Studies in Crystal Engineering: Structure–Reactivity Correlations of Substituted Styrylcoumarins and Related Systems

J. Narasimha Moorthy,[a] **S. D. Samant**[b] **and K. Venkatesan** *[,a]
[a] *Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India*
[b] *University Department of Chemical Technology, Matunga, Bombay 400 019, India*

The solid state photochemical behaviour of 7-hydroxy-4-styrylcoumarin **1** and several of its derivatives and analogues has been investigated. All the compounds with the exception of 7-methoxy-4-styrylcoumarin **2** are photolabile and yield *anti*-HT dimers. It has been observed that chloro substitution in the systems studied does not lead to the expected β-packing mode. The photobehaviour of **1** and **2** has been correlated with their crystal structures. Reasons for α-packing have been examined. The systematics in the arrangement of the carbonyl group and phenyl group of the close neighbours in the crystals of **1**, **2** and a few other cases are presented.

Ever since the geometrical criteria for facile [2 + 2] photocycloaddition in the solid state were established, extensive studies have been pursued to preorganize the reactants in the solid state in a predetermined fashion.[1-4] However, interest has largely been focused on rationalization of the reactivity of β-structures in which the reactive partners are related by a mirror symmetry or design thereof.[2-4] An analysis of α-packed structures characterized by a molecular organization with adjacent molecules related by a centre-of-symmetry with centre-to-centre to distance of *ca.* 4.0 Å has not been a subject of detailed examination.

Photodimerization of coumarins in the solid state have been widely investigated in our laboratories.[5-7] More often than not, the photodimer obtained is mirror symmetric, implying the β-type packing of the precursor monomers. It was observed that 4-styrylcoumarin endowed with two potentially reactive double bonds crystallizes as photoreactive α-packed dimorphs. It was considered worthwhile examining the packing modes and photobehaviour of a few derivatives and analogues of 4-styrylcoumarin. We report herein the correlation between crystal structures and the photobehaviour of 7-hydroxy-4-styrylcoumarin **1** and 7-methoxy-4-styrylcoumarin **2** and the photochemical results of several of their analogues and derivatives.

Experimental

All the derivatives were prepared by a general method consisting of two steps:[8] phenol was condensed with acetone dicarboxylic acid (generated *in situ*) in the presence of conc. sulfuric acid to obtain coumarin-4-acetic acid which was subsequently condensed with corresponding aldehydes in the presence of piperidine. 7-Hydroxy-4-styrylcoumarin was methylated in dry acetone using dimethyl sulfate in the presence of potassium carbonate.

Powdered samples were irradiated in a Rayonet photochemical reactor (λ > 330 nm) at room temp. The progress of the reaction in each case was monitored by ^1H NMR spectroscopy and the dimer yields were calculated from the integrations in the ^1H NMR spectra of the irradiated reaction mixtures. The product dimers were separated by preparative TLC (ethyl acetate–hexane, 20:80) and characterized by comparison of the characteristic ^1H NMR spectral patterns for cyclobutyl protons with those of analogous photodimers documented in the literature.[9-11]

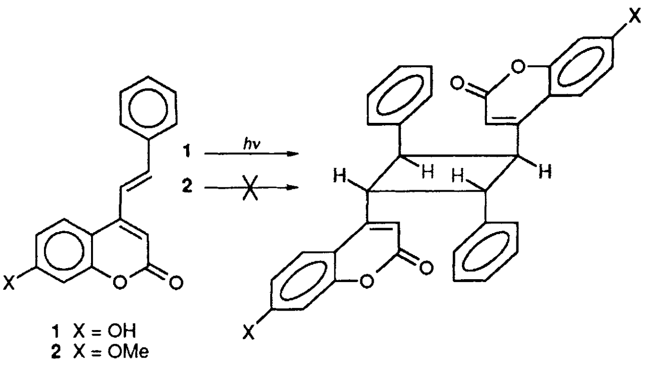
X-Ray Structural Analyses and Refinement.—Single crystals of **1** and **2** were obtained by slow evaporation of their solutions in ethanol and ethanol–chloroform (1:1) mixtures, respectively. Lattice parameters in both the cases were determined by a least-squares procedure to a setting of 25 accurately centred reflections. The data collection for **1** and **2** was accomplished using Ni-filtered Cu-Kα and graphite monochromatized Mo-Kα radiations, respectively, in ω–2θ mode. The intensities of three standard reflections used for checking the stability of the crystals showed only statistical fluctuations. The orientation of the crystal in each case was monitored with the aid of three reflections after the measurement of every 400 reflections. The data were corrected for Lorentz and polarization factors but not for absorption. The structures of both **1** and **2** were solved using SHELXS 86.[12] The program in both the cases, with default parameters, furnished *E*-maps from which all the positions corresponding to the non-hydrogen atoms could be identified. Full-matrix least-squares refinement of the positional parameters, thermal parameters and scale factor was performed using SHELX 76.[13] The positions corresponding to hydrogen atoms in both the cases were located from successive difference-Fourier maps and were included in the refinement for a few cycles. The final refinement of scale factor, positional parameters and anisotropic thermal parameters of non-hydrogen atoms and positional parameters and isotropic thermal parameters of hydrogen atoms converged at *R* values of 0.050 and 0.048 for **1** and **2**, respectively. The details of the data collection and refinement are summarized in Table 1. The final difference-Fourier maps were featureless (Table 1).

