Pergamon

Tetrahedron 54 (1998) 11235–11246

TETRAHEDRON

# Unusual Photodimerization of 7-Fluoro-4-methylcoumarin and 6-Fluoro-4-methylcoumarin in the Solid State

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Received 2 April 1998; revised 29 June 1998; accepted 2 July 1998

**Abstract:** Photodimerization of 7-fluoro-4-methylcoumarin **1** is topochemical while 6-fluoro-4-methylcoumarin **2** does not lead to the expected product based on the topochemical principles. Compound **1** yield an *anti*-HT photodimer with a lower dimer conversion while compound **2** results in a *syn*-HH photodimer. The packing features of **1, 2** and **2a** (the photodimer of **2**) have been unequivocally established by single crystal X-ray diffraction studies. The rationale for the significant lower dimer conversion in **1** is provided. The defect induced dimerization reaction in **2** as a function of temperature is analyzed which verifies that the reaction proceeds with an induction period. The details of the interactions involving fluorine are analyzed. © 1998 Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

The organization of monomer molecules in their crystal structures generally serves as a guideline to predict the stereochemistry of the photodimer.[1] Based on the topochemical principles, the packing of the monomer molecules are classified as α-, β- and γ- type depending upon the distance between the neighboring molecules and the orientation with respect to the centre of inversion or mirror plane.[1] In the α-type crystal, the double bonds of neighboring molecules arrange at a distance of *ca.* 3.7 Å across the centre of inversion to give a centrosymmetric photodimer (*anti*-HT, α-packing mode). The β-type is characterized by a lattice having one axial length of 4.0 ± 0.1 Å yielding a dimer with mirror symmetry (*syn*-HH, β-packing mode) while the photochemically inactive γ-type crystal has the double bonds of neighboring molecules at more than 4.2 Å. Recent studies on fluoro substituted styrylcoumarins and coumarins indicate a preference to β-packing modes and the presence of fluorine appears to serve as a steering agent.[2] Extensive studies on chloro, bromo, methoxy and acetoxy derivatives of coumarin[3] and cinnamic acid[4] have led to the understanding of the packing modes of the monomer molecular units in relation to the substituent pattern. 4-Methylcoumarin has been analyzed to belong to the γ-type lattice and hence photostable.[3b] Substitution of chlorine at the 7 position on coumarin leads to a *syn*-HH

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*PII:* S0040-4020(98)00656-5

photodimer.[3b] Substitution of chlorine at the 6 position also leads to a *syn*-HH photodimer even though the pre-organization of the molecules in the monomer crystal lattice does not permit such conversion.[5] The rationale for this non-topochemical photodimerization is provided by invoking the reaction to originate at a defect site. It is reported that crystals of 7-methoxy-4-methylcoumarin[6] produce two dimers of different stereochemistry *syn*-HH and *syn*-HT when subjected to irradiation in the crystalline state. The formation of the minor product, *syn*-HT is non-topochemical. Work done by several groups has brought to light many cases of substituted anthracenes behaving in a non-topochemical fashion.[7] It was also established through electron microscopic studies that these non-topochemical reactions originate from the defect regions of the crystal lattice.

It is to be noted that the packing in the monomer structures of 6-fluorocoumarin and 7-fluorocoumarin also suggests the formation of *syn*-HH photodimer.[2b] If non-planarity is present in the monomer structures like benzylidene-DL (±)-piperitone, the preference is *anti*-HT packing mode in the crystal lattice.[8] In this article we present an analysis of the photobehaviour of 7-fluoro-4-methylcoumarin **1** and 6-fluoro-4-methylcoumarin **2** in terms of the nature of the crystal packing mode and the effectiveness of the steering capability of fluorine in such molecular assemblies to gain insights into the nature of interactions invoked by fluorine.

