

SOLID-STATE PHOTODIMERIZATION OF COUMARIN
IN THE PRESENCE OF A CRYSTAL LATTICE-CONTROLLING SUBSTANCE

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Abstract - Coumarin, which is known to be photostable in the solid state, underwent photochemical dimerization when admixing a crystal lattice-controlling substance, such as antipyrine and phenanthrene to coumarin to form a mixed crystal. The IR, UV, fluorescence and powder X-ray spectra of the mixed crystals between coumarin and crystal lattice-controlling substances were compared with those of pure coumarin crystal, suggesting that the packing mode of the coumarin crystal has changed by admixing.

In contrast to in gaseous and liquid states, molecules in solid state show little motion, little rotation and no collision to each other. Thus the chemical reactions in the solid state are mainly controlled by the packing arrangement of the molecules in the crystal-line state. It has been found that different products or different product distribution is obtained for many photoreactions in solid state compared with those in solution.¹ Therefore it appeared significant to broaden our knowledge on the role of crystal packing in their solid state photoreactivity.

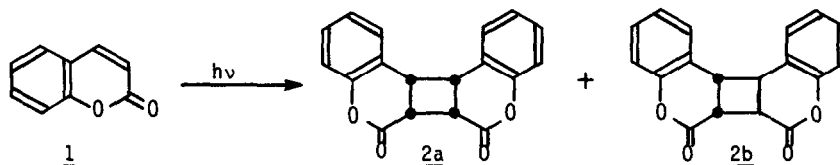
The reactions of cinnamic acids in the crystalline state are well-known example of [2 + 2] photodimerization and the studies by Schmidt and his coworkers have established a correlation between molecular alignment in the reactant crystal and steric configuration of the products.² Schmidt has drawn attention to the fact that photocycloaddition occurs not only when the distance between the double bonds of the reacting cinnamic acid molecules is within about 4.2 Å but also when they are aligned parallel. Recently, there have been great interests in organic reactions in the crystalline state and many such reactions have been studied from the synthetic and mechanistic points of view.³ The utility of such photoreactions as a synthetic tool is limited by the difficulty of achieving the desired type of crystal structure in any given case, since the factors controlling crystal packing are still not fully understood. The reported approaches to "crystal engineering", i.e., controlling packing geometry, have included introduction of Cl...Cl interactions into the crystal structure of aromatic compounds,⁴ complexation with a foreign molecules,⁵ introduction of a substituent into the molecule,⁶ and the strategy involving the strong tendency for oxygen or carbonyl group of esters to pack over the center of the benzene ring of a neighboring molecule.^{2b}

In order to examine factors which affect the molecular packing arrangement, we have studied on the photochemical dimerization of coumarin in the mixed crystal state with several foreign molecules. Coumarin is known to be photostable in the solid state although it readily dimerizes in solution.⁷ However, coumarin photodimerizes in the solid state when it forms a complex with mercuric chloride⁵ and some substituted coumarins are known to photodimerize in the solid states.^{6b} Therefore, our approach appears to be a good molecular framework to study the role of foreign substances in bringing about the preferred molecular packing for photodimerization.

Results and Discussion

Compounds such as antipyrine, phenanthrene, 6-cyano-1,3-dimethyluracil, 5-bromo-1,3-dimethyluracil and 5-iodo-1,3-dimethyluracil were found to modify the crystal of coumarin toward the occurrence of photoreactivity. The mixed crystals were obtained by the resolidification of melted mixtures of coumarin (1) and foreign compounds in certain molecular ratios and irradiated with a high-pressure mercury lamp. The results including reaction conditions and product yields are listed in Table 1. Two known coumarin [2 + 2] photodimers, 2a and 2b, were the only products isolated in these cases. In most cases the syn head-to-head dimer 2a was the sole product, while the mixed crystal with 5-iodo-1,3-dimethyluracil gave anti head-to-head dimer 2b. Similar irradiation of a ternary mixed crystal of coumarin and 5-bromo- and 5-iodo-1,3-dimethyluracil (ratio, 1.7 : 2 : 1) gave a mixture of 2a and 2b (run 7). For the photodimerization of coumarin in solution, syn head-to-head dimer 2a has been reported to be formed from a singlet excited state and anti head-to-head dimer 2b from a triplet excited state.⁷ The quantum yield of the formation of the latter anti dimer 2b has been shown to increase in a heavy atom solvent such as propyl bromide.^{7b} Although the iodine atom of 5-iodo-1,3-dimethyluracil in the mixed crystal may be considered to cause the heavy atom effect to give the coumarin triplet which leads to the anti head-to-head dimer 2b, other interpretations may be operative (see below).

