Effect of Fluoro Substitution on the Packing Motifs of Benzylidene- and Dibenzylidene-cyclopentanones

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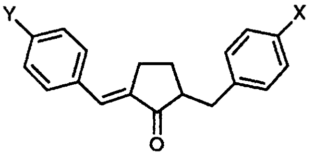
The structure and solid-state reactivity of one fluorinated benzyl(benzylidene)cyclopentanone and two fluorinated dibenzylidenecyclopentanones are reported and the influence of fluoro substitution upon the packing of benzylidenecyclopentanones is discussed. It was shown that intermolecular atom–atom interactions involving the fluoro groups hold sway over the effect of the volume of the substituents upon crystal packing. As a result, the two dibenzylidene compounds have packing motifs very different from that of the unsubstituted parent compound, and thus a different solid-state reactivity pattern. Both the fluorinated dibenzylidene compounds undergo topochemical solid-state dimerisation, whereas the fluorobenzylidene compound was found to be photostable.

Although diffusionless[1] or topochemical solid-state transformations have been known for a long time, they have only become amenable to rationalisation, due to the work of Schmidt *et al.* with (*E*)-cinnamic acids.[2,3] They showed that these reactions are influenced by the geometry of their surroundings, *i.e.* the crystal structure. Since Schmidt's pioneering work, a growing number of other chemical systems which react in the solid state in a similar fashion have been identified.[4,5] Notable among these are the benzyl(benzylidene)cyclopentanone series of compounds[6,7] which not only react homogeneously in the solid state to yield a cyclobutane dimer under UV irradiation, but do so in a single-crystal to single-crystal fashion (a single crystal of monomer is converted into a single crystal of the dimer).

The study of these reactions and solids is important, not only because they result in interesting and useful products (for example, symmetric or chiral cyclobutanes, and highly crystalline or regiospecific polymers), but more importantly, because they represent a means of examining the factors which influence the mode of packing of organic molecules (molecular recognition) in the solid state. These considerations are important in such diverse areas as electronic materials or those with non-linear optical properties, and pharmaceuticals.[4]

In the present paper we study the effect of fluoro substitution on the packing of 2-benzyl-5-benzylidene- (BBCP, see Scheme 1) and 2,5-dibenzylidene-cyclopentanone (DBCP, see Scheme 1). We chose the fluoro substituent because it has a much smaller van der Waals radius (1.35 Å) than other substituents used hitherto, namely Cl (1.80 Å), Br (1.95 Å), Me (2.0 Å), I (2.15 Å), OMe and OH. This allows a method to distinguish between substituent effects due to size and those due to non-bonded interactions, on the crystal packing. In the case that obtains for other members of the BBCP family of compounds, it has been shown that for substitution patterns which do not add significantly to electrostatic intermolecular interactions,[8] size considerations hold sway, and chloro/methyl interchangeability as suggested by Kitaigorodskii is valid;[9] where, however, these interactions are significant, then chloro and methyl substituents behave differently. For example, whereas *p*ClBBCP (see Scheme 1) and *p*MeBBCP are isostructural, *p*ClB*p*BrBCP and *p*MeB*p*BrBCP are not; this difference has been rationalised as being due to differences in the non-bonded interactions of the bromo substituent with the benzyl phenyl group which is bonded to an electron withdrawing group (Cl) in one case, thus imparting partial positive charges to the phenyl carbons, and an electron donating group (Me) in the other.[8]



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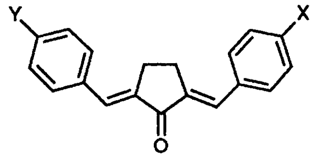

II

Compound	Framework	X	Y
BBCP	I	H	H
*p*ClBBCP	I	*p*-Cl	H
*p*MeBBCP	I	*p*-Me	H
B*p*BrBCP	I	H	*p*-Br
*p*ClB*p*BrBCP	I	*p*-Cl	*p*-Br
*p*MeB*p*BrBCP	I	*p*-Me	*p*-Br
B*p*FBCP	I	H	*p*-F
DBCP	II	H	H
*p*BrDBCP	II	*p*-Br	*p*-Br
*p*FDBCP	II	*p*-F	*p*-F
4FBBCP	II	3,4-di-F	3,4-di-F