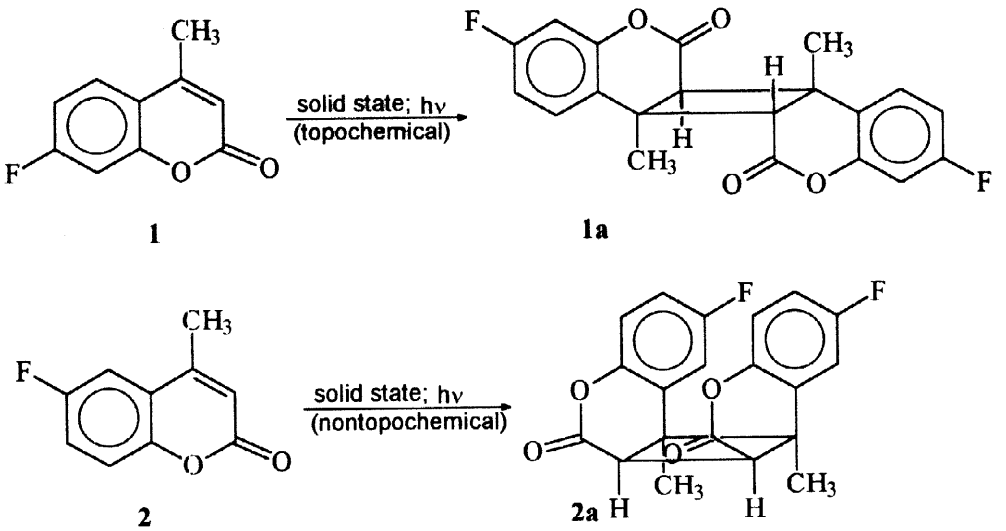
## RESULTS AND DISCUSSION

Compounds **1** and **2** were synthesized and purified by the procedure described in the literature.[9] Crystals were grown from a mixture of 1:2 ratio of chloroform and ethanol. The powder samples of **1** and **2** were irradiated in a Rayonet photochemical reactor ($\lambda_{max}$ = 320 nm ± 20) at room temperature. The progress of the reaction was monitored by $^1$H NMR, IR and thin layer chromatography. The photodimers **1a** and **2a** were separated from their corresponding monomers (**1** and **2**) by column chromatography eluting with 10% ethyl acetate in petroleum ether.

The molecular ion peak at m/z 356 in the mass spectra indicated the formation of photodimers **1a** and **2a** (Scheme 1). This was further confirmed by IR (the C=O stretching frequencies of **1** and **2** are 1720 and 1710 cm$^{-1}$ while those for the corresponding dimers **1a** and **2a** are 1750 and 1760 cm$^{-1}$ respectively) and $^1$H NMR (disappearance of C3-H proton signal in both monomers and the appearance of peaks at around 3.4-3.7δ in photodimers corresponding to cyclobutyl protons).

Generally, the cyclobutyl protons for the *anti* coumarin derivatives[10] resonate near δ 3.4 and methyl singlet at δ 1.2, while the corresponding resonances of the *syn* dimers occur near δ 3.6 and δ 1.7, respectively. The chemical shifts of cyclobutyl protons and methyl singlet in the photodimer of **1a** occur at δ 3.43 and δ 1.27, respectively indicating the stereochemistry is *anti* and from the crystal packing it has been assigned *anti*-HT (Scheme 1). On the other hand, the cyclobutyl protons and methyl singlet of photodimer **2a** appear at δ 3.66 and δ 1.65, respectively indicating the product is *syn* dimer. The stereochemistry *syn*-HH of dimer **2a** is unequivocally established by X-ray crystallography.

Crystals **1** and **2** crystallize in space groups $P2_1/c$ and $P\bar{1}$ respectively consisting of two molecules in the asymmetric unit designated hereafter as **A** and **B** in each case. The perspective views of **1**, **2** and **2a** along with the atomic numbering scheme are shown in Figure. 1, 2 and 3, respectively (thermal ellipsoids are given at 30% probability level).




