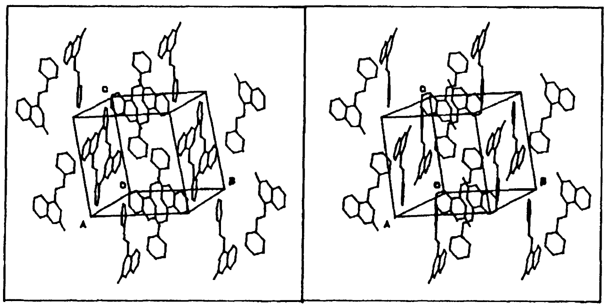


Fig. 2. Stereoscopic drawing of the packing of molecules in the triclinic modification.

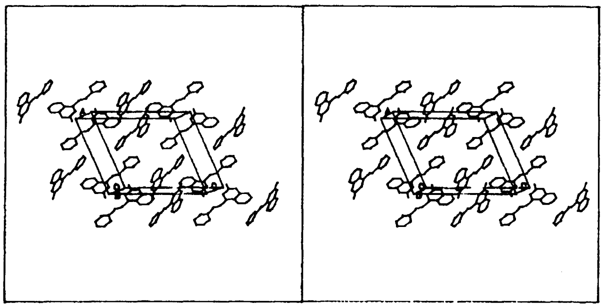


Fig. 3. Stereoscopic drawing of the packing of molecules in the monoclinic modification.

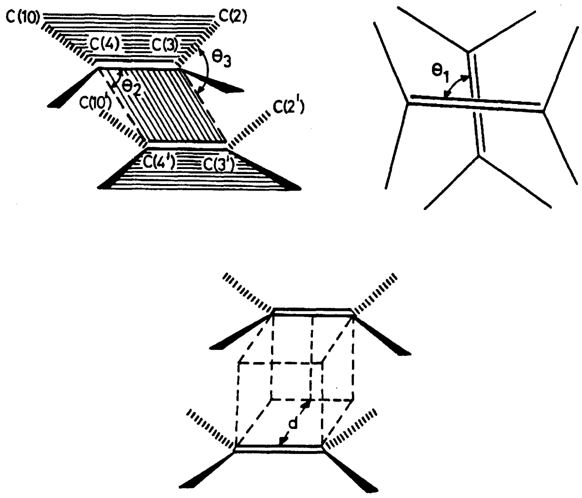


Fig. 4. Geometrical parameters used in the relative representation of the double bonds.

to the ideal values. These values show that the reacting molecules need undergo considerable motion before cyclodimerization ensues. Indeed, it has been noted that in most of the photoreactive compounds, the ideal geometrical conditions are seldom realized. These observations emphasize the fact that there must exist sufficient cavity volume in the crystal lattice permitting the required rotational and translational motions in order to achieve overlap of the orbitals upon excitation. The pyrone double bonds of molecule A and its centrosymmetric partner A′ are juxtaposed at a distance of 4.55 Å, marginally higher than the threshold of ca. 4.2 Å for facile photodimerization. The geometrical parameters $\theta_1=0°$, $\theta_2=52°$, $\theta_3=76°$, and $d=2.8$ Å, however, show that the double bonds are very much off-set from attaining the ideal values. Therefore, dimerization involving styrenic double bond of molecule B and B′ is favored as the π-lobes are better juxtaposed than the pyrone double bonds of A and A′. There are a few cases where the reaction has been observed despite as large center-to-center double bond distance as 4.6 Å,[20] as also a case with unfavorable orientation of reactants.[21,22] The formation of one kind of photodimer in the lattice may facilitate or prohibit the formation of the other. We have reported a case where the formation of nontopochemical dimer is promoted by topochemical dimerization.[23] In the triclinic modification discussed above, the molecular motions during the photodimerization process of the more favorably juxtaposed reactants B seem to hinder the necessary rotational and translational displacements of the less favorably juxtaposed molecule A for dimerization to ensue. This could be a reason for the lower yield of the photodimer in this modification.

