Studies in Crystal Engineering: Topochemical Photodimerization of (±)-*p*-Fluorobenzylidenepiperitone

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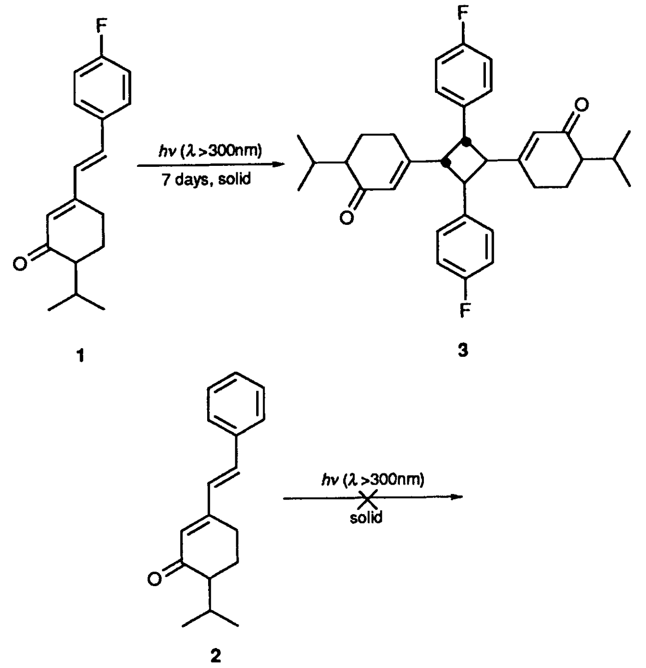
The effect of fluoro substitution on the nature of crystal packing and the solid state photo-behaviour of the title non-planar molecule is examined. The steering capability of fluorine and the role of molecular topology in crystal packing are discussed. Crystallographic evidence for a C–H···F hydrogen bond is provided.

We have recently demonstrated[1] from our studies in crystal engineering that fluorine substitution on coumarin could be utilized to induce β-packing mode, an arrangement required for [2 + 2] photocycloaddition reaction in the solid state to obtain, stereospecifically, the mirror symmetric product. Although it is clear from the literature[2–5] that halogen··· halogen interactions play an important role in the overall three dimensional packing of a molecule, it seems important to consider the influence of the topological features of the organic moiety, namely the overall three dimensional shape of the molecule, on the molecular packing in crystals.[6] It was therefore considered appropriate to further investigate this aspect by choosing an organic system where the combined effects of a steering group and molecular topology are operative on the crystal packing and photobehaviour in the solid state. This paper describes the studies carried out on (±)-*p*-fluorobenzylidenepiperitone (**1**), [(*E*)-3-(*p*-fluorophenylvinyl)-6-isopropylcyclohex-2-enone] in the solid state. It is known[7] that the crystals of unsubstituted (±)-benzylidenepiperitone (**2**) are α-packed and photostable. The question that we address is the following: will fluorine, found to be effective as a β-stack promoter in the case of planar aromatic molecule like coumarin,[1] be successful in achieving the same in the case of non-planar molecules such as **2**?



Scheme 1

Experimental

Compound **1** (m.p. 84 °C) was synthesized by adopting the method of Read and Smith[8] and crystallized from ethanol. Powdered sample of **1** was taken in a petridish (Pyrex glass) and exposed to UV radiation at room temp. using a Rayonet photochemical reactor ($\lambda \geq 300$ nm). The progress of the photoreaction was monitored by thin layer chromatography (TLC). The irradiation was continued until no further increase in the product occurred. Using column chromatography the irradiated sample was separated into its components (monomer and dimer) with chloroform–hexane (60 : 40) as eluent. The yield of the dimer as determined from ^{1}H NMR integration was 35%, significantly lower than the yield observed in the crystals of 6- and 7-fluorocoumarins (*ca.* 100%). The formation of the dimer was confirmed by mass spectral analysis. The NMR spectrum of the dimer revealed, from the absence of styrenic protons, that the reaction occurred across the styrenic double bond and not the enone double bond. Although, in principle, four dimers differing in stereochemistry namely, *syn* head-to-head, *syn* head-to-tail, *anti* head-to-head and *anti* head-to-tail are possible, the dimer **3** could easily be characterized as *anti* head-to-tail from the pattern corresponding to the cyclobutyl protons in the ^{1}H NMR spectrum and by comparison with the other dimers reported in the literature.[9,10] The observations are represented in Scheme 1.