**Scheme 1**

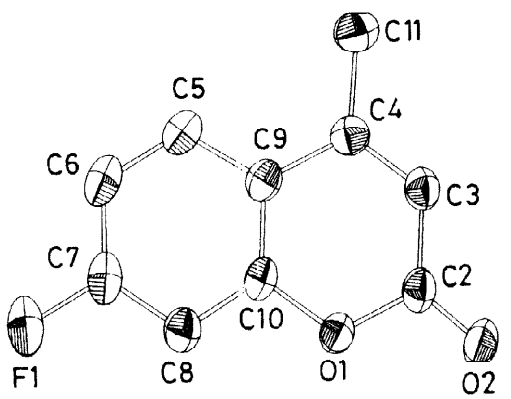



Figure 1. ORTEP plot of **1**

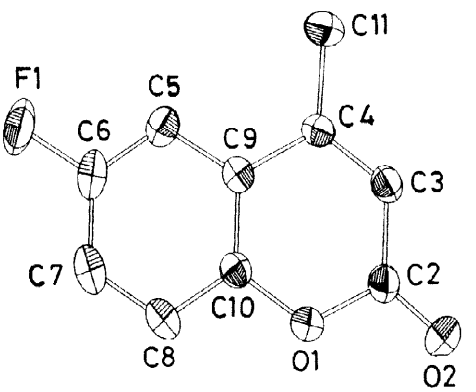



Figure 2. ORTEP plot of **2**

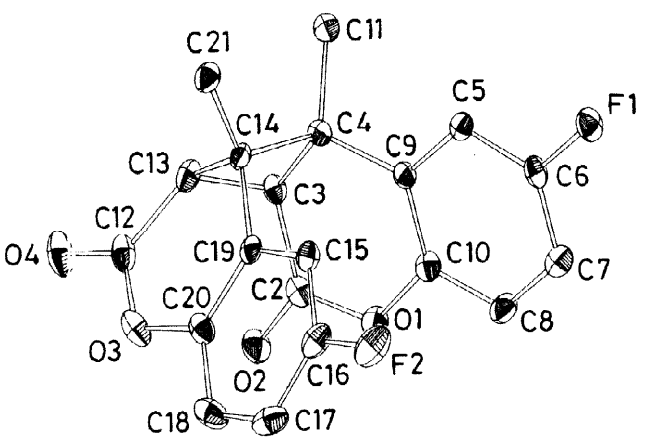



Figure 3. ORTEP plot of photodimer **2a** depicting the formation of a mirror symmetric (syn-HH) dimer

*Structure-Reactivity Correlations of Crystal 1*

For a [2+2] topochemical photoreaction, the centre-to-centre distance between the potentially reactive double bonds should be less than 4.2 Å and the overlap of the π-orbitals of the reactive partners can be identified through the geometrical parameters $\theta_1$, $\theta_2$, $\theta_3$ and d (Figure 4).[17] These parameters should ideally be 0, 90, 90° and 0 Å respectively.[1] The centre-to-centre distance between the reactive centres C(3)=C(4) in molecule **B** and its centrosymmetrically reactive partner **B'** is 4.16 Å while between molecule **A** and its centrosymmetrically related molecule **A'**, the minimum centre-to-centre distance observed is 5.90 Å which is more than the required distance of 4.2 Å and is photostable. It is seen from the packing diagram (Figure 5) that the molecules are related by centre of inversion, upon irradiation to give an *anti*-HT photodimer in the crystalline state. The appropriate geometrical parameters $\theta_1$, $\theta_2$, $\theta_3$ and d values for molecule **B** are 0.0, 112.6, 102.5° and 0.7 Å, respectively. The deviation of these parameters from the ideal values have been observed in many other photolabile crystals and it was shown that the π-orbitals of the reacting partners need not always be exactly parallelly oriented.[11]

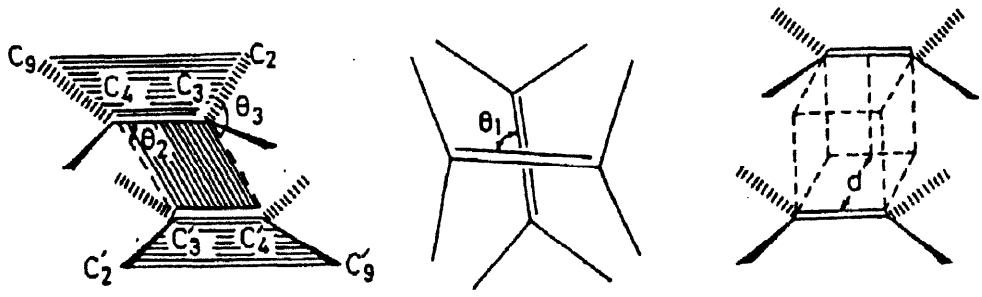



Figure 4. Pictorial representation of $\theta_1$, $\theta_2$, $\theta_3$ and d parameters