Results and Discussion

It has been found that 7-hydroxycoumarin and 7-hydroxy-4-methylcoumarin are photostable.[14,15] In both the cases, an extended network of hydrogen bonding between the hydroxy groups has been shown to result in a crystal packing unfavourable for photodimerization. It is interesting in this context to note that the methylated derivatives *viz.*, 7-methoxycoumarin and 7-methoxy-4-methylcoumarin and photolabile.[16,17] The *o*-methylation destroys the corrugated network of O–H • • • O hydrogen bonds in 7-hydroxycoumarin as well as 7-hydroxy-4-methylcoumarin which results in a packing arrangement of the crystals favourable for photodimerization of 7-methoxycoumarin and 4-methyl-7-methoxy-coumarin. Interestingly, 7-hydroxy-4-styrylcoumarin **1** was found to be photoreactive, whereas 7-methoxy-4-styrylcoumarin **2** was photoinert (Scheme 1). In order to unravel the intermolecular

Table 1 Crystal data and details of refinement

	1	**2**
Molecular formula	$C_{17}H_{12}O_3$	$C_{18}H_{14}O_3$
M_r	264.3	278.3
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	8.535(1)	8.481(2)
b/Å	10.007(2)	5.721(1)
c/Å	15.787(3)	28.271(3)
α/°	90.62(1)	
β/°	92.83(1)	92.26(1)
γ/°	109.56(2)	
V/Å^3	1268.5(4)	1370.6(4)
Z	4	4
D_x/mg m^{-3}	1.384	1.349
Crystal size/mm	0.30 × 0.25 × 0.16	0.4 × 0.3 × 0.15
Radiation used/Å	Cu-Kα, 1.5418	Mo-Kα, 0.7107
μ/cm^{-1}	7.31	0.853
$F(000)$	552	584
θ limit/°	65	25
Mode of data collection	ω–2θ	ω–2θ
No of observed reflections $[\lvert F_o\rvert \geq 3\sigma(\lvert F_o\rvert)]$	3997	2006
Final R	0.057	0.047
Final R_w	0.057	0.060
Weighting function	1.0	$1/(\sigma^2\lvert F_o\rvert + 0.0087\lvert F_o\rvert^2)$
No. of variables	457	246
Residual electron $\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.10, −0.24	0.14, −0.22
Max. Δ/σ	0.01	0.01



Scheme 1

interactions controlling the packing modes of **1** and **2**, the crystal structures of both the compounds were determined.

The crystal data and details of refinement of **1** and **2** are given in Table 1. The two molecules in the asymmetric unit cell of **1** are designated A and B. The perspective views of the molecular structures of **1** and **2** with atom numbering scheme, drawn using the program ORTEP, are shown in Figs. 1 and 2, respectively. The positional and isotropic thermal parameters of the non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre. The coumarin fragments in **1** as well as **2** are planar within the experimental error. The selected torsion angles of interest for both **1** and **2** are given in Table 2. Clearly, the conformations with respect to styryl moiety do not differ significantly.

Short intermolecular contacts in **1** show that the carbonyl oxygen of AO(2) (x, y, z) participates in hydrogen bonding with the hydrogen of the hydroxy group of molecule B translated along the a-axis *i.e.*, B(O3)H ($1 + x, y, z$). The distance B(O3)H ··· AO(2) and the angle B(O3)H–B(O3) ··· AO(2) are 1.95 Å and 158.4°, respectively. However, the hydrogen of the hydroxy group of molecule A remains free. In addition, a total of eight C–H ··· O hydrogen bonds (with H ··· O distances ⩽3.0 Å and C–H ··· O angles in the range 120–180°)[18] are found in **1** and four in **2**. The geometrical parameters of these bonds are recorded in Table 3.