X-ray Structural Investigation.—Single crystals of **1** suitable for X-ray diffraction studies were obtained by slow evaporation from ethanol–chloroform (1 : 1) mixture. Preliminary oscillation and Weissenberg photographs of the crystal indicated that the crystals belong to the triclinic system with $Z = 4$. Three-dimensional intensity data were collected on an Enraf Nonius CAD-4 diffractometer. Lattice parameters were accurately determined by a least squares procedure using 25 carefully centred reflections in the θ-range or 11.2–41.7°. A search for higher symmetry using the program TRACER[11] also suggested the same cell. The intensity data were measured using Nickel-filtered Cu-Kα radiation to a limit of $\theta = 65°$ (h: 0→6, k: −16→16, l: −21→21) in $\omega/2\theta$ scan mode with a pre-scan speed of 5.5° min^{-1} and the final scan was done with a scan speed calculated to satisfy the conditions $\sigma(I)/I \leqslant 0.03$. The intensities of three standard reflections ($1\,\bar{2}\,2, \bar{1}\,\bar{4}\,\bar{4}, \bar{1}\,5\,\bar{3}$), used for checking the stability and orientation of the crystal, showed only statistical fluctuations (±2%). A total of 4888 unique reflections were measured of which 2947 were significant [$|F_o| \geq 4\sigma(F_o)$]. However, since the high angle data ($\theta > 60°$) were quite weak, the data up to $\theta = 60°$ [2591 unique reflections with $|F_o| \geq 4\sigma(F_o)$] alone were used for the structure refinement. The data were corrected for Lorentz and polarization factors but not for absorption. The crystallographic details are provided in Table 1. The structure of **1** was solved by direct methods using

Table 1 Crystallographic details of **1**

Molecular formula	$C_{17}H_{19}OF$
M	258.3
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell parameters	
a/Å	6.032(1)
b/Å	13.833(2)
c/Å	18.180(2)
α/°	78.57(1)
β/°	80.67(1)
γ/°	88.18(1)
V/Å^3	1467.2(3)
Z	4
D_m/g cm^{-3}	1.17
D_x/g cm^{-3}	1.17
Crystal size/mm	0.60 × 0.35 × 0.15
λ/Å	1.5418
T/K	293
μ/cm^{-1}	6.1
F(000)	552
Final R^a	0.082
Goodness of fit	0.94
Number of parameters	325
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ in the final difference Fourier/e Å^{-3}	0.35, −0.19

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

Table 2 Bond lengths involving non-hydrogen atoms with their esds in parentheses

Bond	Distance/Å Molecule-A	Molecule-B
F(1)–C(4)	1.371(8)	1.373(7)
C(1)–C(2)	1.388(9)	1.389(10)
C(1)–C(6)	1.374(8)	1.367(9)
C(1)–3(7)	1.458(7)	1.469(7)
C(2)–C(3)	1.354(9)	1.396(10)
C(3)–C(4)	1.355(10)	1.346(11)
C(4)–C(5)	1.357(11)	1.349(12)
C(5)–C(6)	1.394(9)	1.407(9)
C(7)–C(8)	1.321(8)	1.321(9)
C(8)–C(9)	1.466(7)	1.461(7)
C(9)–C(10)	1.495(7)	1.478(9)
C(9)–C(14)	1.334(7)	1.324(10)
C(10)–C(11)	1.517(7)	1.491(10)
C(11)–C(12)	1.529(8)	1.495(12)
C(12)–C(13)	1.516(7)	1.495(10)
C(12)–C(15)	1.539(7)	1.567(10)
C(13)–O(1)	1.220(7)	1.219(10)
C(13)–C(14)	1.461(7)	1.457(9)
C(15)–C(16)	1.528(9)	1.524(13)
C(15)–C(17)	1.501(10)	1.380(14)
C(15)–C(18)		1.458(20)
C(15)–C(19)		1.539(49)