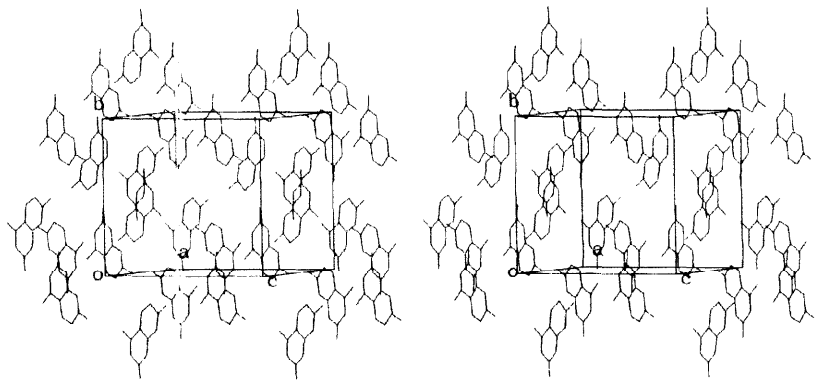


Figure 5. Stereoscopic view of crystal packing of **1**

It may be mentioned that the lower dimer conversion of **1** (20-25%) may be partly due to the fact that only one of the molecules in the asymmetric unit (molecule **B**) is in a reacting situation. Molecule **A** is not favorably positioned for the reaction as the distance of separation between the nearest molecules is as large as 5.90 Å. It is perhaps relevant to draw attention to the reactivities of 4-styryl-6-fluorocoumarin and 4-(3-fluorostyryl) coumarin.[12] Both belong to the space group P1, containing two molecules in the asymmetric unit. In the former, only one of the molecules react giving about ~50% yield while in the latter both molecules react resulting in a much higher yield (~ 80%). It must be stressed that all factors except the particle size which influence the product yield are the same as the irradiation was carried out under identical experimental conditions.

*Structure-Reactivity Correlations of crystal* **2**

Figure 6 is a stereo plot showing the packing of both the molecules A and B in the unit cell. The centre-to-centre distances between the centrosymmetrically related partners (C3=C4) is 4.68 Å in molecule **A** and 6.13 Å in molecule **B**. The separation distance in molecule **B** is clearly well above the normally accepted distance criterion for the bimolecular photoreaction. On the other hand the situation with respect to molecule **A** is not clear. If one assumes that at the separation distance of 4.68 Å (molecule **A**) photodimerization reaction could occur then the expected stereochemistry of the dimer should have corresponded to *anti*-HT. However the photoproduct obtained is *syn*-HH as confirmed by X-ray diffraction studies (Figure 3). The formation of the mirror symmetric photodimer violates the so-called

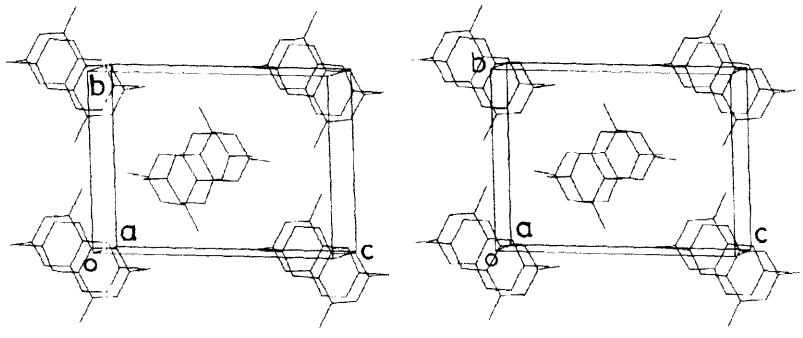



Figure 6. Stereoscopic view of crystal packing of **2**

conformational fixation of the reacting partners in the crystal lattice. It follows that the results cannot be explained on topochemical grounds. Two conclusions emerge from this observation. Firstly the separation distance of 4.68 Å seems to be above the upper limit for the overlap of the π-orbitals of reactive double bonds (C3=C4). It is worth mentioning here that in the crystals of the photoreactive 7-chlorocoumarin, the centre-to-centre distance between the reactive (C3=C4) double bonds is 4.45 Å.[5] It was reported that in the β-form of p-formyl cinnamic acid, the centre-to-centre distance to be 4.825 Å - the longest distance reported for the so-called photolabile crystal.[13] However, recently Harris and