Scheme 1

Experimental

Enones B*p*FBCP (2-benzyl-5-*p*-fluorobenzylidenecyclopentanone), *p*FDBCP [2,5-di-(*p*-fluorobenzylidene)cyclopentanone], and 4FBBCP [2,5-(bis-(3,4-difluorobenzylidene)cyclopentanone] were prepared in the way previously described for the archetypal compounds 2-benzyl-5-benzylidenecyclopentanone and 2,5-dibenzylidenecyclopentanone.[6,7,10]

BpFBCP.—The cyclopentanone–pyrrolidine enamine was prepared in a Dean–Stark apparatus in a toluene solution. The enamine was then allowed to react with benzyl chloride in dioxane to yield 2-benzylcyclopentanone (BCP). The final product B*p*FBCP was obtained by reacting BCP with *p*-fluorobenzaldehyde in methanol, using sodium methoxide as a catalyst. M.p. = 407–408 K; ν/cm^{-1} 1700 (C=O), 1630 (C=C), 1600 (aromatic C=C) and 1218 (C–F) (Found: C, 80.8; H, 5.85. $C_{19}H_{18}FO$ requires C, 81.11; H, 6.45%).

p*FDBCP*.—This compound was prepared from stoichiometric amounts of *p*-fluorobenzaldehyde and cyclopentanone in methanol, with NaOMe as catalyst. M.p. = 512–513 K; ν/cm^{-1} 1680 (C=O), 1620 (C=C), 1500 (C=C, aromatic ring) and 1220 (C–F) (Found: C, 81.65; H, 5.75. $C_{19}H_{14}F_2O$ requires C, 81.70; H, 5.77%).

Table 1 Data collection and refinement details

	B*p*FBCP[17]	4FDBCP	*p*FDBCP
Chemical formula	$C_{19}H_{17}FO$	$C_{19}H_{12}F_4O$	$C_{19}H_{14}F_2O$
M_r	279.31	330.26	296.29
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca*	*P*1	$P2_1/n$
a/Å	8.503(3)	6.789(1)	7.999(2)
b/Å	11.658(4)	13.721(1)	6.112(4)
c/Å	29.655(8)	8.764(1)	29.331(4)
α/°		99.96(1)	
β/°		98.77(1)	96.59(14)
γ/°		94.41(1)	
V/Å^3	2939.6(5)	790.2(3)	1424.5(5)
Z	8	2	4
D_x/g cm^{-3}	1.26	1.39	1.38
Radiation	Mo-Kα	Cu-Kα	Mo-Kα
λ/Å	0.710 69	1.541 78	0.710 69
μ/cm^{-1}	0.49	9.15	0.62
F(000)	1176	336	616
Θ_{max}/°	25	65	25
Total data collected	3036	2927	2866
Total data unique	2569	2676	2499
Total data observed	1245	1626	1174
h min, max	0, 10	−7, 7	−9, 9
k min, max	0, 13	−16, 16	−7, 0
l min, max	0, 35	0, 10	0, 34
R_{int}	0.01	0.01	0.01
Significance test	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$
Parameters refined	207	237	213
R	0.0998	0.0772	0.0560
R_w	0.0889	0.0887	0.0471
Weighting scheme		$[\sigma^2(F) + wF^2]^{-1}$	
w	0.003	0.0017	0.0005
Final cycle			
max Δ/σ	0.006	0.014	0.007
max ΔF peak/e Å^{-3}	0.46	0.78	0.22

Table 2 Atom coordinates (× 10^4) for B*p*FBCP

	x	y	z
C(1)	1051(6)	3212(5)	2505(2)
C(2)	1687(6)	2996(5)	2969(2)
C(3)	1929(6)	1703(5)	2979(2)
C(4)	2303(6)	1365(5)	2494(2)
C(5)	1484(5)	2238(5)	2210(2)
C(6)	684(7)	3518(7)	3346(2)
C(7)	1392(7)	3393(6)	3805(2)
C(8)	917(8)	2545(6)	4099(2)
C(9)	1565(10)	2445(7)	4526(3)
C(10)	2705(9)	3195(8)	4669(2)
C(11)	3183(9)	4042(7)	4385(3)
C(12)	2561(8)	4150(6)	3955(2)
C(13)	1098(6)	2240(5)	1774(2)
C(14)	1373(6)	1430(5)	1418(2)
C(15)	2517(7)	532(6)	1446(2)
C(16)	2720(7)	−199(6)	1085(2)
C(17)	1865(8)	−77(7)	704(2)
C(18)	746(8)	785(7)	658(2)
C(19)	544(7)	1502(6)	1018(2)
O(1)	315(5)	4069(4)	2388(1)
F(1)	2103(6)	−790(4)	358(1)