Table 3 Bond angles involving non-hydrogen atoms with their esds in parentheses

Atoms	Angle/° Molecule-A	Molecule-B
C(6)–C(1)–C(7)	123.2(6)	122.7(6)
C(2)–C(1)–C(7)	119.5(6)	118.2(6)
C(2)–C(1)–C(6)	117.3(6)	119.1(6)
C(1)–C(2)–C(3)	123.1(7)	121.5(6)
C(2)–C(3)–C(4)	117.4(7)	116.6(7)
F(1)–C(4)–C(3)	119.2(7)	117.6(7)
C(3)–C(4)–C(5)	123.4(7)	124.7(7)
F(1)–C(4)–C(5)	117.3(7)	117.7(6)
C(4)–C(5)–C(6)	117.9(7)	118.2(7)
C(1)–C(6)–C(5)	120.9(6)	119.8(6)
C(1)–C(7)–C(8)	127.0(5)	126.0(6)
C(7)–C(8)–C(9)	126.8(5)	126.8(6)
C(8)–C(9)–C(14)	119.5(5)	120.6(6)
C(8)–C(9)–C(10)	120.9(5)	120.4(5)
C(10)–C(9)–C(14)	119.6(5)	119.0(6)
C(9)–C(10)–C(11)	112.0(4)	113.6(6)
C(10)–C(11)–C(12)	111.6(4)	112.8(6)
C(11)–C(12)–C(15)	115.1(4)	119.8(6)
C(11)–C(12)–C(13)	110.1(5)	109.7(6)
C(13)–C(12)–C(15)	112.5(5)	111.7(6)
C(12)–C(13)–C(14)	117.9(5)	117.2(6)
C(12)–C(13)–O(1)	122.0(5)	122.2(7)
O(1)–C(13)–C(14)	120.1(5)	120.5(7)
C(9)–C(14)–C(13)	124.3(5)	124.6(6)
C(12)–C(15)–C(17)	112.3(5)	111.3(8)
C(12)–C(15)–C(16)	109.3(5)	107.8(7)
C(16)–C(15)–C(17)	111.8(5)	114.2(8)
C(12)–C(15)–C(18)		131.9(12)
C(12)–C(15)–C(19)		105.0(19)
C(18)–C(15)–C(19)		95.5(22)