Patterson,[14] based on powder diffraction data, showed that the above structure reported by Nakanishi *et al*[13] actually corresponds to the γ-polymorph not the β-phase for which the separation distance is indeed 4.26 Å which is consistent with Schmidt's generalization for β-type.[1] What is noteworthy in all the photoreactive cases is that the separation distance between the reacting partners is well within ~4.50 Å. The fact that in crystal **2** the molecules do not react topochemically with the centre-to-centre distance between the reactive double bonds C3=C4 being 4.68 Å indicates that it costs much energy to perform translational movement in the direction of the π-orbitals so as to reduce the distance between the reactive bonds. Secondly, the fact that the reaction does take place and that the dimer *syn*-HH is obtained clearly shows that the reaction must occur non- topochemically at defect sites. Incisive studies by Craig and Sarti Fantoni[7] and later by Thomas and co-workers[7b] on the unusual photobehavior in a few cases have revealed the importance of the role of defects in reactivity. It is reasonable to presume the existence of such defects in crystal **2**. In general, defect initiated reactions involve an induction period, because at the beginning of the reaction, the concentration of the defects will be small and there would not be any

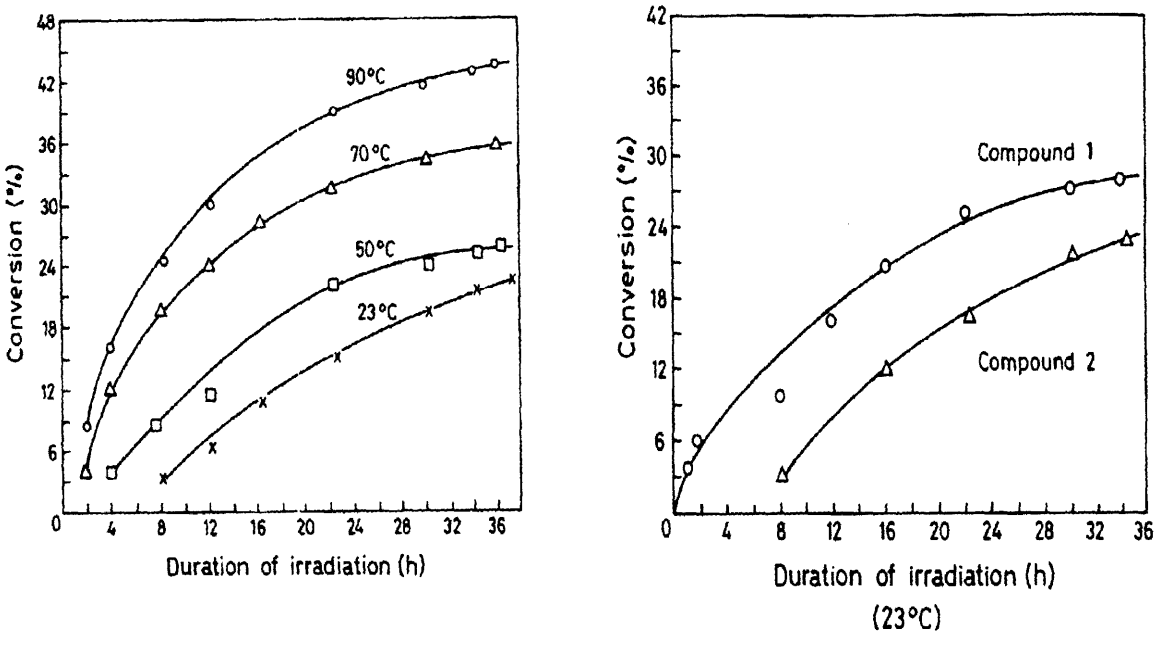



Figure 7. (a) Plot of percentage of conversion of crystal **2** to photodimer **2a** (*syn*-HH) *vs* duration of irradiation . (b) Plot of percentage of conversion of crystal **1** and **2** to photodimers **1a** and **2a**, respectively *vs* duration of irradiation at 23 °C.

appreciable reaction. As the reaction proceeds, the disorder in the crystal lattice grows and allows an appreciable amount of reaction. Crystals **2** were divided into four parts and were kept at different temparatures 23, 50, 70 and 90° C and irradiated. Time of irradiation *vs* dimer conversion plot for **2** shows an induction period which has been found to be characteristic of crystals undergoing photodimerization non-topochemically (Figure 7a).[6] After 4 h of irradiation, the percentage conversion of the samples at 23, 50, 70 and 90° C to the corresponding photodimers were found to be 0, 3, 8 and 12,

respectively. And after about 8 h at temperatures 23, 50, 70 and 90 °C, the percentage of conversion were about 3, 10, 20 and 26%, respectively. Also as the temperature at which the samples were irradiated is increased the induction period was found to decrease. The increase in dimer conversion with temperature could be partly due to the greater rotational and translational motions of the reactant. It has been observed that there is no induction period in crystal **1** (Figure 7b). The fact that the reaction involves a substantial induction period (4 hours) indirectly confirms that the reaction did not originate in the bulk of the crystal. These observations suggest that the defects responsible for the formation of *syn*-HH dimer are not inherently present and that at any rate the defect density cannot be significant prior to irradiation.