4*FBBCP*.—Prepared from stoichiometric amounts of cyclopentanone and 3,4-difluorobenzaldehyde in methanol, with NaOMe as a catalyst. M.p. = 509–511 K; ν/cm^{-1} 1680 (C=O), 1600 (C=C), 1510 (C=C, aromatic ring) and 1220 (C–F) (Found: C, 68.9; H, 3.55. $C_{19}HF_4O$ requires C, 68.68; H, 3.64%). Note: crystallographic analysis indicated the presence of a solvent molecule near to the fluoro substituents of the benzene rings.

The IR spectrum of B*p*FBCP agrees well with that for BBCP, and those for 4FBBCP and *p*FDBCP with that for DBCP. The changes observed during dimerisation are similar to those observed for other members of the BBCP and DBCP families (see for example, refs. 6, 7, 10 and 11).

Table 3 Atom coordinates (× 10^4) for *p*FDBCP

	x	y	z
C(1)	7 002(5)	8 537(6)	167(1)
C(2)	7 977(4)	10 357(6)	399(1)
C(3)	8 252(5)	12 065(6)	46(1)
C(4)	7 438(5)	11 176(6)	−423(1)
C(5)	6 670(4)	8 998(6)	−325(1)
C(6)	8 450(4)	10 257(6)	852(1)
C(7)	9 410(5)	11 769(7)	1 164(1)
C(8)	9 946(5)	13 830(7)	1 034(1)
C(9)	10 841(5)	15 190(8)	1 351(1)
C(10)	11 176(5)	14 474(8)	1 792(2)
C(11)	10 662(6)	12 483(9)	1 941(2)
C(12)	9 770(5)	11 134(8)	1 623(1)
C(13)	5 805(4)	7 553(6)	−603(1)
C(14)	5 302(4)	7 590(6)	−1095(1)
C(15)	5 588(5)	9 325(8)	−1 386(1)
C(16)	5 060(6)	9 258(8)	−1 849(1)
C(17)	4 248(5)	7 403(9)	−2 023(1)
C(18)	3 930(5)	5 655(8)	−1 755(1)
C(19)	4 456(4)	5 765(7)	−1 296(1)
O(1)	6 541(3)	6 902(4)	365(1)
F(1)	12 060(3)	15 808(5)	2 105(1)
F(2)	3 723(4)	7 349(5)	−2 479(1)

Table 4 Atom coordinates (× 10^4) for 4FBBCP

	x	y	z
C(1)	4 064(8)	3 573(4)	8 445(7)
C(2)	5 963(7)	3 219(4)	9 108(6)
C(3)	7 693(8)	3 895(4)	8 940(7)
C(4)	6 829(7)	4 698(4)	8 064(7)
C(5)	4 577(8)	4 488(4)	7 842(6)
C(6)	5 835(8)	2 394(4)	9 760(6)
C(7)	7 362(8)	1 868(4)	10 495(6)
C(8)	6 644(8)	1 023(4)	11 075(7)
C(9)	8 043(8)	496(4)	11 783(7)
C(10)	10 043(8)	760(4)	11 960(7)
C(11)	10 766(8)	1 572(4)	11 410(7)
C(12)	9 397(8)	2 122(4)	10 695(7)
C(13)	3 086(8)	4 960(4)	7 209(6)
C(14)	3 075(8)	5 828(4)	6 503(6)
C(15)	4 850(8)	6 378(4)	6 265(6)
C(16)	4 606(7)	7 186(4)	5 579(6)
C(17)	2 749(8)	7 491(4)	5 122(6)
C(18)	1 023(8)	6 993(4)	5 321(7)
C(19)	1 236(7)	6 169(4)	6 033(7)
O(1)	2 367(6)	3 187(3)	8 416(5)
F(1)	7 677(6)	−338(3)	12 410(6)
F(2)	11 094(6)	122(3)	12 712(5)
F(3)	6 068(6)	7 803(3)	5 191(5)
F(4)	2 980(6)	8 315(3)	4 454(5)

Single crystals for X-ray crystallography were obtained from the slow evaporation of dilute chloroform–methanol solutions. X-Ray data collection was carried out at the SERC facility at Queen Mary and Westfield College, on an Enraf–Nonius four-circle diffractometer, in a manner which has been published elsewhere.[15] No absorption correction was employed.