the program SHELXS-86.[12] Examination of the distribution of the normalized structure factors favoured the choice of centrosymmetric space group, $P\bar{1}$. Using the default options of the program, all the non-hydrogen atoms were obtained from the E-map at stereochemically reasonable positions. The structure was refined using the full-matrix least-squares program, SHELX-76.[13] Isotropic refinement of positional and temperature factors of all non-hydrogen atoms converged to an R-value of 0.189. The two molecules in the asymmetric unit are designated as molecule-A and molecule-B. It was found at the convergence stage of isotropic refinement that the U_{iso} of the carbon atoms C(16) and C(17) of the isopropyl group of molecule-B were high (0.21 and 0.19 Å^2) at the C(15)–C(17) bond length was relatively short (1.38 Å). The difference Fourier map at this stage showed the presence of two peaks of electron density, 0.5 and 0.4 Å^{-3} which appeared to be the minor peaks of C(16) and C(17) of molecule-B. Anisotropic refinement without taking into account these peaks was not satisfactory, the U_{11} value of C(16) and C(17) being high (0.20 and 0.26 Å^2) and the length C(15)–C(17) remaining unsatisfactory (1.37 Å). It was evident from these observations that the isopropyl group is disordered and the two residual peaks mentioned above are the minor positions of the isopropyl carbon atoms C(16) and C(17) of the molecule-B. These minor peaks are designated as C(18) and C(19). At this point all the four carbon atoms C(16), C(17), C(18) and C(19) were left out from the refinement and based on the peak heights in the difference Fourier map, the atoms C(16) and C(17) were given an occupancy of 0.7 each and their disordered counterparts (C18) and C(19) were given occupancy of 0.3 each [*i.e.*, an occupancy of $(1 - x)$ where x is the occupancy of the major peak]. After four cycles of refinement, the occupancies of the four atoms C(16), C(17), C(18) and C(19) converged very close to 0.75, 0.75, 0.25 and 0.25 respectively. These values were fixed during further cycles of refinement. The disordered atoms with minor occupancies, namely C(18) and C(19) were refined only isotropically. As a consequence of the disorder, the bond lengths and angles involving these atoms of the isopropyl group of molecule-B are not very accurate (see Tables 2 and 3).

Full-matrix least-squares refinement of scale factor, positional and anisotropic thermal parameters of the non-hydrogen atoms except C(18) and C(19), as well as positional and isotropic thermal parameters of the hydrogen atoms located from the difference Fourier map was carried out. Atoms C(18) and C(19) were refined only for their positional and isotropic temperature factors. All the hydrogen atoms not identified from the difference Fourier map were stereochemically fixed and were refined for their positional and isotropic thermal parameters. Hydrogen atoms of C(18) and C(19), the disordered carbon atoms with minor occupancy, were not input into the refinement. The quantity minimized in the least-squares refinement was $\Sigma\omega(|F_o| - |F_c|)^2$ where the weighting function w was equal to unity. The refinement converged to a final R-value of 0.082. The final difference Fourier map was essentially featureless with the maximum and minimum values of $\Delta\rho$ being $+0.35$ and -0.19 e Å^{-3} respectively. The fractional atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms, hydrogen atom coordinates, bond lengths and bond angles are deposited at the Cambridge Crystallographic Data Centre (CCDC).*

Results and Discussion

A perspective view of the molecule-A of **1** with the atom-numbering scheme is shown in Fig. 1. The numbering of atoms adopted is the same for both the molecules, A and B. Bond lengths and angles involving the non-hydrogen atoms are given in Tables 2 and 3 respectively. Fig. 2 depicts the packing of the molecules in the crystal.

The bond lengths and angles of the cyclohexenone ring are normal (Tables 2 and 3). In A as well as in B the torsion angles within the cyclohexenone ring (Table 4) indicate the ring to be in a sofa conformation.[14] The torsion angles in A and B, namely, C(13)–C(12)–C(15)–C(16) [−64.7(6)°, −72.5(9)°], C(13)–C(12)–C(15)–C(17) [161.5(7) and 170.6(5)°] as well as the other torsion angles provided in Table 4 clearly show the non-planarity of the molecule as found in *p*-chloro-,[15] *o*-chloro-[16] and *p*-bromo[6] (±)-benzylidenepiperitones.