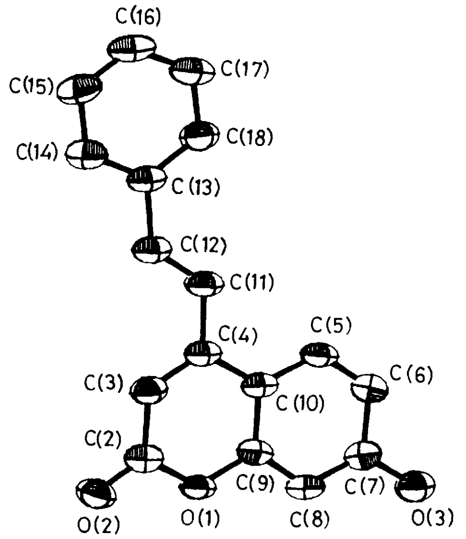


Fig. 1 ORTEP diagram of 7-hydroxy-4-styrylcoumarin **1** with atom labelling scheme. The thermal ellipsoids are at 50% probability level.

The observation that both **1** and **2** as well as the dimorphs of 4-styrylcoumarin[19] are all centrosymmetrically packed prompted the examination of the photobehaviour of a few other derivatives and their analogues (Scheme 2). Remarkably, all the derivatives **3**–**9** were found to undergo efficient photodimerization in the solid state furnishing *anti*-HT dimers (yield *ca.* 70–80%, irradiation for 10–12 h) suggesting that the packing mode in all these cases corresponds to α-type, when the reaction is assumed to be topochemically controlled.

Structure–Reactivity Correlations.—In a topochemical reaction, the overlap of the π-orbitals of the reactive partners should be favourable. If we define θ_1 as the rotation of one of

Table 2 Selected torsion angles of the 4-styrylcoumarin derivatives

Compound		C3–C4–C11–C12	C10–C4–C11–C12	C4–C11–C12–C13	C11–C12–C13–C14	C11–C12–C13–C14
7-Hydroxy-4-styrylcoumarin	A	−10.7(5)	168.2(3)	−177.7(4)	−175.4(4)	4.9(6)
	B	−31.0(6)	148.5(4)	−177.5(3)	178.9(4)	−0.4(6)
7-Methoxy-4-styrylcoumarin		−1.5(4)	178.1(2)	−179.6(2)	4.1(4)	−177.0(2)
4-Styrylcoumarin, prisms	A	−14.7(7)	167.4(4)	179.5(4)	175.5(5)	−4.3(7)
	B	3.2(7)	−174.4(5)	176.7(4)	167.0(5)	−15.3(7)
4-Styrylcoumarin, needles		−10.7(1.2)	166.9(7)	179.6(7)	−173.9(8)	5.3(1.2)

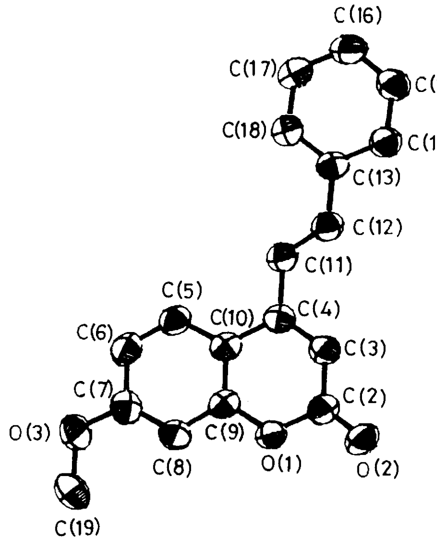


Fig. 2 ORTEP diagram of 7-methoxy-4-styrylcoumarin **2** with atom labelling scheme

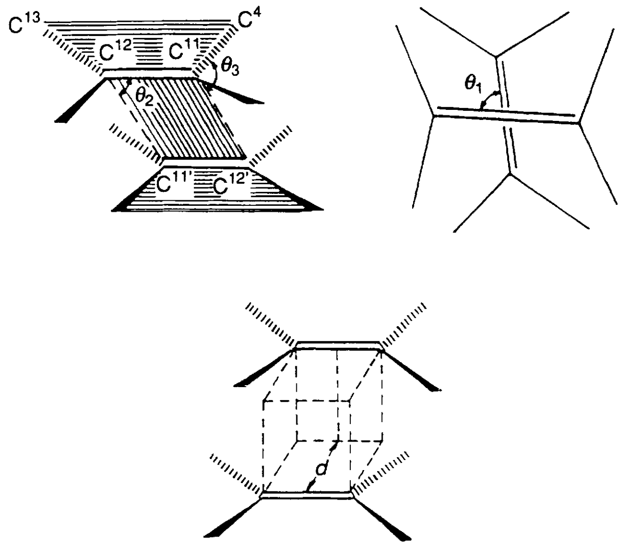
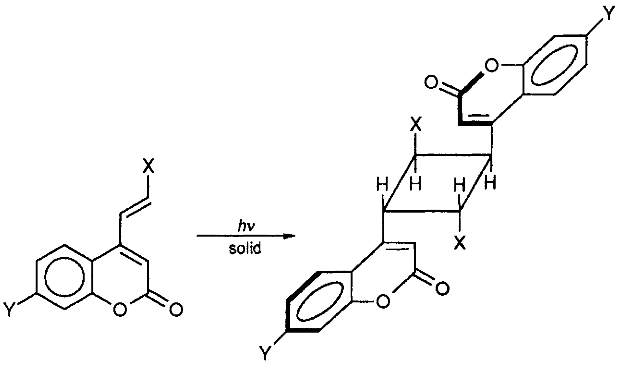


