Pergamon

Tetrahedron 55 (1999) 4095–4108

TETRAHEDRON

Studies in Crystal Engineering: Steering Ability of Fluorine in 4-Styrylcoumarins

Kodumuru Vishnumurthy,[a] Tayur N. Guru Row*[,a,b] and Kailasam Venkatesan[a]

[a] *Department of Organic Chemistry and* [b] *Solid State and Structural Chemistry Unit*
Indian Institute of Science, Bangalore-560 012, India

Received 2 October 1998; revised 14 January 1999; accepted 28 January 1999

Abstract: In continuation of our studies on crystal engineering using fluorine as a steering group, the photobehaviour of di and tri fluoro 4-styrylcoumarins has been examined. It is found that out of the five derivatives, four crystallize into β-packing mode producing *syn*-HH photodimer upon irradiation whereas the parent hydrocarbon produces an *anti* H-T dimer. The packing features of the photolabile crystals of 4-(4-fluorostyryl)-6-fluorocoumarin (**1**), 4-(2,6-difluorostyryl)-6-fluorocoumarin (**2**) and the photodimer (**3a**) of 4-(2,6-fluorostyryl)-7-fluorocoumarin (**3**) have been determined by single crystal X-ray diffraction studies. The stereochemistry of the photodimer of 4-(2-fluorostyryl)-6-fluorocoumarin (**4**) is deduced based on preliminary X-ray crystallographic data. However, 4-(2,6-difluorostyryl) coumarin (**5**) is photoinert. The remarkable steering ability of fluorine is established with the molecular packing in the crystal lattice leading to the formation of *syn* H-H dimer in the above four examples.

INTRODUCTION

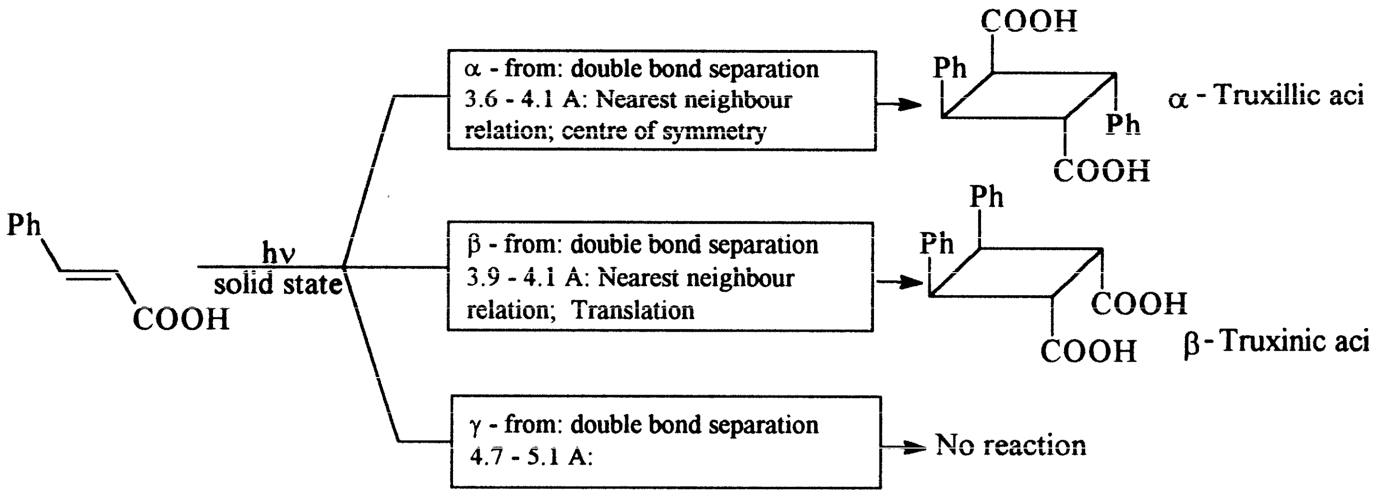
It is well-known that the stereochemistry of the photodimer depends upon the organization of the monomer molecules in the crystal lattice .[1] The packing modes of the monomer molecules are classified into α-, β-, and γ-types depending upon the distance between the neighboring molecules and the symmetry relation between them.[1] In α-type, the double bonds of neighboring molecules are at a distance of *ca.* 3.70 Å across centre of inversion to produce an *anti*-HT (*anti*-head-to-tail, α-packing mode) dimer upon irradiation. In β-type, one of the cell dimension is ~4.0 Å yielding a *syn*-HH (*syn*-head-to-head, β-packing mode) dimer upon irradiation. The photostable γ-type crystal has the centre - to - centre distance between the double bonds

---

E-mail: ssctng@sscu.iisc.ernet.in

PII: S0040-4020(99)00103-9

of neighbouring molecules is more than 4.2 Å (Scheme 1.1).