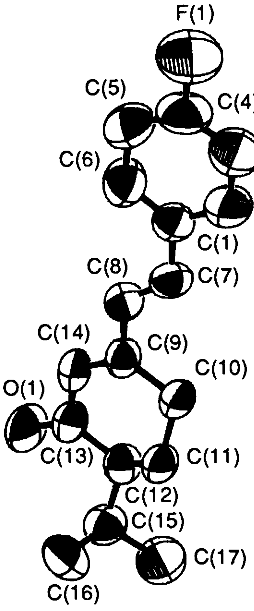


Fig. 1 ORTEP plot of a single molecule of **1** with the atom-numbering scheme

Structure–Reactivity Correlation.—There are two potentially reactive double bonds, namely the styrenic double bond C(7)=C(8) and the enone double C(9)=C(14). Both these double bonds, in principle, could undergo photodimerization. Indeed, double photodimerization has been observed in molecules with multiple reactive double bonds.[17–20] However, irradiation of **1** in the solid state yielded a single product, the *anti* head-to-tail dimer. From the packing diagram of **1** (Fig. 2) it is clear that the centrosymmetrically related pair of double bonds of B, C(7)=C(8) $[x - 1, y + 1, z]$ and C(7)^{i}=C(8)^{i} $[-x + 1, -y, -z + 2]$, react to produce the *anti* head-to-tail dimer. This confirms the stereochemistry of the dimer assigned on the basis of ^{1}H NMR spectra.

For a topochemical [2 + 2] photodimerization reaction, the distance between the potentially reactive double bonds should be less than *ca.* 4.2 Å[2]. In the crystal structure of **1** the centre-to-centre distance of the reacting double bonds, C(7)=C(8) of B and its inversion-related partner C(7)^{i}=C(8)^{i} is 4.13 Å. Further, it is well known that in the topochemical reactions only a minor reorganization of the reactant molecules is necessary to attain ideal geometry required for a given reaction. This necessitates that the reactive double bonds be suitably juxtaposed[21] for a proper overlap of the π orbitals. Fig. 3 illustrates the parameters which are relevant in the context of [2 + 2] photodimerization reaction. In this type of representation where the C(7)=C(8) bond of molecule-B is considered as an example, θ_1 corresponds to rotation of one of the reactive double bonds with respect to the other, θ_2 represents the angle of the parallelogram formed by the double bonds C(8), C(7), C(8)^{i} and C(7)^{i} and θ_3 is a measure of the angle between the least-squares planes passing through C(7), C(8), C(7)^{i}, C(8)^{i} and C(1)^{i}, C(7)^{i} and C(9)^{i}. Ideal values of θ_1, θ_2 and θ_3 are 0, 90 and 90° respectively. Corresponding

Table 4 Selected torsion angles within the cyclohexenone ring

Atoms	Angle/° Molecule-A	Molecule-B
C(14)–C(9)–C(10)–C(11)	−26.3(7)	−21.7(9)
C(9)–C(10)–C(11)–C(12)	54.1(6)	50.2(9)
C(10)–C(11)–C(12)–C(13)	−52.9(6)	−53.8(8)
C(11)–C(12)–C(13)–C(14)	25.5(7)	31.1(9)

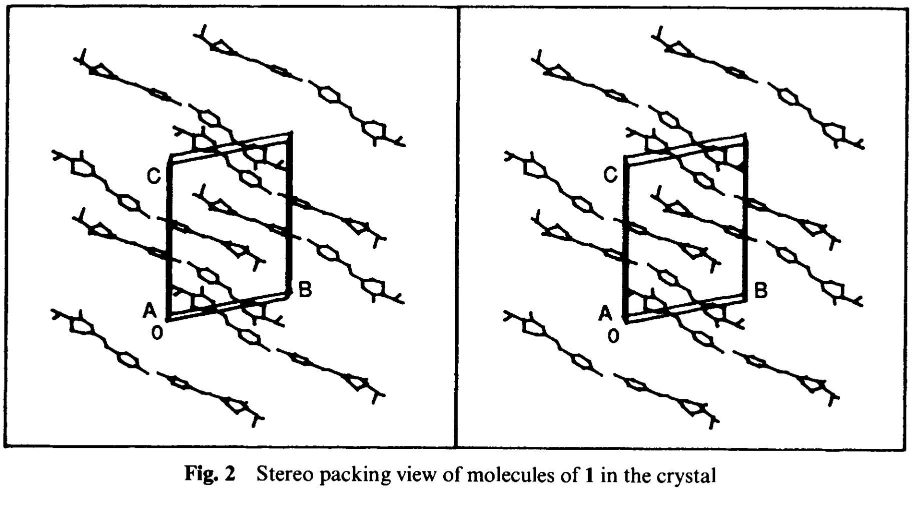


Fig. 2 Stereo packing view of molecules of **1** in the crystal

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* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

