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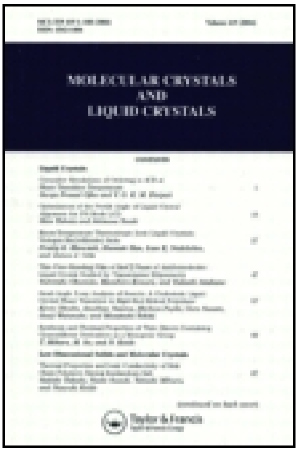

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Fluoro Substitution Effects in the Crystal Packing of Fluorobenzenes

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FLUORO SUBSTITUTION EFFECTS IN THE CRYSTAL PACKING OF FLUOROBENZENES

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Abstract In this paper the effect of fluoro substitution on the packing of the 2-benzyl-5-benzylidene- and 2,5-dibenzylidene-cyclopentanone frameworks will be discussed. We chose the fluoro substituent because it has a much smaller van der Waals radius than other substituents used hitherto, while it is very similar to that of hydrogen. This allows a method to distinguish between substituent effects due to size and those due to non-bonded interactions on the crystal packing. It can be shown that intermolecular atom-atom interactions involving the fluoro groups hold sway over the effect of the volume of the subtituents upon crystal packing. A comparison is made between the F...F contacts in these structures and others published in the literature.

Keywords: fluorine-fluorine interactions, crystal packing, substituent effects, cambridge structural database, fluorobenzenes, solid state photocycloaddition

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INTRODUCTION

The study of diffusionless[1], or topochemical reactions 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[2]. These considerations are important in such diverse areas as electronic materials or those with non-linear optical properties, and pharmaceuticals[3].

This paper discusses the effect of fluoro substitution on the packing of the 2-benzyl-5-benzylidene- and 2,5-dibenzylidene-cyclopentanone frameworks (BBCP and DBCP respectively), and compares these with other fluorobenzenes. We chose the fluoro substituent because it has a much smaller van der Waals radius (135pm) than other substituents used hitherto, namely Cl (180pm), Br (195pm), Me (200pm), I (215 pm), OMe and OH. Furthermore, the van der Waals radius of the fluoro substituent is very similar to that of hydrogen. This allows a method to distinguish between substituent

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effects due to size and those due to non-bonded interactions, on the crystal packing. In the case that obtains for non-fluorinated benzylidene enones, it has been shown[4] that where the substition pattern does not add significantly to electrostatic intermolecular interactions, size considerations hold sway, and chloro-methyl interchangeability as suggested by Kitaigorodskii[5] is valid; where, however, these interactions are significant, then chloro and methyl substituents behave differently.

EXPERIMENTAL

Enones BpFBCP (2-benzyl-5-(4-fluorobenzylidene)cyclopentanone), pFDBCP (2,5-bis-(4-fluorobenzylidene)cyclopentanone), and 4FDBCP (2,5-bis-(3,4-difluorobenzylidene) cyclopentanone), were prepared[6] in the way previously described for the archetypal compounds 2-benzyl-5-benzylidene-cyclopentanone and 2,5-dibenzylidene-cyclopentanone[7,8].

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 400W low-pressure mercury lamp equipped with a pyrex filter ($\lambda >$ 360nm). No means of measuring the UV radiation dose was available. FTIR spectra were recorded on a 1710 Perkin-Elmer spectrometer.

The Cambridge crystallographic database was used to search for structures containing the fluorobenzene moiety using the QUEST90 programme[9]. Statistical and geometric calculations were carried out using GSTAT90. Calculations were carried out on the ULCC Amdahl 5890/300 computer.

DISCUSSION

BpFBCP packs in a photostable packing motif, in such a way that nearest neighbours are related by a glide plane, meaning that the exocyclic double bonds are not parallel, and are separated by a distance in excess of 500 pm. This crystal is thus not expected to exhibit [2+2] cycloaddition, unlike the case for BBCP, the parent structure. The change in packing from BBCP to BpFBCP cannot be rationalised in terms