Fig. 3 Pictorial representation of θ_1, θ_2, θ_3 and d



3 X = Ph; Y = Cl
4 X = 4-ClC$_6$H$_4$—; Y = H
5 X = 4-ClC$_6$H$_4$—; Y = OH
6 X = O[CH]$_3$C—; Y = H
7 X = O[CH]$_3$C—; Y = Cl
8 X = S[CH]$_3$C—; Y = H
9 X = S[CH]$_3$C—; Y = Cl

Scheme 2

the double bonds with respect to the other, θ_2 as the angle of parallelogram formed by the atoms of the double bonds C(11), C(12), C(11') and C(12') and θ_3 as a measure of the angle between the least-squares planes through the atoms C(4), C(11), C(12) and C(13) and C(11), C(12), C(11') and C(12'), their ideal values should be 0, 90 and 90°, respectively (Fig. 3). The displacement of the reactive partners, d, should be 0 Å.

The stereoscopic view of the packing of the molecules in the crystal lattice of **1** is shown in Fig. 4. A careful analysis of the contacts ($\leqslant$4.2 Å) between the non-hydrogen atoms of **1** revealed that C(11)=C(12) double bonds of molecule A and its centrosymmetrically related partner A' are separated by a distance of 3.761 Å. Similarly, the C(11)=C(12) double bonds of molecule B and B' are centrosymmetrically juxtaposed with a distance of separation of 3.963 Å. The calculated parameters θ_1, θ_2, θ_3 and d for the styrenic double bonds of A and A' are 0, 64.7, 88.2° and 0.1 Å, respectively and those for B and B' are 0, 67.1, 85.5° and 0.3 Å, respectively. These values are in the range generally observed for photoreactive crystals.[2,4]

The stereoscopic view of the packing of the molecules in the crystal lattice of **2** is shown in Fig. 5. A search for intermolecular short contacts involving non-hydrogen atoms revealed no contacts between the centrosymmetrically related molecules either across C(3)=C(4) or C(11)=C(12) double bond within 4.5 Å. Also, no favourable contacts were found between C(3)=C(4) and C(11)=C(12) double bonds. The minimum distance at which the molecules are centrosymmetrically related is found to be 5.48 Å with respect to C(3)=C(4) double bond. Hence, **2** is photostable.

C=O ⋯ *π interaction and its role in α-packing.* It transpired from a careful analysis of the short intermolecular contacts in the crystal structure of **1** that the atoms of carbonyl group of the coumarin fragment lie in close proximity of the phenyl ring of the centrosymmetrically related partner. The situation shown in Fig. 6 was observed for the centrosymmetrically related pairs of both the molecules A and B in the asymmetric unit cell of **1**. Indeed, Addadi and Lahav have noted from the analysis of a large number of crystal structures of esters that there exists an attractive interaction between the carbonyl and phenyl groups,

Table 3 Geometrical parameters of the C–H ••• O hydrogen bonds

Atom	Bonded to	C ••• O/Å	C–H–O/°	H ••• O/Å
7-Hydroxy-4-styrylcoumarin				
AO(2)	BC(8)H (1 + *x*, *y*, *z*)	3.54	126.0	2.89
AO(2)	BC(3)H (*x*, 1 + *y*, *z*)	3.54	153.3	2.59
AO(2)	BC(12)H (2 − *x*, 1 − *y*, 2 − *z*)	3.74	128.2	2.97
AO(2)	BC(14)H (2 − *x*, 1 − *y*, 2 − *z*)	3.40	122.7	2.75
BO(2)	AC(3)H (*x*, 1 + *y*, *z*)	3.49	125.5	2.93
BO(2)	BC(14)H (2 − *x*, 2 − *y*, 2 − *z*)	3.62	121.7	2.98
BO(3)	BC(12)H (1 − *x*, 1 − *y*, 2 − *z*)	3.97	147.7	3.00
AO(3)	AC(6)H (1 − *x*, 1 − *y*, 1 − *z*)	3.51	162.1	2.55
7-Methoxy-4-styrylcoumarin				
O(2)	C(3)H (1 − *x*, 1 − *y*, −*z*)	3.92	166.8	2.95
O(2)	C(12)H (1 − *x*, 1 − *y*, −*z*)	3.45	160.8	2.51
O(2)	C(18)H (1 − *x*, −1 − *y*, −*z*)	3.55	154.9	2.65
O(2)	C(19)H (−*x*, 1 − *y*, 1 − *z*)	3.46	137.7	2.60