The results of Table 1 indicate that coumarin crystals became photoreactive to form the photodimers in the cocrystallization with various types of compounds. These foreign compounds are now designated as "crystal lattice-controlling substances. We found, however, that any foreign compounds do not always effect the appearance of photoreactivity to coumarin in the crystalline state. Among tested foreign compounds, naphthalene, 1,4-dimethoxybenzene and 1,4-dichlorobenzene showed no effect. The appearance of photoreactivity in the mixed crystals of coumarin with these crystals lattice-controlling



substances is most probably due to a change of packing mode of coumarin in the crystalline state.

Table 1. Photodimerization of coumarin (1) in the presence of crystal lattice-controlling substances in the solid state.

Run	Crystal lattice-controlling substance (Molar ratio to coumarin) [M.p., °C]	Irradn. time (h) ^a	Product	Isolated yield, % (Yield based on the reacted coumarin, %)
1	Antipyrine (1/3) [110-113]	80 ^b	syn dimer <u>2a</u>	6.8 (d)
2	Antipyrine (1/3)	35	syn dimer <u>2a</u>	10.0 (88)
3	Phenanthrene (1/3) [99]	35	syn dimer <u>2a</u>	3.4 (75)
4	6-Cyano-1,3-dimethyluracil (1/3)[167]	35	syn dimer <u>2a</u>	9.1 (80)
5	5-Bromo-1,3-dimethyluracil (1/3)[180-184]	35	syn dimer <u>2a</u>	5.8 (64)
6	5-Iodo-1,3-dimethyluracil (1/3) [230]	35	anti dimer <u>2b</u>	7.1 (69)
7	2 : 1 mixture of 5-bromo and 5-iodo-1,3-dimethyluracils (3/1.7)	{ 35 35	syn dimer <u>2a</u> anti dimer <u>2b</u>	6.5 (d) 5.2 (d)

^a For the irradiation conditions see Experimental.

^b In this case irradiation was carried out with a 15 W low-pressure mercury lamp.

^c A trace of the anti dimer 2b was detected by TLC analysis.

^d Not determined.

To obtain further informations on the nature of the change of the packing mode in the mixed crystals,⁵ we carried out the spectral examination of the mixed crystals. All the IR spectra of the mixed crystals obtained from the resolidification of melted mixtures of coumarin and the crystal lattice-controlling substances are virtually the same as those of their mechanical mixtures with the same molecular ratio. We found no shift of any absorption, except slight changes in the intensity of some absorption peaks. The result suggests that no strong interaction occurs between coumarin and these crystal lattice-controlling substances in their mixed crystals.

Next, we measured the UV and fluorescence spectra of the mixed crystals in the solid state. Figure 1A and Figure 2 show the UV and fluorescence spectra, respectively, of the coumarin-antipyrine mixed crystal of 1 : 1 molar ratio. It can be seen from Figure 1A that the absorption of coumarin at about 350 nm (shoulder) for the mixed crystal is stronger than that for a simple mechanical mixture of coumarin and antipyrine crystals. Figure 2 shows that the fine structure of the fluorescence spectrum of antipyrine in the solid state disappeared in that of the mixed crystal. These results suggest that some weak interaction occurs between coumarin and antipyrine molecules in the mixed crystal, implying a change of the packing arrangement of coumarin molecules. As seen in Figure 1B, however, there is an increment of the coumarin absorption (ca. 350 nm) of the mixed crystal between coumarin and 1,4-dichlorobenzene as compared with that of the simple mechanical mixture of their crystals. A similar spectral behavior was also observed for the solid-state UV spectrum of the coumarin crystal mixed with other ineffective substances such as 1,4-dimethoxybenzene and naphthalene, indicating that

weak interaction occurs between coumarin and a foreign substance in their mixed crystal.