*Analysis of Short Intermolecular Interactions*

From the intermolecular contacts involving C, H, F and O atoms there is an evidence for the possible presence of both C-H...F-C and C-H...O short contacts in **2** and only C-H...O in compound **1** and its geometrical parameters are depicted in Table 1. There are no F...F inter molecular contacts in both these structures. The van der Waals radii[15] used for the atoms are as follows: C = 1.70, H = 1.20, O = 1.52 and F = 1.47 Å. For the intermolecular C-H...O and C-H...F-C contacts only those with angles greater than 110 ° and H...F and O...H distances < 2.64 and = 2.65 Å, respectively were considered. The analysis of C-F...H-X (X = C, N, O) interactions have shown that these interactions are weaker than C=O...H-X (X = C, N, O).[16] Shimoni and Glusker[17] concluded that even though C-F has only a marginal hydrogen bond acceptor capability there is directionality in its interactions. Such interactions cannot be ignored in predicting the modes of molecular packing in complexes and crystals. Dunitz and Taylor[18] concluded that the chemical factors influencing the strength of hydrogen bond (especially factors influencing hydrogen bond accepting ability) are still not completely understood.

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

| atom | bonded to | C...O/ C...F (Å) | O...H/F...H (Å) | C-H...O/F (°) |
|---|---|---|---|---|
| Crystal **1** | | | | |
| O2(B) | HCA(8) (x, 1+y, z) | 3.37 | 2.53 | 168.1 |
| O1(A) | HCB(3) (x, 1+y, z) | 3.49 | 2.62 | 156.6 |
| O1(B)[1] | HCA(3) (x-1, 1+y,z) | 3.52 | 2.64 | 155.7 |
| O2(A) | HCB(8) (x-1, 1+y, z) | 3.39 | 2.58 | 156.3 |
| Crystal **2** | | | | |
| F1(A) | HCB(11) (x, 1+y, 1+z) | 3.35 | 2.56 | 139.9 |
| O2(B) | HCA(11) (1-x, 1-y, -z) | 3.45 | 2.56 | 153.5 |
| O2(A) | HCB(11) (2-x, 1-y, 1-z) | 3.58 | 2.59 | 168.7 |
| O2(A) | HCB(7) (2-x, -y, 1-z) | 3.49 | 2.61 | 156.4 |

symmetry operation: [1](-x, y, z)

## CONCLUSIONS

It is interesting to note that the replacement of a single hydrogen atom by fluorine dramatically alters the molecular packing. Changes in molecular organization in crystal **1** result in a α-packing mode as against the anticipated β-packing observed in fluoro substituted styrylcoumarins[2a] and 6- and 7-fluorocoumarins.[2b]The formation of syn-HH photodimer in crystal **2** is rationalized in terms of a reaction at defect sites. The fact that the parent 4-methylcoumarin[3b] does not [2+2] photocycloaddition in the solid state while the fluoro derivatives do, brings out the importance of substitution of hydrogen by fluorine. To the best of our knowledge, the fluoro substituted derivative of crystal **2** appears to be the first case where the photodimerization occurs at defect sites non-topochemically.

## EXPERIMENTAL SECTION

**General Methods.** Melting points are uncorrected. Infrared spectra were recorded on Perkin - Elmer 781 and UV spectra on Shimadzu UV 2100. $^1$H (90 MHz) and $^{13}$C (22.5 MHz) NMR spectra were recorded on Jeol FX-90Q spectrometer. The chemical shifts (δ ppm) and the coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for $^1$H) or the central line (77.1 ppm) of $CDCl_3$ for $^{13}$C. In the $^{13}$C NMR spectra off-resonances multiplicities, when recorded, are given in parentheses. 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 parentheses. Elemental analysis was carried out using a Carlo Erba 1106 analyzer.