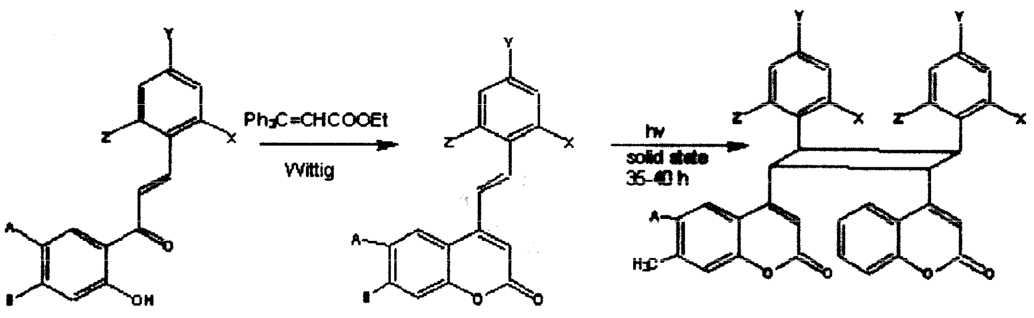


Scheme 1.1

Studies on mono fluoro substituted coumarins lead to the formation of β-packing mode[2a] whereas the parent coumarin has been observed to react in a non-topochemical fashion.[2b] Mono fluoro substitution on 4-styrylcoumarin, however, produces either *anti*-HT or *syn*-HH dimer depending upon the site of substitution .[3] On the other hand, non-planar fluoro substituted benzylidene-DL (±)-piperitone leads to the formation of stereospecific *anti*-HT photodimer.[4] Thus the predictability of fluorine substitution on the packing mode is not as definitive as in the case of chlorine which generates β-packing modes in most cases. [5] To gain further insight into the steering ability of fluorine in engineering crystals, it was considered worthwhile examining the effect of poly substituted fluoro 4-styrylcoumarins on molecular packing and their photobehavior. In this article, we discuss the results of di- and tri- substituted molecules such as 4-(4-fluorostyryl)-6-fluorocoumarin (**1**), 4-(2,6-difluorostyryl)-6-fluorocoumarin (**2**), 4-(2,6-fluorostyryl)-7-fluorocoumarin (**3**), 4-(2-fluorostyryl)-6-fluorocoumarin (**4**) and 4-(2,6-difluorostyryl) coumarin (**5**).

RESULTS AND DISCUSSION

Compounds **1-5** were prepared [6] by condensing the corresponding fluoro-2-hydroxychalcones using the Wittig reagent, $Ph_3P{=}CHCOOEt$, followed by purification by column chromatography using 10% ethyl acetate in petroleum ether as an eluent (Scheme 1.2). The powder samples of **1-5** were irradiated simultaneously in a Rayonet photochemical reactor (λ_{max} = 320 nm ± 20) for *ca.* 35-40 h at room temperature. During irradiation care was taken to expose samples uniformly by shaking the containers at



1. A=Y=F; X=Z=B=H
2. A=X =Z=F; B=Y=H
3. B=X=Z=F; A=Y=H
4. A=X=F; Y=Z=B=H
5. X=Z=F; A=B=Y=H (Photostable)

Scheme 1.2

regular intervals. Irradiation was continued until there was no further increase in the product formation. Compound **5** remains unchanged even after 8 days of continued irradiation. The progress of the photoreaction was monitored by thin layer chromatography (TLC), IR and ^{1}H NMR spectroscopy. The photodimers **1a**, **2a**, **3a** and **4a** were separated from their corresponding monomers (**1**, **2**, **3** and **4**) by column chromatography eluting with 10% ethyl acetate in petroleum ether.

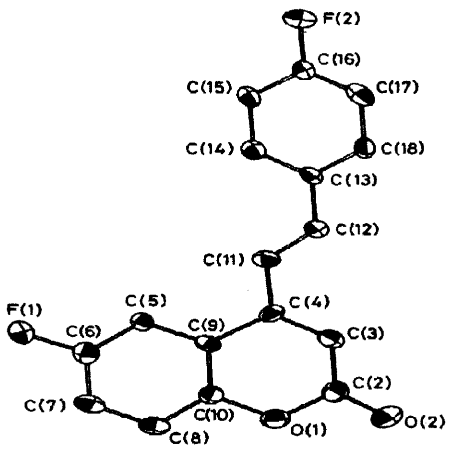
The 4-styrylcoumarin has two potentially reactive double bonds-the pyrone [C (3)=C (4)] and the styrenic double bond [C (11)=C (12)] leading to the formation of eight possible dimers. The photodimers, in principle, can adopt any one of four configurations: *syn*-HH, *syn*-HT, *anti*-HH and *anti*-HT. Upon irradiation, compounds of **1-4** at *ca* 35-40 hours in the crystalline state lead to regio- and stereospecific *syn*-HH photodimers (**1a-4a**) across the styrenic double bond in contrast to the formation of centrosymmetric photoproducts in mono fluoro substituted 4-styrylcoumarins[3b] as well as in parent 4-styrylcoumarins.[7]

The molecular ion peak at m/z 568, 604, 604 and 568 in the mass spectra indicated the formation of photodimers **1a**, **2a**, **3a** and **4a**, respectively (Scheme 1.2). This was further confirmed by IR (the C=O stretching frequencies of **1**, **2**, **3** and **4** are 1735, 1720, 1730 and 1730 cm^{-1} while those for the corresponding dimers **1a**, **2a**, **3a** and **4a** are 1740, 1725, 1730 and 1735 cm^{-1}, respectively) and ^{1}H NMR (disappearance of C11-H and C12-H proton signals in monomers and the appearance of peaks at around 4.3-5.5 δ in photoproducts corresponding to cyclobutyl protons).

IR as well as ^{1}H NMR spectral techniques were used to determine the location of the site [styrenic C11=C12 and pyrone double bonds C3=C4] for photodimerization reaction in the solid state. The integration of cyclobutyl protons of photodimers **1a-4a** in their ^{1}H NMR spectra corresponds to four protons indicating that the [2+2] photocycloadditon is only across the styrenic double bond. In IR spectrum, the carbonyl stretching frequency of the monomers **1-4** and their corresponding dimers **1a-4a** are within 5 cm^{1}

indicating that photodimerization is through the styrenic double bond (dimerization across the pyrone double bond results in deconjugation). The yields of products in all the cases were *ca* 75-85% as determined from the ^{1}H NMR spectra. The configurational assignments were confirmed based on the arrangement of molecules in the crystals. In order to investigate the stereochemistry of the dimers **1a**-**4a** and rationalize the photostability of **5** in terms of crystal packing, the detailed crystallographic analyses of **1**, **2** and **5** were undertaken. Crystals of **1**, **2**, **3a** and **5** were obtained by slow evaporation from 1:2 ratio of chloroform and ethanol. Attempts to obtain suitable X-ray quality crystals of **3** were unsuccessful. The crystals of **3a** (photodimer of **3**) and **4** appeared to be well formed but had a mosaicity distribution over long ranges (peak widths of 1.5 to 2.2 degrees) and hence diffracted poorly. Also the stereochemistry of dimer **3a** was unequivocally established based on the single crystal X-ray diffraction study. Attempts to grow X-ray quality single crystals of **4** and its photodimer **4a** were unsuccessful. However, In view of a short crystallographic axis [a = axis 4.033(1) Å], the reactant crystals corresponds to β-packing mode.