The change of the packing geometry of coumarin during the formation of the mixed crystals with the crystal lattice-controlling substances was directly demonstrated by X-ray powder analysis. Figure 3 shows the X-ray powder diffraction spectra of coumarin crystal, antipyrine crystal and their mixed crystal. A new phase was obviously formed indicating that the packing arrangement of the original coumarin crystal is reduced in the mixed crystal. Thus, while the main diffraction peaks of antipyrine, 11.6° , 19.9° , 23.4° and 30.2° remains in the mixed crystal, the peaks of coumarin, 15.8° , 16.5° , 19.2° , 19.9° , 22.8° , 31.4° and 36.3° , become very weak and the peaks for a new crystal packing arrangement, 13.2° , 21.5° and 28.5° , are observed.

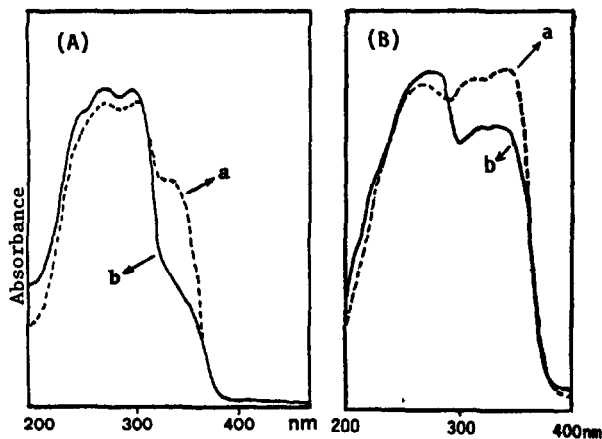


Figure 1. UV spectra in the solid state. (A) Coumarin and antipyrine; (B) coumarin and 1,4-dichlorobenzene. (a) 1 : 1 Mixed crystal; (b) 1 : 1 mechanical mixture.

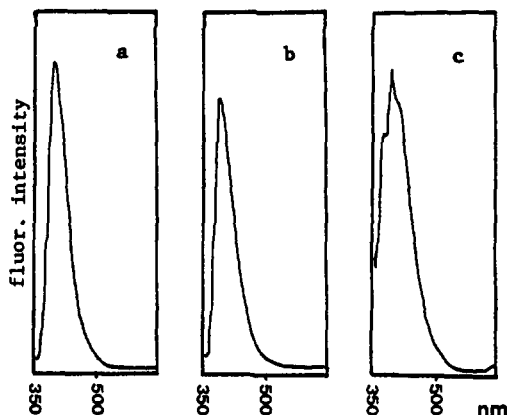


Figure 2. Fluorescence spectra in the solid state. (a) Coumarin; (b) mixed crystal of coumarin and antipyrine; (c) antipyrine.

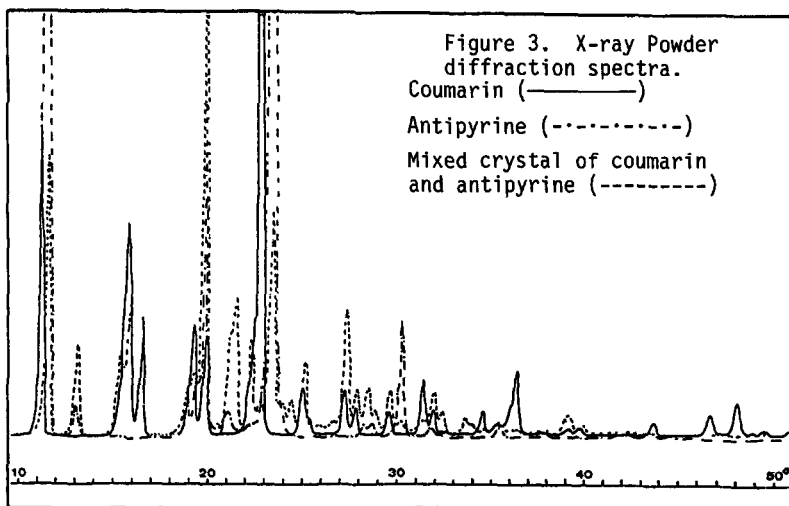


Figure 3. X-ray Powder diffraction spectra. Coumarin (—) Antipyrine (· · · · ·) Mixed crystal of coumarin and antipyrine (— — — — —)

Table 2. New peaks of the X-ray powder diffraction spectra of the mixed crystals between coumarin and crystal lattice-controlling substances in the molar ratio of 1 : 1.