The structures were solved using SHELXS-86, SHELX-76 and were studied by PLUTO-78 and private programs, on a variety of computers (IBM-3081, Cambridge, and Pyramid, Brunel). Table 1 gives the structure solution and collection data. Structures were solved by direct methods and refined by full-matrix least-squares techniques. Hydrogens were located from difference maps and refined isotropically, whilst all other atoms were refined anisotropically.

Table 5 Bond lengths (Å) and angles (°) for B*p*FBCP

C(2)–C(1)	1.498(8)	C(5)–C(1)	1.481(9)
O(1)–C(1)	1.229(8)	C(3)–C(2)	1.522(10)
C(6)–C(2)	1.533(9)	C(4)–C(3)	1.523(9)
C(5)–C(4)	1.495(8)	C(13)–C(5)	1.332(8)
C(7)–C(6)	1.495(9)	C(8)–C(7)	1.379(10)
C(12)–C(7)	1.401(10)	C(9)–C(8)	1.385(11)
C(10)–C(9)	1.373(12)	C(11)–C(10)	1.362(11)
C(12)–C(11)	1.386(10)	C(14)–C(13)	1.435(9)
C(15)–C(14)	1.432(10)	C(19)–C(14)	1.384(8)
C(16)–C(15)	1.380(9)	C(17)–C(16)	1.350(9)
C(18)–C(17)	1.391(11)	F(1)–C(17)	1.338(8)
C(19)–C(18)	1.366(9)		
C(5)–C(1)–C(2)	109.0(6)	O(1)–C(1)–C(2)	125.5(7)
O(1)–C(1)–C(5)	125.5(6)	C(3)–C(2)–C(1)	103.5(6)
C(6)–C(2)–C(1)	113.7(6)	C(6)–C(2)–C(3)	117.1(6)
C(4)–C(3)–C(2)	105.5(5)	C(5)–C(4)–C(3)	105.0(6)
C(4)–C(5)–C(1)	107.7(6)	C(13)–C(5)–C(1)	120.8(6)
C(13)–C(5)–C(4)	131.5(6)	C(7)–C(6)–C(2)	113.7(6)
C(8)–C(7)–C(6)	121.8(7)	C(12)–C(7)–C(6)	120.8(7)
C(12)–C(7)–C(8)	117.3(7)	C(9)–C(8)–C(7)	121.5(8)
C(10)–C(9)–C(8)	120.7(8)	C(11)–C(10)–C(9)	118.8(8)
C(12)–C(11)–C(10)	121.4(8)	C(11)–C(12)–C(7)	120.3(8)
C(14)–C(13)–C(5)	132.2(5)	C(15)–C(14)–C(13)	123.3(6)
C(19)–C(14)–C(13)	120.5(6)	C(19)–C(14)–C(15)	116.2(7)
C(16)–C(15)–C(14)	119.4(7)	C(17)–C(16)–C(15)	121.1(8)
C(18)–C(17)–C(16)	121.8(7)	F(1)–C(17)–C(16)	119.7(8)
F(1)–C(17)–C(18)	118.5(7)	C(19)–C(18)–C(17)	116.8(7)
C(18)–C(19)–C(14)	124.7(7)		

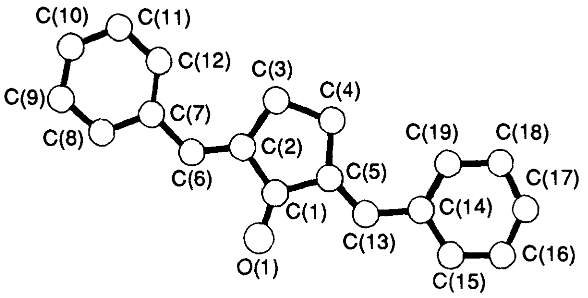

Fig. 1 Numbering scheme for the benzyl(benzylidene)- and the dibenzylidene-cyclopentanone frameworks

Solid state reactivity was determined by comparing Fourier-transform infrared (FTIR) spectra taken before and after irradiation by UV radiation. The UV-source used was a water-cooled 400 W low-pressure mercury lamp equipped with a Pyrex filter (λ > 360 nm). No means of measuring the UV radiation dose was available. FTIR spectra were recorded on a 1710 Perkin-Elmer spectrometer.