Structure **1** contains two molecules in the asymmetric unit designated hereafter as **A** and **B**. The perspective views of **1** (molecule **A**), **2**, **3a** and **5** along with the atomic numbering scheme are depicted in Figure 1, 2, 3 and 4, respectively (thermal ellipsoids are given at 30% probability level).



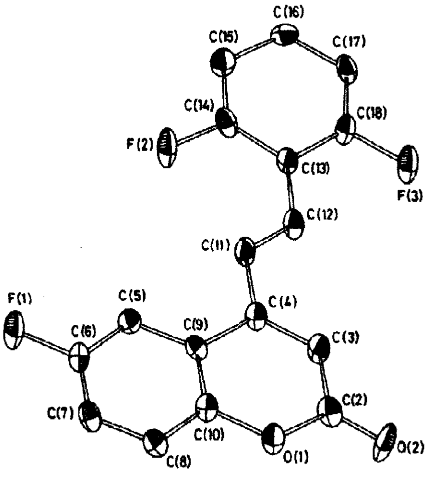


Figure 1. ORTEP plot of **1** (Molecule **A**) Figure 2. ORTEP plot of 2

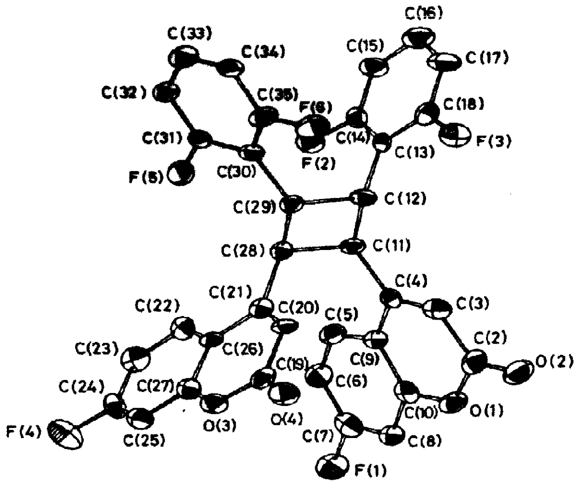


Figure 3. ORTEP plot of photodimer **3a**

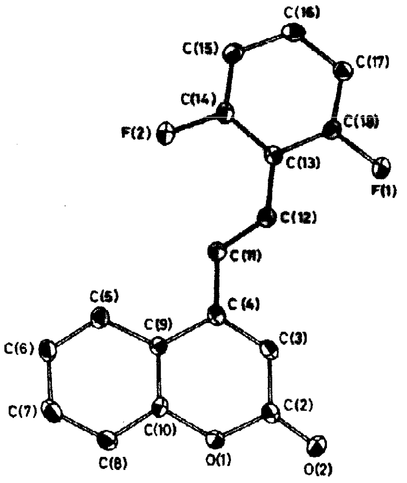


Figure 4. ORTEP plot of 4

Structure-Reactivity Correlations

To achieve [2+2] topochemical photodimerization reactions in the solid state, the centre-to-centre distance between the reactive double bonds should be less than *ca.* 4.2 Å and also the overlap of the π-orbitals of the reactive partners should be favorably juxtaposed (Figure 5).[1] 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 (11), C (12), C (11') and C(12'), 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'), and d is the displacement distance between the reactive partners, C(11) = C(12), C(11') = C(12'). The ideal values of θ_1, θ_2, θ_3 and d for topochemical photodimerization reaction are 0, 90, 90° and 0 Å respectively.[5b] In crystal **1**, the centre-to-centre distance between the reactive partners of styrenic double bonds (C11=C12) and the pyrone double bonds (C3=C4) of their translated molecules along *b* axis is 3.810 Å (same for both **A** and **B**) and in crystal **2** it is 3.867 Å along the *a*-axis. In crystal **5**, the minimum centre-to-centre distance observed between the styrenic and pyrone double bonds and their centrosymmetrically related counterparts are 6.614 and 6.092 Å, respectively and hence the crystals are photostable. The values of θ_1, θ_2, θ_3 and d for the styrenic double bonds of molecules **A** and **A'** in crystal **1** are 0.0, 66.7, 75.7° and 0.9 Å, respectively and those for **B** and **B'** 0.0, 75.9, 100.0° and 0.6 Å. In crystal **2** these values are 0.0, 104.5, 75.1° and 0.8 Å.

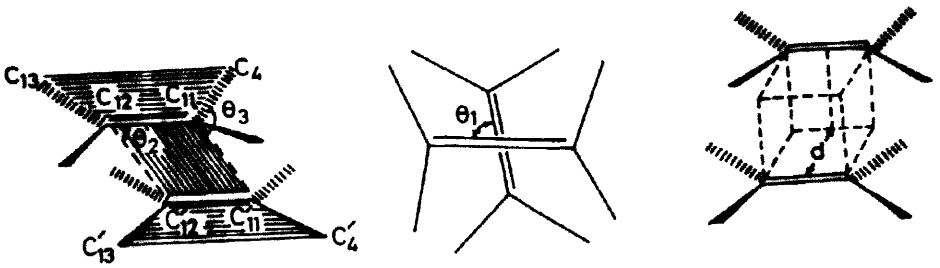


Figure 5. Pictorial representation of θ_1, θ_2, θ_3 and d parameters.

Though these values differ from the ideal values, the dimerization across the styrenic bond takes place, which is indeed, confirmed by the ^{1}H NMR and IR spectra. In fact, in most cases, it is observed that the values for θ_1, θ_2, θ_3 and d do not correspond to the ideal values.[3,5b] This is attributed to orientational flexibility of the reactants in the reaction cavity.