Crystal lattice-controlling substance	New peaks (°)					
Antipyrine	13.2	21.5	28.5			
Phenanthrene	17.7	20.8	21.8	25.5	26.2	
6-Cyano-1,3-dimethyluracil	17.2					
5-Bromo-1,3-dimethyluracil	16.3	21.2	24.3	29.4		
5-Iodo-1,3-dimethyluracil	23.4	24.5	31.8	32.6	34.2	
Ineffective substance:						
1,4-Dichlorobenzene	22.5	27.5	29.9	30.7	31.6	32.2
1,4-Dimethoxybenzene	22.4	24.3	28.1	28.2	28.4	
Naphthalene	22.4	22.6				

Table 3. Dependence of the substrate ratio upon the yield of the photodimerization of coumarin in the mixed crystal with antipyrine.^a

Molar ratio (antipyrine : coumarin)	2 : 1	1 : 1	1 : 2	1 : 3	1 : 4	1 : 5	1 : 6
% Yield of coumarin photodimer <u>2a</u>	3.5	5.0	7.5	10.0	8.5	6.5	4.0

^a For the reaction conditions see Experimental.

Similar results were obtained for the UV, fluorescence and X-ray diffraction spectra of other photoreactive mixed crystals. The data for the X-ray diffraction spectra are listed in Table 2. In conclusion, the new packing arrangements of coumarin by its interaction with the crystal lattice-controlling substances in the mixed crystals are considered to become suitable geometries for the photocycloaddition reaction to form the dimers 2a and 2b. It should be mentioned that the photochemically unreactive mixed crystals, namely ones with 1,4-dichlorobenzene, 1,4-dimethoxybenzene and naphthalene, also show the peaks for new crystal packing arrangements as listed in Table 2 as well as the peaks for the original coumarin and foreign substance crystals. In these cases the new crystal packing arrangements occur most probably for the foreign substances but not for coumarin.

As a possible interpretation, the new crystal packing arrangement could arise in the following sequence. When the melted mixture of coumarin and a crystal lattice-controlling substance is cooled, the foreign molecule first crystallizes probably because of its much higher melting point than that (69-70°C) of coumarin (Table 1) and then coumarin crystallizes on the surface of the nascent microcrystals of the foreign molecule to form the new phase of the photoreactive packing arrangement. 5-Iodo-1,3-dimethyluracil may induce the crystallization of coumarin into a different photoreactive packing arrangement giving anti head-to-head dimer 2b. In case of 1,4-dichlorobenzene (m.p. 51-54°C), 1,4-dimethoxybenzene (m.p. 55-56°C) and naphthalene (m.p. 79°C) which have a melting point

Table 4.
Final atomic coordinates
for non-hydrogen atoms.

	x	y	z
C11	0.3983(3)	0.0491(3)	0.8902(3)
C12	0.3437(3)	-0.0579(3)	0.8793(3)
C13	0.2342(3)	-0.0784(3)	0.9482(3)
C14	0.1843(3)	0.0067(4)	1.0214(3)
C15	0.2407(4)	0.1125(3)	1.0285(3)
C16	0.3499(3)	0.1343(3)	0.9633(3)
C21	0.1175(3)	-0.0676(3)	0.6501(3)
C22	0.1734(3)	-0.1692(3)	0.6830(3)
C23	0.0932(3)	-0.2591(3)	0.7112(3)
C24	-0.0380(3)	-0.2465(3)	0.7063(4)
C25	-0.0907(3)	-0.1444(4)	0.6733(3)
C26	-0.0144(3)	-0.0530(3)	0.6451(3)
C31	0.3992(3)	-0.1468(2)	0.7983(3)
C32	0.3149(3)	-0.1793(2)	0.6839(3)
C33	0.3845(3)	-0.0873(3)	0.6111(3)
C34	0.4947(3)	-0.0927(3)	0.7084(3)
C1	0.5621(3)	0.0153(3)	0.7417(3)
C2	0.3183(3)	0.0262(3)	0.6067(3)
O1	0.6576(2)	0.0490(2)	0.6949(2)
O2	0.3714(2)	0.1143(2)	0.5882(2)
O3	0.5116(2)	0.0803(2)	0.8313(2)
O4	0.1893(2)	0.0294(2)	0.6208(2)