Results and Discussion

Tables 2, 3 and 4, present the positional parameters of non-hydrogen atoms for compounds B*p*FBCP, *p*FDBCP and 4FBBCP, respectively, whilst tables of positional parameters for hydrogen, thermal parameters for all atoms, and tables of observed and calculated structure factors have been deposited as supplementary material. Fig. 1 shows the numbering scheme for all three structures. For B*p*FBCP, the benzylidene moiety corresponds to atoms C-5–C-13, C-14–C-19. Tables 5, 6 and 7 contain the bond lengths and angles for B*p*FBCP, *p*FDBCP and 4FBBCP, respectively.

Table 6 Bond lengths (Å) and angles (°) for *p*FDBCP

C(2)–C(1)	1.480(6)	C(5)–C(1)	1.464(6)
O(1)–C(1)	1.234(5)	C(3)–C(2)	1.504(6)
C(6)–C(2)	1.338(5)	C(4)–C(3)	1.550(7)
C(5)–C(4)	1.508(7)	C(13)–C(5)	1.339(6)
C(7)–C(6)	1.456(6)	C(8)–C(7)	1.397(6)
C(12)–C(7)	1.399(6)	C(9)–C(8)	1.384(6)
C(10)–C(9)	1.364(6)	C(11)–C(10)	1.371(7)
F(1)–C(10)	1.363(5)	C(12)–C(11)	1.380(7)
C(14)–C(13)	1.454(6)	C(15)–C(14)	1.397(6)
C(19)–C(14)	1.399(6)	C(16)–C(15)	1.376(6)
C(17)–C(16)	1.375(7)	C(18)–C(17)	1.366(7)
F(2)–C(17)	1.356(5)	C(19)–C(18)	1.367(6)
C(5)–C(1)–C(2)	109.6(4)	O(1)–C(1)–C(2)	124.2(4)
O(1)–C(1)–C(5)	126.2(4)	C(3)–C(2)–C(1)	108.4(4)
C(6)–C(2)–C(1)	119.7(4)	C(6)–C(2)–C(3)	131.9(3)
C(4)–C(3)–C(2)	106.7(4)	C(5)–C(4)–C(3)	106.3(4)
C(4)–C(5)–C(1)	109.0(4)	C(13)–C(5)–C(1)	119.7(4)
C(13)–C(5)–C(4)	131.3(3)	C(7)–C(6)–C(2)	131.5(4)
C(8)–C(7)–C(6)	123.9(4)	C(12)–C(7)–C(6)	117.7(5)
C(12)–C(7)–C(8)	118.4(5)	C(9)–C(8)–C(7)	120.6(5)
C(10)–C(9)–C(8)	118.4(5)	C(11)–C(10)–C(9)	123.5(5)
F(1)–C(10)–C(9)	118.5(6)	F(1)–C(10)–C(11)	117.9(5)
C(12)–C(11)–C(10)	117.8(5)	C(11)–C(12)–C(7)	121.2(6)
C(14)–C(13)–C(5)	131.2(4)	C(15)–C(14)–C(13)	124.9(5)
C(19)–C(14)–C(13)	118.1(5)	C(19)–C(14)–C(15)	117.0(4)
C(16)–C(15)–C(14)	121.8(5)	C(17)–C(16)–C(15)	118.0(5)
C(18)–C(17)–C(16)	122.9(5)	F(2)–C(17)–C(16)	117.7(5)
F(2)–C(17)–C(18)	119.4(5)	C(19)–C(18)–C(17)	118.1(5)
C(18)–C(19)–C(14)	122.2(5)		