**Irradiation procedure.** The finely powdered crystalline samples of **1** and **2** placed at a distance of *ca.* 30 cm from the Rayonet photochemical lamps ($\lambda_{max}$ = 320 nm ± 20 ) were irradiated simultaneously for about 35-45 h. 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 irradiation. Irradiation was continued until there was no further increase in the product formation. The photoproducts were separated from their monomers by column chromatography on silica gel using 10% ethylacetate in petroleum ether as eluent. The percentage of conversion is 20-25% in **1** and 25-30% in **2** as determined from $^1$H NMR.

**3-Fluorophenyl acetate and 4-Fluorophenyl acetate.** 3-Fluorophenyl acetate[7a] and 4-fluoro-phenylacetate[7b] 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.[7c] 4-fluoro-2-hydroxyacetophenone; mp 25-26 °C (lit.[7d] 24 °C); 5-fluoro-2-hydroxy acetophenone; mp 56-58 °C (lit[7b]. mp 56.5-57 °C).

**Fluoro-methylcoumarins (1 and 2).** These compounds were synthesized according to the method described in the literature.[7] A mixture of fluoro-2-hydroxy acetophenone (1.211g, 5 mmol) and [ethyl

(triphenyl phosphoranylidene) 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% ethyl acetate in petroleum ether as an eluant. Recrystallization from 1:2 ratio of chloroform/ethanol yielded colourless needles.

**7-Fluoro-4-methylcoumarin (1).** Yield 82%, m.p. 129-132 °C; UV $\lambda_{max}$ (ethanol) 306.5 nm; IR (nujol): 1720, 1600, 1375, 1265, 1140, 1120, 1060, 975 $cm^{-1}$; $^1H$ NMR: δ 7.59 (1H, dd, J=10.3, 6.4 Hz, H-5), 6.9-7.15 (2H, m, H-6 and H-8), 6.25 (1H, s, H-3), 2.43 (3H, s, aromatic methyl); $^{13}C$ NMR: δ 159.98 (C-2), 113.61 (C-3), 151.86 (C-4), 126.2 (d, $J_{c-f}$ = 9.7 Hz, C-5), 103.97 (d, $J_{c-f}$ =24.5 Hz, C-6), 164.1 (d, $J_{c-f}$ =253.5 Hz, C-7), 111.9 (d, $J_{c-f}$=22.1 Hz, C-8), 116.54 (C-9), 154.4 (d, $J_{c-f}$=12.2 Hz, C-10), 18.48 (C-11); LRMS m/z 178 ($M^+$, 68 %), 151 (79), 149 (100), 121 (12), 101 (15), 75 (16), 51 (12); Anal. Calcd. for $C_{10}H_7FO_2$: C, 67.42 ; H, 3.96 %. Found C, 67.34; H, 3.85 %.

**6-Fluoro-4-methylcoumarin (2).** Yield 85%; m.p. 166-169 °C; UV $\lambda_{max}$ (ethanol) 319 nm; IR (nujol): 1710, 1370, 1485, 1425, 1255, 1155, 920 $cm^{-1}$; $^1H$ NMR: δ 7.2-7.4 (3H, m, H-5, H-7 and H-8), 6.35 (1H, s, H-3), 2.42 (3H, s, aromatic methyl); $^{13}C$ NMR: δ 160.20 (C-2), 115.88 (C-3), 151.53 (C-4), 110.25 (d, $J_{c-f}$ = 24.3 Hz, C-5), 158.68 (d, $J_{c-f}$=243.90 Hz, C-6), 118.93 (d, $J_{c-f}$=24.84 Hz, C-7), 118.5 (d, $J_{c-f}$=7.0 Hz, C-8), 120.5 (d, $J_{c-f}$= 71. Hz, C-9), 149.58 (C-10), 18.48 (C-11); LRMS m/z 178 ($M^+$, 86 %), 151 (47), 149 (100), 121 (9), 101 (13), 75 (10). Anal. Calcd. for $C_{10}H_7FO_2$: C, 67.42 ; H, 3.96 %. Found C, 67.36; H, 3.88 %:

**Photodimer (*anti*-HT) (1a).** Yield 92.5 % (based on recovery of 77.5% starting material); m.p. 205-207 °C; UV $\lambda_{max}$ (ethanol) = 276 nm; IR (nujol): 1750, 1620, 1580, 1470, 1385, 1280, 955, 825, 715 $cm^{-1}$; $^1H$ NMR: δ 6.9-7.2 and 7.48-7.65 (6H, m, aromatic protons), 3.43 (2H, s, cyclobutyl protons), 1.27 (6H, s, methyl protons); LRMS m/z 356 ($M^+$, 28 %), 279 (5), 179 (100), 151 (100), 150 (100), 121 (42). Anal. Calcd. for $C_{20}H_{14}F_2O_4$: C, 67.42; H, 3.96 %. Found C, 67.34; H, 3.87%.