Analysis of Short Intermolecular Interactions

The intermolecular contacts involving C, H, F and O atoms show the existence of both C-H...F-C and C-H...O interactions in **1**, **2** and **5** (Figure 6 and 7). In addition to these contacts, crystal **2** has two F...F intermolecular interactions less than the sum of the van der Waals radii.[8]. Only those intermolecular C-H...O and C-H...F-C contacts with angles greater than 120° and H...F and O...H distances < 2.64 and < 2.65 Å, respectively are taken into account (Table 1). Based on the Cambridge Structural Database (CSD), the question of presence or absence of C-H...F interaction has been discussed at length by different investigators.[9-12] Shimoni and Glusker conclude that the C-F...H-X (X = C, N, O) interactions are much weaker than C=O...H-X (X = C, N, 0) [10a] but their role in the prediction of molecular packing in the crystals can not be overlooked.[10b] Howard *et. al* have concluded that the C-H...F contacts have very little significance in terms of energy.[11] Recently, Taylor and Dunitz[12] have carried out statistical analysis of Cambridge Structural Database and Brookhaven Protein Data Bank and concluded that fluorine hardly acts as a hydrogen bond acceptor .

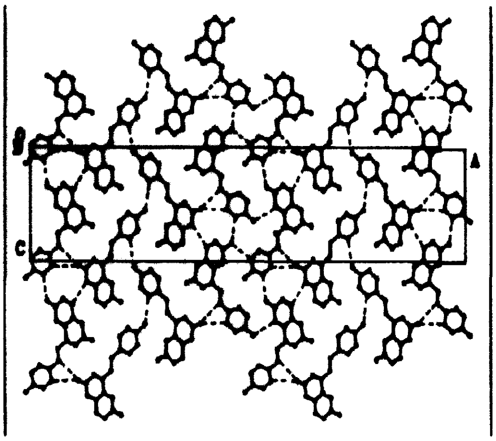


Figure 6. C-H...O and C-H...F short intermolecular contacts pattern crystal **1**

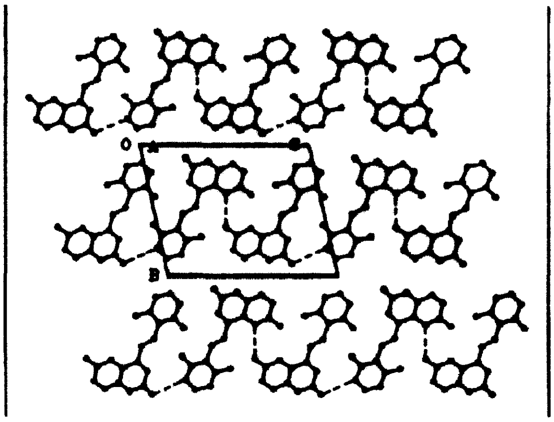


Figure 7. C-H...O, C-H...F and F...F short intermolecular contacts pattern crystal **2**

Table 1. Geometrical parameters of F...F, C-F...H-C and C-H...O short contacts*

atom bonded to	C...O/F(Å)	H...O/F(Å)	C-H...O/F (°)
Compound **1**			
BO(2) AC(12)H (x, 1+y, z)	3.64	2.65	154.5
BO(2) AC(14)H (x, 1+y, z)	3.51	2.62	157.3
BO(1) AC(8)H (x, y, 1+z)	3.43	2.49	159.4
AF(1) AC(15)H (x, y, 1+z)	3.07	2.57	118.9
AF(2)^1 AC(5)H (1-x, 1-y, 1/2+z)	3.55	2.55	164.0
AF(1) AC(17)H (2-x, -y, 1/2 + z)	3.39	2.44	153.5
BF(2)^2 BC(18)H (3/2-x, 3/2+y, 1/2 +z)	3.47	2.46	149.9
Compound **2**			
O(2)^3 C(17)H (1-x, 1-y, 2-z)	3.48	2.60	150.4
F(1) C(5)H (2-x, 1-y, 1-z)	3.46	2.59	158.4
		F...F	
F(3)^4 F(3) (-x, 1-y, 1-z)		2.89	
F(2) F(1) (2-x, 1-y, 1-z)		2.79	
Compound **5**			
O(2) C(11)H	3.37	2.59	140.6
O(2) C(16)H	3.25	2.55	129.3
O(2)^5 C(15)H (1-x, 1-y, 1-z)	3.36	2.45	166.5
F(1)^6 C(6)H (2-x, -y, -z)	3.27	2.64	125.0

Symmetry operation: ^{1}(x-1, y, 1+z); ^{2}(x, y+1, z); ^{3}(1+x, y, z); ^{4}(x, y, z-1); ^{5}(1+x, 1+y, 1+z); ^{6}(x, 1+y, 1+z):

*The van der Waal radii used[9] for C = 1.70, H = 1.20, O = 1.52 and F = 1.47 Å.

CONCLUSIONS

The dramatic change in the assembly of 4-styrylcoumarin molecules in the crystal lattice by the replacement of hydrogen atom by fluorine can be anticipated. But what is interesting is that the changes made are so designed as to bring about β-packing mode in four compounds (**1**, **2**, **3** and **4**). However, it cannot be said unequivocally that the presence of C-H...F interaction is solely responsible for this packing mode. In this connection the photoinertness of compound **5** even though there is a C-H...F interaction is noteworthy. It may be pointed out that the stereochemistry of dimers obtained in parent[7] and mono fluoro substituted 4-styrylcouamrins corresponds to *anti* H-T.[3b] Also, among the five monofluoro substituted 4-styrylcoumarins reported recently, two lead to the formation of centrosymmetric products and two others lead to mirror symmetric dimers and one remains photostable.[3] The observation that di- and tri- fluoro substitution in the 4-styrylcoumarin favour β-packing mode is significant. It seems reasonable to conclude that long range coloumbic interactions between fluorine atoms and the remaining interactions such as F...H, F...C and F...X seem to control the molecular assembly in addition to other interactions such as C-H...O, π...π, C=O ...π etc.