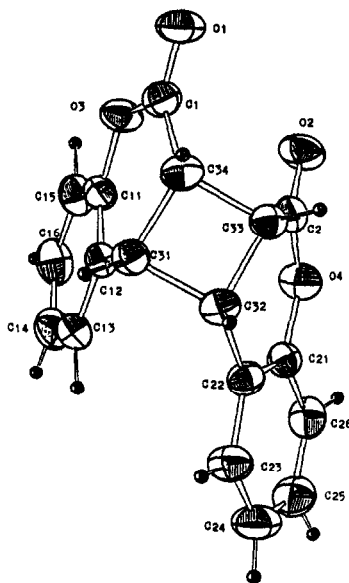


Table 5.
Bond distances (Å) and angles (°) of 2a with
estimated standard deviations in parenthesis.

C11-C12	1.390(4)	C21-C26	1.393(4)	C31-H31	0.96(3)
C11-C16	1.388(4)	C21-O4	1.410(4)	C32-C33	1.539(4)
C11-O3	1.411(4)	C22-C23	1.390(4)	C32-H32	0.95(3)
C12-C13	1.407(4)	C22-C32	1.489(4)	C33-C34	1.559(4)
C12-C31	1.500(4)	C23-C24	1.384(5)	C33-C2	1.507(4)
C13-C14	1.393(5)	C23-H23	0.90(4)	C33-H33	0.96(3)
C13-H13	1.08(4)	C24-C25	1.370(6)	C34-C1	1.497(4)
C14-C15	1.381(6)	C24-H24	0.90(4)	C34-H34	0.98(3)
C14-H14	0.92(4)	C25-C26	1.382(5)	C1-O1	1.201(4)
C15-C16	1.385(5)	C25-H25	0.91(4)	C1-O3	1.362(4)
C16-H16	1.11(4)	C31-C32	1.568(4)	C2-O4	1.365(4)
C21-C22	1.378(4)	C31-C34	1.555(4)		
C12-C11-C16	123.4(3)	C23-C22-C32	123.0(3)	C31-C32-H32	111.(2)
C12-C11-O3	123.1(3)	C22-C23-C24	121.0(4)	C33-C32-H32	108.(2)
C16-C11-O3	113.4(3)	C22-C23-H23	115.(2)	C32-C33-C34	88.1(2)
C11-C12-C13	116.7(3)	C24-C23-H23	124.(2)	C32-C33-C2	114.8(3)
C11-C12-C31	121.4(3)	C23-C24-C25	120.0(4)	C32-C33-H33	115.(2)
C13-C12-C31	122.0(3)	C23-C24-H24	124.(3)	C34-C33-C2	113.1(3)
C12-C13-C14	120.4(3)	C25-C24-H24	116.(3)	C34-C33-H33	117.(2)
C12-C13-H13	116.(2)	C24-C25-C26	120.8(3)	C2-C33-H33	108.(2)
C14-C13-H13	123.(2)	C24-C25-H25	118.(3)	C31-C34-C33	88.5(2)
C13-C14-C15	121.1(3)	C26-C25-H25	121.(3)	C31-C34-C1	120.0(3)
C13-C14-H14	119.(3)	C21-C26-C25	118.2(3)	C31-C34-H34	111.(2)
C15-C14-H14	119.(3)	C21-C26-H26	117.(2)	C33-C34-C1	118.2(3)
C14-C15-C16	119.7(4)	C25-C26-H26	125.(2)	C33-C34-H34	108.(2)
C14-C15-H15	123.(2)	C12-C31-C32	115.2(3)	C1-C34-H34	110.(2)
C16-C15-H15	116.(2)	C12-C31-C34	110.6(3)	C34-C1-O1	124.7(3)
C11-C16-C15	118.7(3)	C12-C31-H31	112.(2)	C34-C1-O3	117.8(3)
C11-C16-H16	119.(2)	C32-C31-C34	87.2(2)	O1-C1-O3	117.5(3)
C15-C16-H16	122.(2)	C32-C31-H31	112.(2)	C33-C2-O2	124.0(3)
C22-C21-C26	122.3(3)	C34-C31-H31	117.(2)	C33-C2-O4	118.6(3)
C22-C21-O4	122.6(3)	C22-C32-C31	122.1(3)	O2-C2-O4	117.4(3)
C26-C21-O4	115.1(3)	C22-C32-C33	115.0(3)	C11-O3-C1	121.8(2)
C21-C22-C23	117.7(3)	C22-C32-H32	110.(2)	C21-O4-C2	122.5(2)
C21-C22-C32	119.3(3)	C31-C32-C33	88.7(2)		