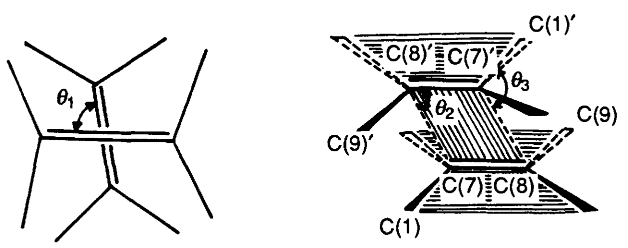

Fig. 3 Pictorial representation of θ_1, θ_2 and θ_3

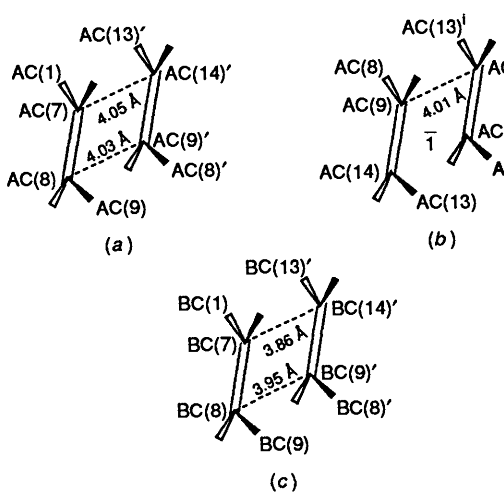

Fig. 4 Schematic representation of the three pairs of potentially reactive double bonds

Table 5 Geometries of C–F ··· F interactions

REFCODE	Contact	H ··· F/Å	C–H ··· F/°	Inter/ Intra
BIGSUF	C(15–)H15 ··· F2	2.10	130.1	Inter
	C(26–)H26 ··· F2	2.54	136.0	Inter
BUJNID	(C1–)H1 ··· F1	2.64	113.0	Inter
CIJLOW	(C6–)H4 ··· F2	2.60	118.9	Intra
	(C6–)H5 ··· F1	2.37	152.8	Inter
	(C6–)H5 ··· F3	2.27	116.0	Inter
COVJIG	(C4–)H4 ··· F1	2.50	156.3	Inter
CUGBOV	(C12–)H1 ··· F5	2.28	114.0	Intra
DFACAM	(C11–)H3 ··· F1	2.40	128.2	Inter
FBENZA01	(C3–)H3 ··· F1	2.60	171.0	Inter
FIXWEO	(C8–)H81 ··· F1	2.59	138.9	Inter
FMANIL	(C18–)H5 ··· F22	2.55	148.2	Inter
FODYAY	(C3–)H3 ··· F1	2.63	143.5	Inter
	(C6–)H63 ··· F1	2.50	97.9	Intra
NPOFNP	(C9–)H3 ··· F1	2.63	132.2	Inter
PFBZCY	(C5–)H5 ··· F1	2.66	153.0	Inter

values of these parameters observed in the crystal structure of **1** are 0, 112.3 and 83.8°. Similar deviations ($\theta_1 = 0$, $\theta_2 = 87.1$ and $\theta_3 = 66.8°$) were observed in the photoreactive crystals of (±)-*p*-chlorobenzylidenepiperitone[15] as well. This would mean that in the ground state geometry, the π-orbitals of the reactive double bonds do not overlap exactly and appreciable translational and rotational displacements are necessary before the onset of dimerization. It was concluded from lattice-energy calculations[22] that in photoreactive crystals there is sufficient cavity volume and hence freedom for the reacting partners to re-orient themselves in the lattice.