Table 7 Bond lengths (Å) and angles (°) for 4FDBCP

C(2)–C(1)	1.484(8)	C(5)–C(1)	1.481(9)
O(1)–C(1)	1.226(7)	C(3)–C(2)	1.481(8)
C(6)–C(2)	1.356(8)	C(4)–C(3)	1.550(9)
C(5)–C(4)	1.510(9)	C(13)–C(5)	1.344(9)
C(7)–C(6)	1.444(9)	C(8)–C(7)	1.425(8)
C(12)–C(7)	1.376(8)	C(9)–C(8)	1.375(9)
C(10)–C(9)	1.356(9)	F(1)–C(9)	1.375(7)
C(11)–C(10)	1.374(9)	F(2)–C(10)	1.364(7)
C(12)–C(11)	1.386(9)	C(14)–C(13)	1.434(8)
C(15)–C(14)	1.434(8)	C(19)–C(14)	1.395(8)
C(16)–C(15)	1.359(8)	C(17)–C(16)	1.382(8)
F(3)–C(16)	1.375(7)	C(18)–C(17)	1.361(8)
F(4)–C(17)	1.369(7)	C(19)–C(18)	1.389(8)
C(5)–C(1)–C(2)	107.9(5)	O(1)–C(1)–C(2)	126.3(6)
O(1)–C(1)–C(5)	125.8(6)	C(3)–C(2)–C(1)	110.0(5)
C(6)–C(2)–C(1)	117.7(6)	C(6)–C(2)–C(3)	132.3(5)
C(4)–C(3)–C(2)	106.8(5)	C(5)–C(4)–C(3)	106.1(5)
C(4)–C(5)–C(1)	109.1(5)	C(13)–C(5)–C(1)	118.9(6)
C(13)–C(5)–C(4)	132.0(5)	C(7)–C(6)–C(2)	131.5(5)
C(8)–C(7)–C(6)	115.5(6)	C(12)–C(7)–C(6)	125.8(6)
C(12)–C(7)–C(8)	118.7(6)	C(9)–C(8)–C(7)	117.6(6)
C(10)–C(9)–C(8)	122.5(6)	F(1)–C(9)–C(8)	127.0(6)
F(1)–C(9)–C(10)	110.5(6)	C(11)–C(10)–C(9)	120.8(6)
F(2)–C(10)–C(9)	110.7(6)	F(2)–C(10)–C(11)	128.5(6)
C(12)–C(11)–C(10)	118.2(6)	C(11)–C(12)–C(7)	122.1(6)
C(14)–C(13)–C(5)	132.6(5)	C(15)–C(14)–C(13)	123.8(6)
C(19)–C(14)–C(13)	118.4(6)	C(19)–C(14)–C(15)	117.8(6)
C(16)–C(15)–C(14)	117.3(6)	C(17)–C(16)–C(15)	122.9(6)
F(3)–C(16)–C(15)	127.6(6)	F(3)–C(16)–C(17)	109.4(6)
C(18)–C(17)–C(16)	121.9(6)	F(4)–C(17)–C(16)	109.6(6)
F(4)–C(17)–C(18)	128.5(6)	C(19)–C(18)–C(17)	116.2(6)
C(18)–C(19)–C(14)	123.9(6)		

The packing of B*p*FBCP is similar to that for most other benzylidene-substituted BBCPs. The only reactive member of the series, in addition to BBCP, is B*p*BrBCP, these two having very similar packing motifs. If Br is substituted by Me or Cl however, the packing motif is changed to a photostable one. The following rationalisation was made of these observations: The difference in packing arises because the bromo substituent enters into numerous intermolecular Br ••• H contacts thanks to its polarisability; these contacts are maximised in the photoreactive motif, where molecules are related by a centre of symmetry. In the case that obtains for the Me- and