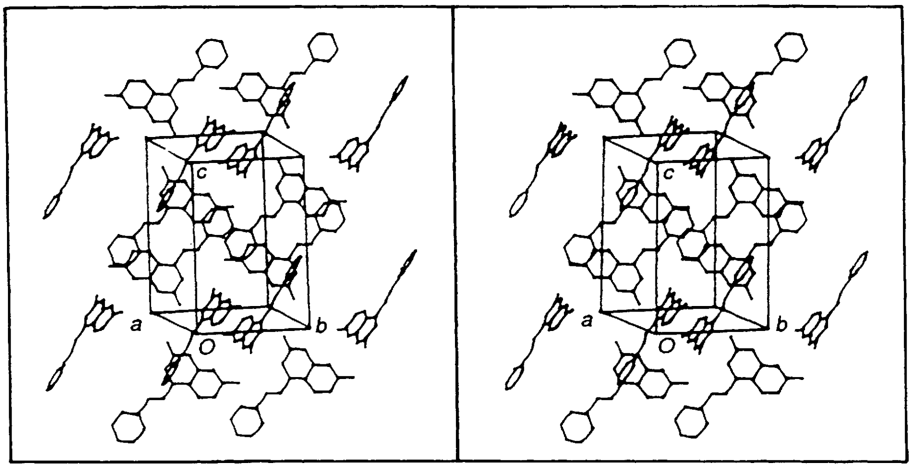


Fig. 4 Stereoscopic view of the crystal packing of **1**

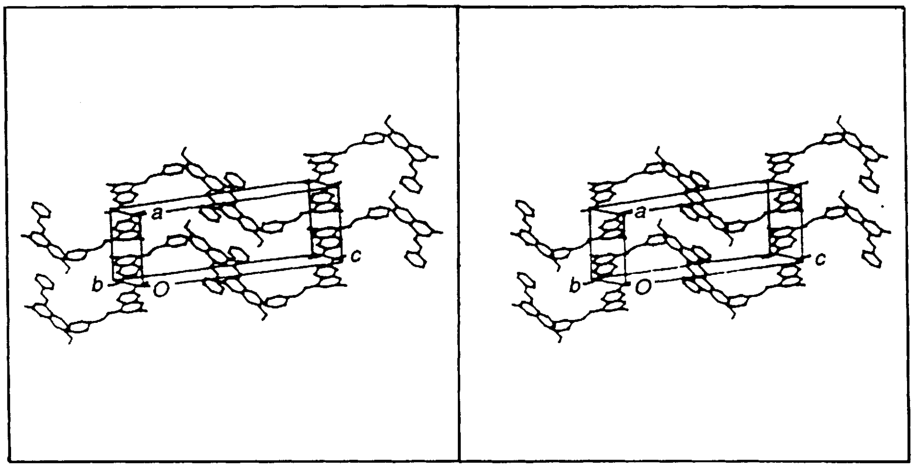


Fig. 5 Stereoscopic view of the crystal packing of **2**

referred to as C=O ••• π interaction, of adjacent molecules which would juxtapose the double bonds at a distance of 4.0 Å.[20] Utilizing this observation, they designed a class of compounds for asymmetric dimerization and polymerization and successfully demonstrated that the attractive interaction between the carbonyl group of the ester and the phenyl rings of the adjacent molecules could be employed to bring about the required proximity and orientations between the molecules in the crystal lattice to furnish, upon irradiation, chiral [2 + 2] cycloaddition dimers, oligomers and polymers. An electrostatic interaction has been supposed to operate between the electron deficient phenyl group and the electron rich oxygen atom of the carbonyl group.[21]

In the light of the above reports, the hypothesis that the derivatives **3**–**9** effectively employ, in the centrosymmetric arrangement, the C=O ••• π interaction, besides the potential π ••• π interactions appears reasonable. The efficient formation of centrosymmetric *anti*-HT photodimers from all the derivatives clearly indicates α-type packing mode. This also implies that the C=O ••• π interaction prevails even when the

Table 4 Geometrical parameters for carbonyl oxygen with respect to the phenyl ring