As mentioned earlier, there are two crystallographically independent molecules of **1** in the asymmetric unit; molecule-A and molecule-B. As is clear from Fig. 2 the double bonds between A and B are too far apart to react. From the molecular packing diagram (Fig. 2) it is also clear that there is no symmetry operation which brings the C(7)=C(8) double bonds of A and B close enough for the reaction to occur. In addition to the above, there are no proximal C(7)=C(8) contacts (< 4.2 Å) between molecules of A. Thus, of the two molecules present in the asymmetric unit, molecule A does not have any favourable C(7)=C(8) contacts and it is only between the molecules of B that the reaction can take place. This implies a maximum expected yield of only 50% and hence the observed yield of 35% seems reasonable.

From the calculation of intermolecular distances, it is found that there are other close contacts (< 4.2 Å) involving the enone double bond, C(9)=C(14). Such pairs of double bonds (where both ends of the double bond involved are distances less than *ca.* 4.2 Å apart) are depicted in Fig. 4. The θ_1, θ_2 and θ_3 values observed for these potentially reactive pairs of double bonds namely, (i) C(7)=C(8) of A and C(14)ⁱ=C(9)ⁱ $[-x + 1, -y + 1, -z + 1]$ of A, (ii) C(9)=C(14) of A and C(14)ⁱ=C(9)ⁱ $[-x + 1, -y + 1, -z + 1]$ of A and (iii) C(7)=C(8) $[x - 1, y + 1, z]$ of B and C(9)ⁱ=C(14)ⁱ $[-x + 1, -y, -z + 2]$ of B are: (i) $\theta_1 = 7.6$, $\theta_2 = 99.8$, $\theta_3 = 71.7°$; (ii) $\theta_1 = 0$, $\theta_2 = 70.4$, $\theta_3 = 88.8°$; and (iii) $\theta_1 = 5.4$, $\theta_2 = 84.6$, $\theta_3 = 79.1°$, respectively. However, from TLC as well as from ^{1}H NMR spectra it is clear that there is only one photodimer *viz*., the one involving centrosymmetrically related C(7)=C(8) double bonds. There is no evidence whatsoever for the presence of any other dimer in the irradiated sample.

Absence of reactions in spite of favourable arrangement has been coming to light in the recent years.[5,23–26] Indeed, from the investigations of different (±)-benzylidenepiperitones such cases are known. For example, in the unsubstituted (±)-benzylidenepiperitone[7] and *o*-chlorobenzylidenepiperitone[16] the potentially reactive double bonds are favourably juxtaposed but the crystals are photoinert. The probable reason for the lack of solid-state photoreactivity in these cases is explained in terms of steric compression which may develop between the reactive molecules and the nearest neighbours in their excited state geometries.

Steering Ability of Fluoro Group vs. *Influence of Molecular Topology on Crystal Packing*.—As mentioned at the outset one of the primary aims of the present investigation was to examine whether the fluoro group could be used to steer non-planar organic systems to the β-packing mode. The results of this study show that the molecules of *p*-fluorobenzylidenepiperitone adopt the α-packing mode and *not* the anticipated β-type observed in the case of planar aromatic molecules such as 6- and 7-fluorocoumarins.[1]

It is noteworthy that the molecules in the crystals of (±)-benzylidenepiperitone,[7] the *p*-chloro,[15] *o*-chloro,[6] *p*-bromo[6] as well as *p*-fluoro discussed in this paper have been found to adopt, without exception, the α-packing mode, irrespective of the presence or absence of steering groups such as Cl, Br and F. On the other hand, it has been shown[5] that all the chloro-, bromo- and fluoro-coumarins studied so far adopt the β-packing mode. Unlike coumarins, all the benzylidenepiperitones mentioned above are non-planar with the cyclohexenone ring adopting a sofa conformation (see Table 4). Further, in all these cases, there is an isopropyl group which is quite anisotropic in shape. It seems reasonable to conclude that the overall non-planarity of the molecules would prevent efficient close packing of this moiety in the β-arrangement. These observations lead to the conclusion that molecular topology takes precedence over the β-steering ability of fluorine in determining the packing mode of a non-planar system.