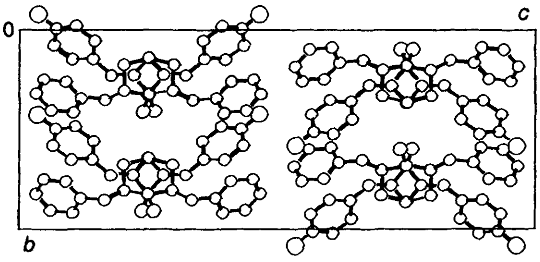

Fig. 2 Packing diagram for B*p*FBCP viewed along the *a* axis

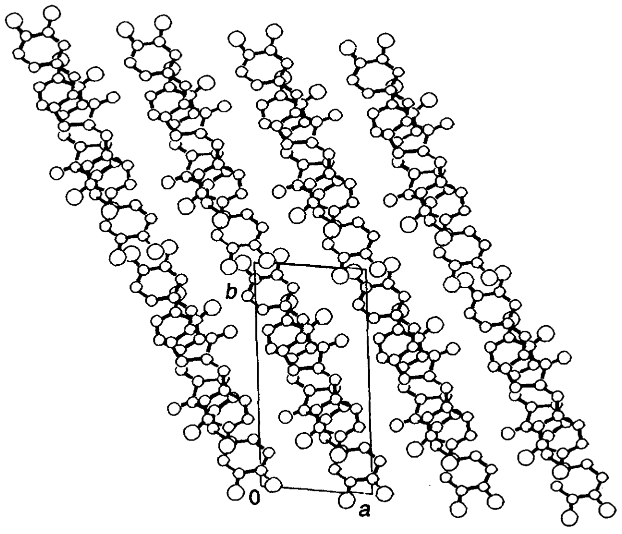

Fig. 3 View of the 4FBBCP crystal structure along the *c* axis

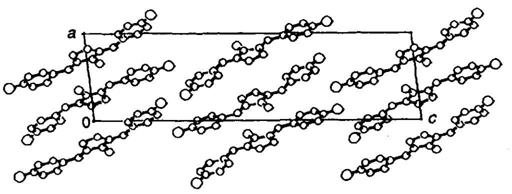

Fig. 4 The *p*FDBCP crystal structure viewed along the *b* axis

Cl-substituted molecules, these contacts are not advantageous, and packing is steered in such a way as to accommodate the increased volume of the benzylidene moiety. This results in a photostable packing motif, where nearest neighbours are related by a glide plane. The exocyclic double bonds (C-5 • • • C-13) are no longer parallel, and are separated by distances in excess of 4.7 Å.

B*p*FBCP packs (see Fig. 2) in such a way that nearest neighbours are related by a glide plane. The exocyclic double bonds (C-5–C-13) are related by a glide plane, and are thus not parallel. The bond to bond separation is in excess of 5 Å. This is not a geometry which is conducive to [2 + 2] cycloaddition, and no reaction is observed. The benzylidene fragment is almost planar, and subtends an angle of 73° with the benzyl phenyl ring. It is apparent that the change in packing from BBCP to B*p*FBCP cannot be rationalised in terms of volume changes, given the similarity of the van der Waals radii of F (1.35 Å) and H (1.2 Å). It is clear that the change in packing has to be associated with strong intermolecular interactions involving F.

*p*FDBCP and 4FBBCP have both been shown to undergo solid-state photoreaction involving the exocyclic double bonds. These changes have been observed from changes in the FTIR spectra, *i.e.* a reduction in the peak corresponding to C=C stretching at ν 1620 cm^{-1} for *p*FDBCP and at ν 1600 cm^{-1} for 4FDBCP, and a shift in position and shape change to the peak corresponding to C=O carbonyl stretch. These changes are far more easily discernible than in the case of DBCP, where observations were made more difficult by the broadening of the infrared spectra. This broadening was due to the formation of amorphous product. For both crystals, nearest neighbour molecules are related by a centre of symmetry.

For 4FBBCP, the bond centre to bond centre separation (C-5–C-13 to C5′–C-13′) was found to be 4.30 Å. This is a geometry which permits topochemical [2 + 2] photoreaction, although the separation is one of the longest observed so far. Fig. 3 shows a packing diagram for this structure. In order to obtain good convergence of the structure solution, two additional atoms near the fluoro substituents, with partial occupancy factors were needed. These are probably due to the presence of solvent molecules round the fluorine atoms. The molecule as a whole is flat, since the two benzylidene moieties subtend an angle of only 4° between them. This is in contrast to DBCP, where the two moieties subtended an angle of 10°. Furthermore, in DBCP the molecule possesses a two-fold axis, which is coincident with a crystallographic one. For *p*BrDBCP, the molecule possesses a mirror plane of symmetry. In *p*FDBCP as well as 4FBBCP, the molecule does not possess such symmetry. This confirms that in spite of the rigidity of the molecule, the torsional freedom round C-3–C-4, C-13–C-14 and C-6–C-7 is enough to produce small changes which would give rise to these differences in the configuration of the benzylidene cyclopentanone carbon framework.

*p*FDBCP shows a double bond to double bond separation of 4.12 Å, which is again favourable for topochemical reaction. The molecule as a whole is essentially planar, and the two benzylidene moieties subtend a dihedral angle of only 3° between them. Fig. 4 contains a packing diagram for this structure.