Compound	$\theta_1/°$	$\theta_2/°$	$d_1/Å$	$d_2/Å$	$d_3/Å$
7-Hydroxy-4-styrylcoumarin A	52.3	6.1	4.52	3.44	2.93
B	66.0	29.7	4.36	2.70	3.42
4-Styrylcoumarin B	60.8	14.8	4.50	4.20	1.60
Benzylidene-(±)-piperitone	95.9	8.8	4.28	3.25	2.78
α-Acetylaminocinnamic acid	60.9	9.3	4.04	3.74	1.53
2-Benzyl-5-benzylidenecyclopentanone	74.2	9.3	5.15	4.20	3.00
p-Fluorobenzylidene-(±)-piperitone	74.4	1.5	4.70	3.70	2.90
p-Chlorobenzylidene-(±)-piperitone	64.1	2.9	4.3	3.40	2.63
Geometrical parameters for carbonyl carbon with respect to the phenyl ring					
7-Hydroxy-4-styrylcoumarin A	113.37		3.90	3.42	1.87
B	97.85		4.02	3.18	2.46
4-Styrylcoumarin B	104.11		4.04	3.18	1.25
Benzylidene-(±)-piperitone	68.65		4.57	3.46	2.98
α-Acetylaminocinnamic acid	72.17		3.61	3.53	0.76
2-Benzyl-5-benzylidenecyclopentanone			4.96	4.07	2.83
p-Fluorobenzylidene-(±)-piperitone	90.70		4.57	3.74	2.63
p-Chlorobenzylidene-(±)-piperitone	99.59		3.90	3.50	1.72

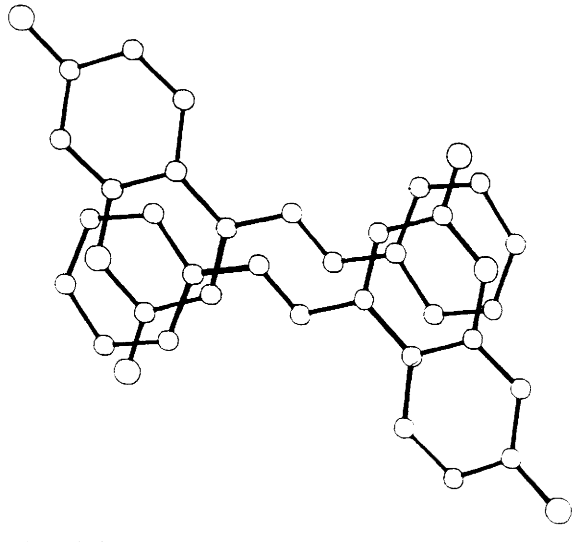


Fig. 6 Relative orientation of the centrosymmetrically related molecules of **1**

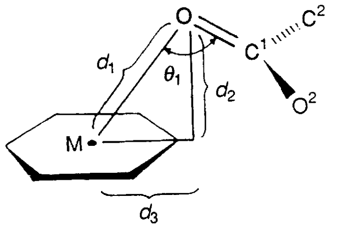


Fig. 7 Pictorial representation of the geometrical parameters

phenyl group is replaced by *p*-chlorophenyl, furyl and thiophenyl groups.

It is relevant in this context to note that several cases which crystallize in α-mode and hence undergo photodimerization to yield stereospecifically *anti*-HT dimers have been reported in the literature.[21–30] It turns out that the juxtaposition of the carbonyl group over the phenyl rings can be visualized in all the cases between the centrosymmetrically related pairs. Similar considerations can be extended to all the cinnamic acids which produce *anti*-HT dimers. However, a perusal of the results of photodimerization of a number of cinnamic acids revealed that when other potential interactions such as Cl···Cl or O–H···O hydrogen bonds predominate the crystal packing, the influence of weaker C=O···π interaction, perhaps, gets obscured. A few derivatives of cinnamic acids, *e.g.* 3,4-dichloro-, *o*-, *p*- and *m*-chloro-[23] 3,4-methylenedioxycinnamic acids[24] pack in β-fashion owing to other interactions. Perhaps a combined effect of π···π as well as C=O···π(aryl) interactions, in the present 4-styrylcoumarin and related systems, between the centrosymmetrically arranged partners leads to α-packing.

Geometry of Spatial Orientation of Carbonyl Group with respect to the Phenyl Group.—The approach-geometry of carbonyl group with respect to the phenyl ring of the centrosymmetrically generated counterpart was defined using the parameters θ_1, θ_2, d_1, d_2 and d_3 (Fig. 7): θ_1 refers to the angle between the C(1)=O(1) bond and the line joining the midpoint of the phenyl ring; θ_2, the angle between the plane of the phenyl ring and the least-squares plane comprised of the atoms O(1), O(2), C(1) and C(2); the parameter d_1 is the length of the line connecting carbonyl O(1) [or C(1)] and the midpoint *M* of the phenyl ring; d_2, the length of the perpendicular to the plane of the phenyl ring passing through O(1) [or C(1)] atom and d_3, the horizontal displacement of O(1) [or C(1)] from the midpoint of phenyl group when projected on to the least-squares plane of the phenyl ring.