The reactivity of the monoclinic modification follows directly from topochemical considerations (Fig. 3), reaction proceeding fast and yielding 100% in about 10 h of irradiation. The pyrone double bonds (C3=C4)

Table 6. Selected Torsion Angles with Their esd's in Parentheses

Atoms	Prisms, $P\bar{1}$ Molecule A (Angle/°)	B	Needles $P2_1/c$ (Angle/°)
C(3)–C(4)–C(11)–C(12)	−14.7(7)	3.3(7)	−10.7(12)
C(10)–C(4)–C(11)–C(12)	167.4(4)	−174.4(5)	167.0(8)
C(4)–C(11)–C(12)–C(13)	179.5(4)	176.7(4)	179.6(7)
C(11)–C(12)–C(13)–C(14)	175.5(5)	167.0(5)	−173.9(8)
C(11)–C(12)–C(13)–C(18)	−4.3(7)	−15.3(7)	5.3(12)

of the centrosymmetrically related pairs are well juxtaposed ($\theta_1=0°$, $\theta_2=70°$, $\theta_3=75°$, and $d=0.96$ Å) and are at a distance of 3.57 Å.

There are no notable differences in the conformations of 4-styrylcoumarin in both the modifications. The torsion angles of relevance are given in Table 6. However, crystallization of the two forms from the same experimental set up, as noted earlier, is suggestive of their near energetic equivalence, despite apparent significant difference in their packing motifs. According to Bernstein, the polymorphic modifications differ in their van der Waals interaction energies only by 1—2 kcal mol^{-1}.[15] From the observation that the chances of obtaining triclinic crystals were more from a number of crystallization experiments with varying degrees of saturation and different solvent compositions, we believe that the triclinic prisms are thermodynamically more stable than the monoclinic needles. It should be mentioned that the differential scanning calorimetric experiments for both the modifications showed no evidence of phase transition.

C–H···O type of bonding in crystals has been recognized recently as one of the important interactions in determining the molecular packing.[24] In the crystal structures of triclinic and monoclinic modifications, there are 15 and 5 short contacts respectively involving C, H, and O atoms in a distance range of C···O≤4.0 Å with O···H distances ranging from 2.5 to 3.0 Å. The triclinic crystals appear to derive the extra stabilization from these weak but important C–H···O interactions.

Conclusions

Many cases involving the photodimerization of polymorphs leading to dimers of different configuration, but of same reaction site are known. To our knowledge, this appears to be the first illustrative example of dimorphs of a molecule endowed with two reaction sites producing regiochemically different photodimers in a stereospecific fashion.

Experimental

4-Styrylcoumarin (**I**) was synthesized by condensing coumarin-4-acetic acid with benzaldehyde in presence of piperidine.[25] Crystallization from chloroform and hexane (1 : 3) mixture yielded a crop of both prisms and needles which could be easily separated. The samples were powdered and irradiated in a Rayonet photochemical reactor ($\lambda \geq 320$ nm) at room temperature. Both the dimers **II** and **III** were isolated as insoluble white powders from ethanolic solutions of irradiated mixtures. The progress of reaction in the case of needles was monitored by ^{1}H NMR spectroscopy. Since the irradiated mixture of prisms posed solubility problem, the sample was irradiated for 24 h and the photodimer was filtered as a white solid from ethanolic solution. The isolated yield was 45%.

X-Ray Structural Analysis and Refinement. Single crystals of both prisms and needles suitable for X-ray diffraction studies were obtained from chloroform–hexane (1 : 3) mixture by slow evaporation at room temperature. Since the single crystals of needles were long, they were cut and used for X-ray structural studies. The three dimensional intensity data for both the modifications were collected on an Enraf–Nonius CAD-4 diffractometer. The intensity of the three standard reflections measured in both the cases after every 3600 seconds of exposure showed only statistical variations. Corrections were applied for Lorentz and polarization factors and not for absorption. The structure in the case of prisms was solved by using the direct methods program SHELXS 86.[26] The program with default parameters revealed the positions corresponding to all the atoms of two molecules A and B in the asymmetric unit cell. In the case of needles, molecular replacement methodology was used. Patterson search using the structure obtained from triclinic modification as a known fragment with PATSEE routine which is an integrated part of SHELXS 86 furnished all the non-hydrogen atoms. SHELX 76[27] was used for full-matrix least-squares refinement. The positions of hydrogen atoms in both the cases were located from successive difference Fourier maps and were refined for a few cycles. The final difference Fourier maps were featureless. The crystal data and details of refinement are provided in Table 1. Tables of anisotropic thermal parameters of non-hydrogen atoms, fractional coordinates and isotropic thermal parameters of hydrogens bond lengths and angles involving hydrogens, and the complete F_o-F_c data are deposited as Document No. 66047 at the office of the Editor of Bull. Chem. Soc. Jpn.

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