Since nearest neighbour molecules for double bonds in both *p*FDBCP and 4FBBCP are for molecules related by a centre of symmetry, and with bond-centre to bond-centre distances conducive to topochemical reaction, it is expected that the product will be a substituted cyclobutane with a centre of symmetry, by analogy with BBCP and DBCP.[5] Changes in the FTIR spectra upon irradiation, confirm the formation of such a product. Dimerisation was also indicated by mass spectrometry of irradiated samples. The ^{1}H NMR spectrum (60 MHz) for irradiated *p*FDBCP, showed a signal at $\delta = 4.41$, which was assigned to the two cyclobutane (or oxetane) hydrogen atoms. Examination of an irradiated sample of *p*FDBCP by thin layer chromatography (TLC), however, indicated the presence of two products. It is suggested that in addition to the centrosymmetric cyclobutane product, an oxetane was also obtained; favourable contacts of 3.58 Å for O-1 • • • C-5 in *p*FDBCP and of 4.30 Å in 4FBBCP between centrosymmetric pairs have been identified. Oxetane formation has been observed in other enone solid-state transformations. It was not possible to isolate the products for further characterisation. Comparison of the peak height ratios (C=C double bond stretch to carbonyl stretch) for *p*FDBCP and 4FBBCP before irradiation and after 5 h exposure, indicated that reaction had resulted in the removal of 50% of monomer.

An examination of the formation of mixed crystals of DBCP with *p*FDBCP[11,12] indicated from the variation of melting point with composition, that the solid solutions formed were non-ideal. This was in contrast with the *p*ClBBCP and *p*MeBBCP pair,[13] where an ideal solid solution was obtained. This again indicates that in spite of the proximity of the van der Waals radii for H and F, these are not interchangeable. That a solid solution was obtained, was indicated by the fact that upon irradiation mixed dimers were obtained, as well as those of DBCP and *p*FDBCP only.

It is suggested that the differences in molecular symmetry between DBCP and its fluorinated analogues are due to the intermolecular interactions of the fluoro substituents. Closest intermolecular F · · · F contacts were found to be 3.38 Å for 4FBBCP, and 3.93 Å for *p*FDBCP. For B*p*FBCP, shortest F · · · F contact was in excess of 5 Å. These distances are well in excess to the sum of the van der Waals radii for two fluoro substituents. The small size of this atom in addition to its high electronegativity, probably has the effect of repelling other fluoro substituents. This is unlike chloro substitutions, where short Cl · · · Cl contacts are often observed, especially where dichloro substituents are present in the benzene ring. These interactions have often been used in crystal engineering, to steer molecules to lie parallel to each other. It appears that fluoro substitution will also steer planar molecules towards such a configuration that nearest neighbour molecules are parallel or antiparallel to each other. This is probably due to the fact that the strong electron withdrawing effect of the fluoro substituent induces $\delta+$ charges on the phenolic carbons attached to them; close contacts between these rings and fluoro substituents on neighbouring molecules bearing $\delta-$charges will occur. In the case of planar molecules, these contacts are maximised for molecules related by a centre of symmetry.

In the case of B*p*FBCP, however, a centrosymmetric packing motif would bring the fluoro group in proximity to the benzyl group which is unsubstituted. To obtain the contacts described from the dibenzylidene molecules, one needs to pack two B*p*FBCP molecules parallel to each other. Since these molecules are not planar, such a motif would be highly inefficient. Instead, these contacts are achieved by forcing the molecule in a non-reactive motif.

The mechanism for dimer formation has been discussed in detail elsewhere[16] and is believed to be a non-concerted reaction between a ground-state molecule and triplet excited state molecule, resulting in a cyclobutane ring where closest intermolecular contacts involve two carbon–carbon double bonds, or formation of an oxetane, where the reactant groups are one double bond and one carbonyl.

That symmetrically substituted dibenzylidenecyclopentanones are photoreactive is contrary to Kaupp's observations.[14] However, the peculiar nature of fluoro substitution and the network of intermolecular interactions in which these groups take part, is probably responsible for this discrepancy. The fact that fluoro substitution leads to packing motifs in the DBCP series which are markedly different from those adopted where other substituents are employed, augurs well for their use in crystal engineering techniques, so as to achieve desirable solid-state reactivity.

Acknowledgements

The preparation and preliminary study of the solid-state reactivity of the fluorinated enones, were carried out as part of a final-year project in this department by SEH. We are grateful to the SERC and Professor M. B. Hursthouse for data collection, to Professor P. G. Sammes for useful discussions, and acknowledge the financial support of Brunel University (BRIEF Award).

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Paper 1/00653E
Received 11*th February* 1991
Accepted 15*th April* 1991