Figure 4.
Stereodrawing of a single
molecule of photodimer 2a.

lower than or comparative to that of coumarin, coumarin will first crystallize to form photochemically unreactive packing arrangement.

To gain further insight on this crystal lattice-controlling phenomenon, the photo-reaction of the mixed crystals having various ratios of antipyrine to coumarin was examined. As shown in Table 3, the highest yield of dimer 2a was obtained with the mixed crystal of 1 : 3 antipyrine-coumarin ratio and the yield of 2a decreased as the ratio became either lower or higher than 1 : 3. The exact nature of this phenomenon remains

to be further elucidated.

For the rigorous confirmation of the molecular structure of syn head-to-head dimer 2a, an X-ray crystallographic analysis was carried out to give the structure of Figure 4. The crystal data are follows: $C_{18}H_{12}O_4$; $M = 292.28$; monoclinic; space group $P2_1/n$; its unit cell parameters, $a = 10.461(3)$, $b = 11.785(2)$, $c = 10.974(2)$ Å; $\beta = 91.12(2)^\circ$; $Z = 4$; $D_{calc} = 1.432$ g/cm³. The atom positions, bond distances and bond angles are tabulated in Table 4 and Table 5.

Experimental

¹H-NMR, IR, UV and solid fluorescence spectra were recorded on a JEOL PMX-60 spectrometer, a PYE UNICAM SP3-300 spectrometer, a Shimadzu UV-240 spectrometer and a Shimadzu RF-540 spectrophotometer, respectively. X-ray powder diffraction diagrams were obtained on a D/Max-III A X-ray diffractometer. The crystal and molecular structure of compound 2a was determined on an ENRAF-NONIUS diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Mass spectra were recorded on a 7070E-HE mass spectrometer. Photoreaction of coumarin in the mixed crystal state.

With antipyrine. The mixed crystal was prepared by melting a mixture of coumarin (0.44 g, 3.0 mmol) and antipyrine (0.188 g, 1.0 mmol) followed by cooling the melt and was irradiated, after powdering, with a 300 W high-pressure mercury lamp under nitrogen for 35 h. Column chromatographic separation of the irradiated crystal on silica gel (Qing Dao 300; chloroform-ethyl acetate, 5 : 1 v/v) gave the coumarin photodimer 2a (10.0 % yield), m.p. 274-276°C (lit. m.p. 279-280°C^{8b}), which was identified by comparison of the melting point and mass and ¹H-NMR spectra with those of an authentic sample prepared according to the reported method.⁸ Irradiation of the mixed crystal with a 15 W low-pressure mercury lamp for 80 h followed by the similar work-up gave 2a in 6.8 % yield.

The mixed crystal of coumarin and antipyrine having a different molar ratio was irradiated with a 300 W high-pressure mercury lamp under nitrogen for 35 h and worked up similarly to give 2a. The results are listed in Table 3.

With phenanthrene. The mixed crystal of coumarin (3 mmol) and phenanthrene (1 mmol) was prepared as above and irradiated in the same manner to give 2a in 3.4 % yield.

With 6-cyano-1,3-dimethyluracil. The mixed crystal of coumarin (3 mmol) and 6-cyano-1,3-dimethyluracil⁹ (1 mmol) similarly gave 2a in 9.1 % yield.

With 5-bromo-1,3-dimethyluracil. The mixed crystal of coumarin (3 mmol) and 5-bromo-1,3-dimethyluracil¹⁰ (1 mmol) similarly gave 2a in 5.8 % yield. In this case, TLC analysis of the reaction mixture revealed the formation of a trace of anti head-to-head photodimer 2b.