**Photodimer (*syn*-HH) (2a).** Yield 97.5 % (based on recovery of 72.5% starting material);; mp 217-220 °C; UV $\lambda_{max}$ (ethanol) = 274.6 nm; IR (nujol): 1760, 1685, 1575, 1480, 1455, 1235, 1155, 920, 855, 730 $cm^{-1}$; $^1H$ NMR: δ 6.51-7.0 (6H, m, aromatic protons), 3.66 (2H, s, cyclobutyl protons), 1.65 (6H, s, methyl protons); LRMS m/z 356 ($M^+$, 24 %), 279 (3), 191 (20), 179 (100), 178 (100), 151 (100), 150 (100), 121 (35), 101 (47). Anal. Calcd. for $C_{20}H_{14}F_2O_4$: C, 67.42; H, 3.96 %. Found C, 67.31; H, 3.82 %.

**X-ray analysis**

**Crystal 1**. A colorless needle-shaped crystal with the dimensions 0.45 x 0.40 x 0.34 mm was used for data collection. Intensity data was collected on an Enraf-Nonius CAD4 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 = 9.515 (1), b = 12.923 (2), c = 14.004 (2) Å, β = 107.12 (2)°, V = 1645.7(4) $Å^3$, Z = 8, $D_{(cal)}$ = 1.438 g $cm^{-3}$, linear absorption coefficient, μ = 0.115 $cm^{-1}$ and formula weight = 178.16 for

$C_{10}H_7FO_2$, F (000) = 736. The total number of reflections was 2518 and those with I > 2 σ (I) was 1702. The final R (on $F^2$) = 0.059 and Final $R_w$ (on $F^2$) = 0.167. The largest difference peak/hole = 0.30/-0.45 e. $A^{-3}$.

**Crystal 2**. A colorless needle shaped crystal with the dimensions 0.45 x 0.40 x 0.30 mm was used for data collection. Intensity data was collected on an Enraf-Nonius CAD4 diffractometer using Ni filtered Cu-Kα in ω-2θ mode at 293 K. The crystal was determined to be triclinic, space group P1, a = 7.162 (2), b = 8.857 (1), c = 12.999 (2) Å, α = 86.96 (1), β = 100.59 (2)°, γ = 93.47 (2)°, V = 808.3 (3) $Å^3$, Z = 4, $D_{(cal)}$ = 1.464 g $cm^{-3}$, linear absorption coefficient, μ = 0.994 $cm^{-1}$ and formula weight = 178.16 for $C_{10}H_7FO_2$, F (000) = 368. The total number of reflections was 2385 and those with I > 2 σ (I) was 1636. The final R (on $F^2$) = 0.049 and Final $R_w$ (on $F^2$) = 0.119. The largest difference peak/hole = 0.21/-0.30 e. $A^{-3}$.

**Crystal 2a**. A colorless needle shaped crystal with the dimensions 0.8 x 0.80 x 0.20 mm was used for data collection. Intensity data was collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα in ω-2θ mode at 293 K. The crystal was determined to be orthorhombic, space group $Pna2_1$, a = 16.500 (3). b = 13.358 (2), c = 7.325 (1) Å, V = 1614.5 (4) $Å^3$, Z = 4, $D_{(cal)}$ = 1.466 mg $m^{-3}$, linear absorption coefficient, μ = 0.117 $cm^{-1}$ and formula weight = 356.31for $C_{20}H_{14}F_2O_4$, F (000) = 736. The total number of reflections was 1706 and those with I > 2 σ (I) are 1257. The final R (on $F^2$) = 0.048 and Final $R_w$ (on $F^2$) = 0.080. The largest difference peak/hole = 0.21/-0.19 e. $A^{-3}$.

The structures of **1**, **2** and **2a** were solved using direct method SHELXS-86.[19] 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.[20] 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.

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