EXPERIMENTAL SECTION

General methods. Melting points were measured with a Buchi apparatus and are uncorrected. Infrared spectra (IR) were recorded on Perkin - Elmer 781 and Ultravoilet (UV) spectra on Shimadzu UV 2100. ^{1}H NMR 90 and 200 MHz spectra were recorded on Jeol FX-90Q and Bruker AC200, respectively. The chemical shifts (δ ppm) and the coupling constants (Hz) are reported in the standard fashion with reference to internal tetramethylsilane. Low-resolution mass spectra (LRMS) measurements were carried out with a Jeol JMS-DX 303 GC-MS instrument using a direct inlet mode. Relative intensities of the ions are given in parenthesis. Elemental analysis was carried out using a Carlo Erba 1106 analyzer.

3-Fluorophenyl acetate and 4-fluorophenyl acetate. 3-Fluorophenyl acetate[6a] and 4-fluorophenylacetate[6b] were synthesized by literature procedures.

4-Fluoro-2-hydroxyacetophenone and 5-fluoro-2-hydroxyacetophenone. Both were synthesized from the above corresponding fluorophenyl acetates by following the literature procedures.[6c] 4-Fluoro-2-hydroxyacetophenone; mp 25-26 °C (lit.[6d] 24 °C); 5-fluoro-2-hydroxy acetophenone; mp 56-58 °C (lit[6b] mp 56.5-57 °C).

The following were prepared by the representative procedure described below:

1-(5-Fluoro-2-hydroxyphenyl)-3-(4-fluorophenyl)-2-propen-1-one.[6] To a solution of 5-fluoro-2-hydroxyacetophenone (10 mmol) in ethanol (4 ml) was added dropwise a solution of 50% aq. NaOH (4 mL) while stirring to get a homogeneous paste. To this paste was added dropwise a solution of 4-fluorobenzaldehyde (15 mmol) in ethanol (3 mL). After keeping this overnight in the refrigerator the reaction mixture was decomposed with dil. HCl (2N). The yellow precipitate was filtered off and washed with 10 mL of distilled water to remove the traces of HCl and dried under reduced pressure. The residue was subjected to column chromatography on silica gel using 5% ethylacetate in petroleum ether as eluent. Recrystallization from ethanol gave yellow needles.

Yield 90 %; mp 179-181 °C; IR (nujol); 1650, 1590, 1510, 1380, 1170, 1030, 980, 840 cm^{-1}; ^{1}H NMR, (CDCl$_3$, 90 MHz), δ: 6.91 (2H, t, J = 7.2 Hz), 7.3 (1H, dd, J = 6.9 and 2.8 Hz), 7.42 (2H, t, J = 8.1 Hz), 7.5 – 8.0 (4H, m), 12.5 (1H, s, Ar-OH); Anal. Calcd. for $C_{15}H_{10}F_2O_2$: C, 69.23 ; H, 3.87 %. Found C, 69.16; H, 3.83 %.

3-(2,6-Difluorophenyl)-1-(5-fluoro-2-hydroxy phenyl)-2-propen-1-one. Yield: 92%; mp 131-133 °C. IR (nujol), 1635, 1600, 1565, 1380, 1340, 1250, 1210, 755 cm^{-1}; ^{1}H NMR, (CDCl$_3$, 90 MHz) δ: 6.93 (1H, dd, J = 7.1 and 3 Hz), 7.2 (1H, t, J = 7.8 Hz), 7.28 – 7.56 (3H, m), 7.61 – 8.0 3H, m), 12.45 (1H, s, Ar-OH); Anal. Calcd. for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26 %. Found C, 64.69; H, 3.21 %.

3-(2,6-Difluorophenyl)-1-(4-fluoro-2-hydroxyphenyl)-2-propen-1-one. Yield 92%; mp 135-137 °C; IR (nujol): 1630, 1600, 1555, 1330, 1255, 1200, 750 cm^{-1}; ^{1}H NMR, (CDCl$_3$, 90 MHz), δ: 6.52 (2H, t, J = 7.8), 6.61 (1H, dd, J = 7.1) and 2.8), 6.66 – 7.2 (3H, m), 7.28 – 8.1 (3H, m), 13.05 (1H, s, Ar-OH); Anal. Calcd. for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26 %. Found C, 64.67; H, 3.23 %.

3-(2-Fluorophenyl)-1-(5-fluoro-2-hydroxyphenyl)-2-propen-1-one. Yield 93%; mp 118-121 °C; IR (nujol): 1635, 1590, 1550, 1350, 1150, 800, 765, 730 cm^{-1}; ^{1}H NMR, (CDCl$_3$, 90 MHz), δ: 6.92 (1H, dd, J = 6.9 and 2.8 Hz), 7.2 (2H, t, J 7.1 Hz), 7.41 (1H, dd, J = 7.1 and 3.1 Hz), 7.52 – 8.1 (5H, m), 12.6 (1H, s, Ar-OH); Anal. Calcd. for $C_{15}H_{10}F_2O_2$: C, 69.23 ; H, 3.87 %. Found C, 69.14; H, 3.81 %.

3-(2,6-Difluorophenyl)-1-(2-hydroxyphenyl)-2-propen-1-one. Yield 88%; mp 107-109 °C IR (nujol): 1640, 1620, 1580, 1375, 1210, 1025, 1000, 780, 750, 720, 730 cm^{-1}; ^{1}H NMR, (CDCl$_3$, 90 MHz), δ: 6.9-8.02 (8H, m), 7.89 (1H, dd, J = 7.2 and 2.5 Hz), 12.65 (1H, s, Ar-OH); Anal. Calcd. for $C_{15}H_{10}F_2O_2$: C, 69.23 ; H, 3.87 %. Found C, 69.14; H, 3.83 %.