The values of these parameters calculated with respect to O(1) and C(1) of the carbonyl group for the centrosymmetrically related pairs of A and B in 7-hydroxy-4-styrylcoumarin are provided in Table 4. To examine the trend of the approach geometry of the carbonyl group with respect to the phenyl group, these parameters were calculated for the centrosymmetrically related pairs in 4-styrylcoumarin,[19] benzylidene-(±)-piperitone,[31] α-aminoacetylcinnamic acid,[20] *p*-chlorobenzylidenepiperitone,[32] *p*-fluorobenzylidenepiperitone[33] and 2-benzyl-5-benzylidenecyclopentanone.[25,26]

It is clear from the values of θ_2 that the least-squares plane through the atom C(1) and those bonded to it is essentially coplanar with the plane of the phenyl ring, but displaced with respect to one another as may be seen from the values of d_3. It is important to record the observation that the carbonyl carbon in all but 2-benzyl-5-benzylidenecyclopentanone was found to produce contacts ($\leqslant 3.8$ Å) with at least two sp^2 carbon atoms of the phenyl ring. From purely qualitative considerations, the relatively acidic carbonyl carbon is the one which would be expected to interact with the electron rich phenyl carbons.

The Role of Chloro Group.—The overall three dimensional packing of a particular compound is a net result of the intermolecular interactions such as C···C, C···H, C···O, Cl $\cdots$ Cl, $\pi \cdots \pi$, *etc.* The non-bonded Cl $\cdots$ Cl attractive interactions have been recognized to contribute effectively to the stacked packing of planar aromatic compounds.[34] For example, 6-chloro-, 7-chloro- and 4-methyl-6-chloro-coumarins are all β-packed.[5] However, the chloro substitution is not effective in non-planar aromatic compounds as has been discussed recently.[35] It was considered worth examining if chloro substitution would steer styrylcoumarins and related systems into β-packing mode. However, all the chloro substituted derivatives **3**–**5**, **7** and **9** were found to yield invariably centrosymmetric *anti*-HT dimers suggesting that the chloro group is ineffective in inducing β-packing mode. Indeed, in the analogous totally non-planar benzylidene-(±)-piperitones studied by Venugopalan *et al.*, no short contacts between Cl $\cdots$ Cl groups were observed.[11,32] In as much as the dimers obtained upon irradiation of **3**–**5**, **7** and **9** are *anti*-HT, the Cl $\cdots$ Cl interactions in these cases are unlikely. However, it may be noted that all the chloro derivatives investigated are monosubstituted. The effect of dichloro substitution in the present systems has not been investigated.

Influence of the Methoxy Group.—As can be seen from Table 2, the conformations of the photolabile **1** and photostable **2** molecules with respect to the styryl moiety are similar. The least-squares plane of the phenyl ring of the styryl fragment makes an angle of 6.2° in **1A**, 31.6° in **1B** and 2.3° in **2** with respect to the least-squares plane of the coumarin fragment. It is evident from these angles and the torsion angles involving the methoxy group, *i.e.*, C(19)–O(3)–C(7)–C(6) = $-177.9(2)°$ and C(19)–O(3)–C(7)–C(8) = $2.4(3)°$ that 7-methoxy-4-styryl coumarin **2** is approximately planar. As has been noted so far, the methoxy substitution leads to photoinertness. In this context, the photoreactivities of methoxy derivatives of coumarin are noteworthy: 8-methoxycoumarin is photoreactive and furnishes *anti*-HT dimer;[5] 7-methoxy-4-methylcoumarin undergoes topochemical (major *syn*-HH dimer) as well as non-topochemical photodimerization (minor *syn*-HT dimer);[17] 7-methoxycoumarin photodimerizes (*syn*-HT) despite the fact that the reactive double bonds of proximal molecules are rotated by an angle of 65°, but with the distance of separation between the double bonds being *ca.* 4.0 Å.[16] In contrast, **2** is photostable, despite being planar. The bulky methoxy group does not permit close packing of **2** which is also reflected from the densities of **1** and **2** which are 1.384 and 1.349 gm cm^{-3}, respectively. That compound **2** is α-packed is probably owing to the fact that the molecules can effectively employ the $\pi \cdots \pi$ and the C=O $\cdots$ π interactions (described above) in the centrosymmetric arrangement. The dependence of molecular topology on the crystal packing and hence the photoreactivity has recenty been examined.[35] Clearly, methoxy substitution cannot be employed for achieving photodimerization with unique product stereochemistry.