From the intermolecular distances and angles involving C, H and F atoms there is evidence for the presence of a C–H ··· F interaction between molecule A and B of **1**: C(5)B ··· F(1)A $[x + 1, y, z] = 3.26(1)$, H(5)B ··· F(1)A = 2.22(9) Å; C(5)B–H(5)B ··· F(1)A = 153(7)°. The existence of a

C–H ⋯ F interaction was first observed in the crystals of 6- and 7-fluorocoumarins. As there was no earlier report on the crystallographic evidence for the existence of a C–H ⋯ F hydrogen bond, the crystallographic data of fluoro substituted organic systems were retrieved from the Cambridge Structural Database[27] (1989, Version 3.4, 71 630 entries) for further analysis. From the list of references obtained, the following cases were omitted: (*a*) the metal complexes; (*b*) ionic structures; (*c*) structures which are disordered; (*d*) structures with high (> 10%) *R*-factor; (*e*) structures with any other halogen besides fluorine; and (*f*) crystal structures of all stereochemically complex molecules. Thus, the above stringent and fairly broad based criteria adopted in choosing the structures resulted in a very limited data available for the analysis.

The geometry of C–H ⋯ F interactions observed in the crystal structures is summarized in Table 5. The van der Waals radii used were: C = 1.75, H = 1.20, F = 1.47 Å.[28] Both inter- and intra-molecular contacts are included. The C–H ⋯ F angles less than 90° were ignored in the case intramolecular contacts while for the intermolecular contacts, only those with C–H ⋯ F angles greater than 110° were considered. It may be mentioned that the short intramolecular interactions may sometimes be due to the geometric constraints of the molecule. Such contacts were also omitted. It is worth emphasizing that in a majority of the structures, the H ⋯ F intermolecular short contacts (2.67 Å) are observed even though the hydrogen atom involved is not activated (acidic). In other words, the carbon atom involved in the C–H ⋯ F interaction is bonded to neither N nor O. This could be due to the fact that fluorine is the most electronegative atom[29] (F = 4.0, O = 3.5, N = 3.0). In view of the limited data available for the analysis of the C–H ⋯ F type of interaction it is not possible to comment upon the nature of these interactions. As the geometric characteristics of the C–H ⋯ F interaction (H ⋯ F and C–H ⋯ F) are similar to those used for C–H ⋯ O hydrogen bonds,[30,31] it seems reasonable to call the observed C–H ⋯ F interaction a hydrogen bond. However it is to be noted that the atom F is not polarizable, as oxygen is.

Conclusions

The fluoro substitution does not lead to the anticipated β-packing of the molecules of (±)-benzylidinepiperitone. The significant conclusion emerging from this study as well as from crystal packing in all the benzylidenepiperitones studied so far is that the topological aspect, namely the non-planar character of the molecule controls the nature of molecular packing in the crystal. In the crystals of all the benzylidenepiperitones investigated so far, the α-packing is favoured, suggesting greater packing efficiency of this class of molecules in the α-packing mode rather than in the β-mode. The formation of the centrosymmetric dimer **3** upon irradiation of crystals of **1** is rationalized in terms of crystal packing. There are no F ⋯ F contacts less than the sum of the van der Waals radii (2.94 Å) in **1**. However, C–H ⋯ F interaction first identified in the crystal structures of 6- and 7-fluorocoumarins[1] is observed in the crystal structure of **1** as well. From a survey of the Cambridge Structural Database, crystallographic evidence for the existence of C–H ⋯ F hydrogen bond has been obtained. That the parent compound, namely (±)-benzylidenepiperitone, does not photodimerize in the crystalline state whereas the fluoro-derivative does, brings out, in a subtle way, the importance of fluoro-substitution.

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