The following were prepared by the representative procedure described below:

4-(4-Fluorostyryl)-6-fluorocoumarin (1) [General procedure for all the di-fluoro compounds]. A mixture of the corresponding fluoro chalcone (1.211g, 5 mmol) and [ethyl (triphenylphosphoranylidene) acetate], ($Ph_3P{=}CHCOOEt$) (2.613 g, 7.5 mmol) in toluene (20 mL) was refluxed for 24 h. The reaction mixture was cooled and the solvent was evaporated under reduced pressure. The crude residue was subjected to column chromatography on silica gel using 10% ethylacetate in petroleum ether as eluent. Recrystallization from chloroform and ethanol (1:2 ratio) gave pale yellow needles. yield 82%; mp 202-205 °C; UV λ_{max} (ethanol): 329.5 nm; IR (nujol): 1735, 1650, 1600, 1500, 1410, 1200, 1150, 960, 870, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.64 (1H, s, H-3), 7.1-7.4 (6H, m), 7.47 (1H, dd, J = 8.8 and 2.6 Hz. H-5), 7.59 (2H, dd, J = 8.7 and 5.4 Hz, H-14, and H-18; LRMS (m/z): 284 (M^+ 100 %), 267 (91), 256 (73), 239 (27), 227 (51), 207 (28), 201 (23), 189 (27), 133 (21). Anal. Calcd. for $C_{17}H_{10}F_2O_2$: C, 71.83 ; H, 3.55 %. Found C, 71.76; H, 3.49 %.

4-(2,6-Difluorostyryl)-6-fluorocoumarin (2). yield 90 %; mp 178-181 °C; UV λ_{max} (ethanol): 315 nm ; IR (nujol): 1720, 1620, 1575, 1480, 1380, 1240, 1210, 1005, 880, 830, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 6.65 (1H, s, H-3), 7.0 (2H, t, J = 8.7 Hz, H-15 and H-17), 7.2-7.5 (5H, m), 7.6 (1H, d, J = 16.4 Hz, H-12); LRMS (m/z): 302 (M^+ 100 %), 274 (50), 254 (25), 245 (17), 225 (20), 189 (32) 136 (13); Anal. Calcd. for $C_{17}H_9F_3O_2$: C, 67.56, H, 3.00 %. Found C, 67.51; H, 2.94 %.

4-(2,6-Difluorostyryl)-7-fluorocoumarin (3) yield 85%; mp 205-208 °C; UV λ_{max} (ethanol): 310.5 nm ; IR (nujol): 1730, 1620, 1390, 1280, 1220, 1140, 1005, 975, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.58 (1H, s, H-3), 6.25-7.2 (4H, m), 7.33 (1H, t, J = 8.3 Hz), 7.35 (1H, d, J = 16.4 Hz, H-11), 7.66 (1H, d, 16.4, H-12), 7.76 (1H, dd, J = 8.6 and 6.0 Hz); LRMS (m/z): 302 (M^+ 100 %), 274 (55), 261 (10), 254 (27), 245 (19), 225 (19), 219 (6), 189 (27), 127 (12); Anal. Calcd. for $C_{17}H_9F_3O_2$: C, 67.56, H, 3.00 %. Found C, 67.53; H, 2.96 %.

4-(2-Fluorostyryl)-6-fluorocoumarin (4) yield 90 %; mp 198-201 °C; UV λ_{max} (ethanol): 324 nm ; IR (nujol): 1730, 1650, 1625, 1580, 1500, 1420, 1390, 1250, 1170, 960, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 6.61(1H, s, H-3), 7.1 (2H, t, J = 8.5 Hz, H-15 and H-17), 7.3-7.5 (5H, m), 7.69 (2H, t, J = 16.4 Hz); LRMS (m/z): 284 (M^+ 100 %), 267 (75), 256 (54), 236 (18), 227 (35), 207 (26), 201 (15), 189 (32), 133 (18); Anal. Calcd. for $C_{17}H_{10}F_2O_2$: C, 71.83; H, 3.55 %. Found C, 71.73; H, 3.47 %.

4-(2,6-Difluorostyryl) coumarin (5). yield 86 %; mp 158-161 °C; UV λ_{max} (ethanol): 308.5 nm ; IR (nujol): 1720, 1630, 1600, 1390, 1285, 1240, 1210, 1180, 1140, 1005, 955, 785 cm^{-1}; ^{1}H NMR ($CDCL_3$, 200 MHz) δ 6.63 (1H, s, H-3), 6.9 (2H, t, J = 8.6 Hz, H-15 and H-17), 7.2-7.5 (4H, m), 7.57 (1H, t, J = 7.7 Hz), 7.7 (1H, d, J = 16.4, H-12 and H-17), 7.77 (1H, d, 7.2 Hz); LRMS (m/z): 284 (M^+ 100 %), 256 (49), 243 (10), 236 (27), 227 (20), 207 (21), 201 (10), 171 (27) 118 (11), 63 (10); Anal. Calcd. for $C_{17}H_{10}F_2O_2$: C, 71.83; H, 3.55 %. Found C, 71.78; H, 3.51 %.

Irradiation procedure. The finely powdered crystalline samples of **1-5** placed at a distance of 30 cm from the Rayonet photochemical lamps (λ_{max} 320 nm, ±20) were irradiated simultaneously for about 35-40 hours. Compound **5** remain unchanged even after 8 days of continuous irradiation. During irradiation care was taken to expose samples uniformly by shaking the containers at regular intervals. Uniform temperature in the irradiation chamber was ensured by keeping a cooling fan on during the irradiation. Irradiation was continued until there was no further increase in the product formation.

Photodimer (1a). yield 78-80 %; mp 212-215 °C; UV λ_{max} (ethanol): 323 nm ; IR (nujol): 1740, 1710, 1585, 1525, 1500, 1430, 1390, 1250, 1175, 975 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.36 (1H, d, J = 8 Hz, H-11), 4.72 (1H, d, 8 Hz, H-12), 6.5 (1H, s, H-3), 7.17 (1H, s), 7.4 (1H, t, J = 8.8 Hz), 7.65-7.75 (2H, m), 7.8-8.0 (2H, m), 8.3-8.4 (2H, m); LRMS (m/z): 568 (M^+ 24 %), 459 (8), 446 (20), 403 (13), 351 (25), 284 (100), 267 (80), 256 (58), 239 (20), 227 (29), 201 (12), 189 (20); Anal. Calcd. for $C_{34}H_{20}F_4O_4$: C, 71.83, H, 3.55 %. Found C, 71.78; H, 2.50 %.