With 5-iodo-1,3-dimethyluracil. The mixed crystal of coumarin (3 mmol) and 5-iodo-1,3-dimethyluracil¹¹ (1 mmol) prepared as above was irradiated in the same manner. Separation using silica gel chromatography (petroleum ether-ethyl acetate, 5 : 1 v/v) gave dimer 2b in 7.1 % yield, m.p. 177-179°C (lit. m.p. 179-181°C^{8b}), which was identified by comparison of the melting point and mass and ¹H-NMR spectra with those of an authentic sample prepared by the known method.⁸

X-ray crystallography.

A colorless cubic crystal of the coumarin dimer 2a, $C_{18}H_{12}O_4$, having approximate dimension of 0.70 x 0.70 x 0.70 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo K α radiation on an ENRAF-NONIUS CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal incident beam monochromator. Unique reflections of 2503 were collected in the range of $7^\circ < \theta < 10^\circ$ using ω - 2θ scan mode, in which 2088 reflections were considered to be observed. The intensities of the reflections were reduced to the amplitudes of structure factors and Lp correction and absorption correction were applied. The structure was solved by direct method (MULTAN 82). Most of non-hydrogen atoms were located from an E-map. The remaining non-hydrogen atoms were found in the succeeding difference Fourier synthesis. The coordinates of hydrogen atoms were calculated. In the final structure refinement by the full matrix least-square method, the anisotropic

thermal parameters of coordinates of non-hydrogen atoms and the isotropic thermal parameters of hydrogen atoms were refined. The final R factors are $R = 0.050$ and $R_w = 0.058$.

References

1. For example, T. Matsuura, Y. Sata, K. Ogura and M. Mori, Tetrahedron Letters **1968**, 4627; W. K. Appel, Z. Q. Jiang, J. R. Scheffer and L. Walsh, J. Am. Chem. Soc. **1983**, 105, 5354.
2. a) M. D. Cohen and G. M. J. Schmidt, J. Chem. Soc. **1964**, 1996.
b) G. M. J. Schmidt, Pure Appl. Chem. **1971**, 27, 6479.
3. For recent reviews, see V. Ramamurthy and K. Venkatesan, Chem. Rev. **1986**, 86, 433; V. Ramamurthy, Tetrahedron, **1986**, 42, 5753; M. Hasegawa, Chem. Rev. **1983**, 83, 507.
4. a) M. D. Cohen, B. S. Green, Z. Ludmer and G. M. J. Schmidt, Chem. Phys. Lett. **1970**, 7, 486.
b) B. S. Green and G. M. J. Schmidt, Tetrahedron Letters, **1970**, 4249.
c) B. S. Green and L. Hellor, J. Org. Chem. **1974**, 39, 196.
d) J. A. R. P. Sarma and G. R. Desiraju, Accounts Chem. Res. **1986**, 19, 222.
5. J. Bregnan, K. Osaki, G. M. J. Schmidt and F. I. Sonntag, J. Chem. Soc. **1964**, 2021.
6. a) W. Jones, S. Ramdas, C. R. Theocharis, J. M. Thomas and N. W. Thomas, J. Phys. Chem. **1981**, 85, 2594.
b) N. Ramasubbu, T. N. G. Row, K. Venkatesan, V. Ramamurthy and C. N. R. Rao, J. Chem. Soc. Chem. Commun. **1982**, 178.
7. a) H. Morrison, H. Curtis and T. Medowell, J. Am. Chem. Soc. **1966**, 88, 5415.
b) R. Hoffman, P. Wells and H. Morrison, J. Org. Chem. **1971**, 36, 102.
8. a) C. H. Krauch, S. Farid and G. O. Schenck, Chem. Ber. **1966**, 99, 625.
b) R. Anet, Can. J. Chem. **1962**, 40, 1249.
c) G. O. Schenck, I. V. Wilucki and C. H. Krauch, Chem. Ber. **1962**, 95, 1409.
9. S. Senda, K. Hirota and T. Asao, J. Org. Chem. **1975**, 40, 353.
10. S. Y. Wang, J. Org. Chem. **1959**, 24, 11.
11. P. K. Chang and A. D. Welch, J. Med. Chem. **1959**, 6, 428.