Conclusions

The photochemical results clearly show that α-packing is preferred in all the derivatives **3**–**9**, as in the case of **1** with the substituents such as furyl, thiophenyl, phenyl and *p*-chlorophenyl groups effectively bringing about no changes in the overall packing pattern. It is observed that the monochloro substitution is not effective enough in inducing β-form. Indications are that the C=O $\cdots$ π(aryl) interaction contributes to enhance the stability of the crystal structure in α-mode.

Acknowledgements

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References

1 G. M. J. Schmidt, in *Solid State Photochemistry*, ed. D. Guinsburg, Weinheim and New York, 1976.
2 V. Ramamurthy and K. Venkatesan, *Chem. Rev.*, 1987, **87**, 433.
3 *Organic Solid State Chemistry*, ed. G. R. Desiraju, Elsevier, Amsterdam, 1987.
4 V. Ramamurthy and K. Venkatesan, *Photochemistry in Organized and Constrained Media*, ed. V. Ramamurthy, 1991, p. 487.
5 K. Gnanaguru, N. Ramasubbu, K. Venkatesan and V. Ramamurthy, *J. Org. Chem.*, 1985, **50**, 2337.
6 J. N. Moorthy and K. Venkatesan, *J. Org. Chem.*, 1991, **56**, 6957.
7 J. N. Moorthy, K. Venkatesan and R. G. Weiss, *J. Org. Chem.*, 1992, **57**, 3292.
8 S. D. Samant, personal communications.
9 L. H. Leenders, E. Schouteden and F. C. de Schryver, *J. Org. Chem.*, 1992, **57**, 276.
10 P. Venugopalan, R. G. Weiss and K. Venkatesan, *J. Org. Chem.*, 1992, **57**, 276.
11 P. Venugopalan, PhD. Thesis, Indian Institute of Science, Bangalore, India, 1991.
12 G. M. Sheldrick, SHELXS 86, *Program for Crystal Structure Solution*, Gottingen University, 1986.
13 G. M. Sheldrick, SHELX 76, *Program for Crystal Structure Solution*, University of Cambridge, Cambridge, 1976.
14 S. Shimizu, S. Kashino and M. Haisa, *Acta Crystallogr., Sect. B*, 1975, **31**, 1285.
15 K. Ueno, *Acta Crystallogr., Sect. C*, 1985, **41**, 1786.
16 N. Ramasubbu, T. N. Guru Row, K. Venkatesan, V. Ramamurthy and C. N. R. Rao, *J. Chem. Soc., Chem. Commun.*, 1982, 178.
17 J. N. Moorthy and K. Venkatesan, *J. Mater. Chem.*, 1992, **2**, 675.
18 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.
19 J. N. Moorthy and K. Venkatesan, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1.
20 L. Addadi and M. Lahav. *Pure Appl. Chem.*, 1979, **39**, 1269.
21 K. Ueno, H. Nakanishi, M. Hasegawa and Y. Sasada, *Acta Crystallogr. Sect. B*, 1978, **34**, 2034.
22 M. D. Cohen, G. M. J. Schmidt and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2000.
23 G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2014.
24 G. R. Desiraju, R. Kamala, B. H. Kumari and J. A. R. P. Sarma, *J. Chem. Soc., Perkin Trans. 2*, 1984, 181.
25 W. Jones, S. Ramdas, C. R. Theocaris and J. M. Thomas, *J. Phys. Chem.*, 1981, **85**, 2594.
26 H. Nakanishi, W. Jones, J. M. Thomas, M. B. Hursthouse and M. Motevalli, *J. Phys. Chem.*, 1981, **85**, 3636.
27 G. Kaupp, E. Jostkleigrewe and H. T. Hermann, *J. Chem. Soc.*, 1982, **21**, 435.
28 E. Waschen, R. Matusch, D. Krampity and K. Hartke, *Liebigs Ann. Chem.*, 1978, 2137.
29 S. Mohr, *Tetrahedron Lett.*, 1979, 2461.
30 D. Lawrenz, S. Mohr and B. Wendlander, *J. Chem. Soc., Chem. Commun.*, 1964, 863.
31 K. Kanakapushpam, V. Ramamurthy and K. Venkatesan, *Acta Crystallogr., Sect. C*, 1990, **43** 1128.
32 P. Venugopalan and K. Venkatesan, *Acta Crystallogr., Sect. B*, 1990, **43**, 826.
33 V. Amarendra Kumar and K. Venkatesan, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2429.
34 M. D. Cohen, A. Elgavi, B. S. Green, Z. Ludmer and G. M. J. Schmidt, *J. Am. Chem. Soc.*, 1972, **94**, 6776.
35 P. Venugopalan, T. Bharati Rao and K. Venkatesan, *J. Chem. Soc., Perkin Trans. 2*, 1991, 981.

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