Photodimer (2a). yield 81-85 %; mp 223-226 °C; UV λ_{max} (ethanol): 321.5 nm ; IR (nujol): 1725, 1635, 1590, 1480, 1390, 1280, 1245, 1020, 970, 840, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.78 (1H, d, J = 8 Hz, H-11), 5.38 (1H, d, 8 Hz, H-12), 6.56 (1H, s, H-3), 6.79 (2H, t, J = 8.5 Hz, H-15 and H-17), 7.0-7.4 (4H, m); LRMS (m/z): 604 (M^+ 25 %), 477 (28), 352 (38), 324 (45), 302 (100), 274 (80), 254 (35), 225 (26), 189 (42), 136 (16); Anal. Calcd. for $C_{34}H_{18}F_6O_4$: C, 67.56, H, 3.00 %. Found C, 67.51; H, 2.94 %.

Photodimer (3a). yield 75-78 %; mp 210-213 °C; UV λ_{max} (ethanol): 309 nm ; IR (nujol): 1730, 1615, 1575, 1480, 1240, 1170, 1110, 955, 830, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.76 (1H, d, J = 8 Hz, H-11), 5.44 (1H, d, 8 Hz, H-12), 6.47 (1H, s, H-3), 6.6-7.3 (5H, m), 7.44 (1H, dd, J = 8.9 and 5.8 Hz); LRMS (m/z): 604 (M^+ 20 %), 577 (10), 464 (10), 449 (12), 351 (15), 302 (100), 274 (48), 254 (25), 245 (18), 225 (18), 189 (25); Anal. Calcd. for $C_{34}H_{18}F_6O_4$: C, 67.56, H, 3.00 %. Found C, 67.48; H, 2.92 %.

Photodimer (4a). yield 78-81 %; mp 225-228 °C; UV λ_{max} (ethanol): 321 nm ; IR (nujol): 1735, 1620, 1575, 1490, 1440, 1240, 1165, 1100, 955, 825, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.98 (1H, d, J = 8 Hz, H-11), 5.35 (1H, d, 8 Hz, H-12), 6.74 (1H, s, H-3), 6.91 (1H, d, 6.9 Hz), 7.41 (2H, t, J = 8.8 Hz, H-15 and H-17), 7.5-7.62 (5H, m), 7.7-7.95 (2H, m); LRMS (m/z): 568 (M^+ 15 %), 540 (8), 459 (10), 446 (8), 431

(8), 403 (8), 284 (100), 267 (65), 256 (48), 227 (15), 189 (20); Anal. Calcd. for $C_{34}H_{20}F_4O_4$: C, 71.83, H, 3.55 %. Found C, 71.76; H, 2.48 %;

X-ray analysis

Crystal 1. A pale yellow colored needle-shaped crystal with the dimensions 0.50 x 0.40 x 0.25 mm^3 was used for data collection. Intensity data was collected on a Siemens-P4 diffractometer using monochromated Mo-Kα in ω-2θ mode at 163 K. The crystal was determined to be orthorhombic, space group $Pna2_1$, a = 56.767 (6), b = 3.810 (1), c = 11.739 (3) Å, V = 2538.9 (1) $Å^3$, Z = 8, $D_{(cal)}$ = 1.487 g cm^{-3}, linear absorption coefficient, μ = 0.117 cm $^{-1}$ and formula weight = 284.25 for $C_{17}H_{10}F_2O_2$, F (000) = 1168. The total number of reflections was 2569 and those with I > 2 σ (I) was 2098. The final R (on F^2) = 0.049 and Final R_w (on F^2) = 0.071. The largest difference peak/hole = 0.17/-0.15 e. A^{-3}.

Crystal 2. A pale yellow colored needle-shaped crystal with the dimensions 0.45 x 0.30 x 0.50 mm^3 was used for data collection. Intensity data was collected on an Enraf-Nonius CAD-4 diffractometer using monochromated Mo-Kα in ω-2θ mode at 293 K. The crystal was determined to be triclinic, space group P 1, a = 3.867 (1), b = 11.563 (3), c = 14.595 (3) Å, α = 77.66 (2), β = 88.45 (2), γ = 87.35 (2)°, V = 636.7 (3) $Å^3$, Z = 2, $D_{(cal)}$ = 1.576 g cm^{-3}, linear absorption coefficient, μ = 0.132 cm $^{-1}$ and formula weight = 302.24 for $C_{17}H_9F_3O_2$, F (000) = 308. The total number of reflections was 1649 and those with I > 2 σ (I) was 698. The final R (on F^2) = 0.059 and Final R_w (on F^2) = 0.136. The largest difference peak/hole = 0.28/-0.34 e. A^{-3}.

Crystal 4. The crystal structure **4** could not be refined [a = 4.033 (1); b = 11.640 (2); c = 13.893 (3) Å; α = 78.17 (2); β = 88.45 (2); γ = 86.64 (3)°; V = 637.17 $Å^3$; Z = 4; space group = P1] as the number of observed reflections were insufficient.

Crystal 5. A pale yellow colored needle-shaped crystal with the dimensions 0.40 x 0.35 x 0.20 mm^3 was used for data collection. Intensity data was collected on a Siemens-P4 diffractometer using monochromated Mo-Kα in ω-2θ mode at 163 K. The crystal was determined to be triclinic, space group P 1, a = 7.021 (1), b = 8.442 (2), c = 11.697 (2) Å; α = 87.23 (1); β = 72.69 (1); γ = 74.40 (1)°; V = 637.1 (2) $Å^3$, Z = 2, $D_{(cal)}$ = 1.482 g cm^{-3}, linear absorption coefficient, μ = 0.116 cm $^{-1}$ and formula weight = 284.25 for $C_{17}H_{10}F_2O_2$, F (000) = 292. The total number of reflections was 1666 and those with I > 2 σ (I) was 1098. The final R (on F^2) = 0.047 and Final R_w (on F^2) = 0.088. The largest difference peak/hole = 0.19/-0.22 e. A^{-3}.

Crystal 3a. A colorless needle-shaped crystal with the dimensions 0.35 x 0.40 x 0.30 mm^3 was used for data collection. Intensity data was collected on an Enraf-Nonius CAD-4 diffractometer using monochromated Mo-Kα in ω-2θ mode at 293 K. The crystal was determined to be monoclinic, space group $P2_1/c$, a = 12.379 (4), b = 15.889 (3), c = 13.354 (4) Å, β = 103.36 (3)°, V = 2555.5 (1) Å^3, Z = 4, $D_{(cal)}$ = 1.571 g cm^{-3}, linear absorption coefficient, μ = 0.132 cm^{-1} and formula weight = 604.48 for $C_{34}H_{18}F_6O_4$, F (000) = 1232. The total number of reflections was 3838 and those with I > 2 σ (I) was 1662. The final R (on F^2) = 0.118 and Final R_w (on F^2) = 0.227. The largest difference peak/hole = 0.63/-0.49 e. A^{-3}.

The structures of **1**, **2** ,**5** and **3a** were solved using direct method SHELXS-86.[15a] Using the default option of the program, all the positions corresponding to the non-hydrogen atoms could be identified from the E map. Full matrix least-squares refined using SHELXL-93.[15b] In the final cycles of the refinement the hydrogen atoms were fixed using the option HFIX in SHELXL-93 and were refined as riding hydrogens. Anisotropic thermal parameters of non-hydrogen atoms, atomic coordinates, bond lengths and bond angles involving hydrogen atoms will be deposited at the Cambridge Crystallographic Data Centre (CCDC).

ACKNOWLEDGEMENTS

We thank UGC (KVM), INSA (KV) and DST, India (TNG) for financial assistance. We also gratefully acknowledge Prof. Ward T. Robinson, University of Canterbury for data collection on compounds of **1** and **5**.

REFERENCES

1. Cohen M. D.; Schmidt, G. M. J.; *J. Chem. Soc.*, **1964**, 1996; Cohen, M. D.; Schmidt, G. M. J.; Sonntag, F. I.; *J. Chem. Soc.*, **1964**, 2000; Schmidt, G. M. J.; *J. Chem. Soc.*, **1964**, 2014.
2. (a) Amarendra Kumar, V.; Begum, N. S.; Venkatesan, K.; *J. Chem. Soc., Perkin Trans.* 2, **1993**, 463.
   (b) Marrison, H.; Curtis, H.; McDowell, T.; *J. Am. Chem. Soc.*, **1966**, 88, 5415; Hoffman, R.; Wells, P.; Marrison, H.; *J. Org. Chem.*, **1971**, 36, 102.
3. (a) Vishnumurthy, K.; Guru Row, T. N.; Venkatesan, K.; *J. Chem. Soc., Perkin Trans.* 2, **1996**, 1475.
   (b) Vishnumurthy, K.; Guru Row, T. N.; Venkatesan, K.; *J. Chem. Soc., Perkin Trans.* 2, **1997**, 615.
4. Amarendra Kumar, V.; Venkatesan, K.; *J. Chem. Soc., Perkin Trans.* 2, **1993**, 2429.
5. (a) Desiraju, G. R.; *Crystal Engineering: The design of organic solids*, Elsevier, Amsterdam, **1989**.
   (b) Ramamurthy,V,; Venkatesan,K.; Chem .Rev. 87, **1987**, 433.
6. (a) Chen, F. C.; Chang, C. T.; Lin, C. H.; J. Formosan. Sci., **1952**, 6, 81; (b) Corse, J.; Ingraham,, L. L. *J. Org. Chem.*, **1951**, 16, 1345; (c) Amin, G. C.; Shah, N. M.; *Org. Synth. Collct.* Vol. III, 281; (d)

Chang, C. T.; **Chen**, F. C.; *J. Chem. Soc.*, **1961**, 3155; (e) Joshi, U. K.; **Kelkar**, R. M.; **Paradkar**, **M**. V.; ***Indian Chem.*** *Soc.*, **1983**, 22, 151.

7. **Narasimha Moorthy**, J.; Venkatesan, K.; *Bull. Chem. Soc. Jpn.*, **1994**, 67, 1.
8. **Bondi**. **A**.; *J. Phys. Chem.*, **1964**, 68, 441.
9. **Murray-Rust**, P.; Stallings, W. C.; Monti, C. T.; Preston, R. K.; Glusker, J. P.; *J. Am. Chem. Soc.*, **1983**, 105, 3206; Howard, J. A. K.; Hoy, V. J.; O' Hagan, D.; Smith, G. T.; *Tetrahedron*, **1996**, 52, 12613; Castano, C. F.; Foces, C. F.; Cano, F. H.; Claramunt, R. M.; Escolatico, C.; Fruchier, A.; Elguero, J.; *New J. Chem.* **1997**, 21, 195.
10. Shimoni, L.; Glusker, J. P.; *Structural Chem.*, **1994**, 5, 383; (b) Shimoni, L.; Glusker, J. P.; Bock, C. W.; *J. Phys. Chem.*, **1995**, 99, 1194.
11. Howard, J. A. K.; Hoy, V. J.; Hagan, D.; Smith, T.; *Tetrahedron*, **1996**, 52, 12613.
12. Dunitz, J. D.; Taylor, R.; *Chem. Eur. J.*, **1997**, 3, 89; Dunitz, J. D.; *Mol. Cryst. Liq. Cryst.*, **1996**, 279, 209.
13. (a) Sheldrick, G. M.; SHELXS 86, *Program for Crystal Structure Solution*, Gottingen University, **1986**; (b) Sheldrick, G. M.; SHELXL 93, *Program for Crystal Structure Determination*, Gottingen University, **1993**.