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Table I

List of Refcodes obtained from the QUEST90 Search

AFBIPH ANLCLA BABZAF BACYAF BAJMEE BANGOM BARBOL BAWPUK BAZHOZ BCFPLA
BDIXNB BEDLUR BFPDZB BIBLON BIBSEK BICCAR BIHMUA BIKDII BIKDOO BIMCEF
BIPKEQ BIPPIZ BIPPOF BITCEM BIWZIO BMPFPN BOFVOH BOHWIE BOKHOY BOLNAR
BPFPDS BPPFBP BRFLBZ BUCYED BULJIB BUNKOK BUTYUK BUWLOU BXCPAF CACPIF
CACPOL CACXOT CADGIX CADMUP CAFVAG CEBYAJ CEBYEN CEGSOW CEKYUM CEPGUZ
CEVGUF CFBXMO CFHBZP CFPARH CFPNIB CFTPVP CHCFMO CIDGAX CIPRIC CIRKAP
CNIFPC COGHOV COSJUP COSRIL COTDIY COTFEW COTFIA COVJIG COWKII COYSUE
CPAZCO CPFPCO CPFPRH CPFVLV CUGPEZ CUPMAB CUVDOM CUXWAT CUYLUD DABCEO
DAHSAG DALYAQ DAMBUO DAMREO DASMUF DATHOV DBOFBP DEBJEZ DEBKAW DECFDP
DEDJEB DEHBOH DENWUO DENXAV DENXEZ DERYAA DEVFOZ DFBENV DFNAPH DFPPTP
DFPSLO DIFHUV DIKDEG DIKJOW DILDIL DILDOR DIRXUX DISLUM DIWBOA DIZLAZ
DIZLED DIZVIR DMAFBZ DOCRIW DODTAR DODYUQ DODZAX DOHKEQ DOHKIU DOMVUW
DORFAR DOVZUJ DOWMEH DPFPPO DRPRDL DTFNPS DUGTUU DUHLEX DUNCIY DUTPUD
DUXFUX DUZJUD DUZLIT EPFPPT FABGOE EANFAB FANWAS FAPJOV FAPTUL FAPVAT
FASGEL FAVBUZ FAVTAX FAXREB FAZFAN FAZMOA FBPAZD FBYTMO FEBWIS FEBWOY
FECSUB FEFBIB FEKXEY FELCAA FEPXAS FETDUF FEWMOJ FGEBIA FGEBIB FHIPRP
FICCEZ FIHGEI FIHHIN FIRRON FIVVOV FIXVOX FIXWOY FLBIPC FLBZHG FLBZOS
FLCPNI FLDAZP FLGEHG FLNAPH FLPHHG FLTHAN FLUBIP FMPCBN FNTSBZ FOFFAH
FOJSAY FORGAU FOSHUQ FOTPEJ FOYHUW FPAMHG FPAPAR FPBUTP FPBXZL FPCLET
FPFAZP FPHBPI FPIRCO FPZCRU FSEANT FUCXOQ FUCXUW FUFVAD FUMBUK FUPMOS
FUVNEP GABTEI GALJAE GAMPEP GANYUP GAZJAS GEMMAM GEVPIG GEVPUS GEXJAU
GEYLOL GEZPEG GIDPUE GIGBUT GIJREW GIKBOR GILWON GIRMAV GIRXUA GIRXUA
HALDOL HALOPB HFHYZW HMOFAS HXDYFS IFPPAU JAGSIT JANPIX JAPJAL JARSEA
JAWGUJ JAXJAT JEDUIW KABWAL KACHEB KAHVEU KAJPAM KAMCIK KAPSID KASPAV
KAWFUJ KAWZAJ KAWZEN KEGMAK KEGMEO KEGMIS KEGMOY KEGMUE KEJTOI KEKBOR
KEKBUX KTFPHT LIPFAZ MEBRHA MEBRHB MEFPHN METOFB MPFPNI MSTFNI NFPHSO
NONFBP NPOFNP NTNFBP OFBZDO PASOFP PCUFBZ PEMFAC PEYOFB PFBIPH PFBZAC
PFBZAD PFBZCY PFDPAY PFICRH PFLBPH PFPBTI PFPHGE PFPSIL PFPVAP PFTENT
PFTPAN PFTRPH PFZPSO PLASAU RTFBCP SABBIG SACWUO SAHGAJ SAHWAZ SAHWED
SAMXOT SANXAG SAPNUS SAPPAA SAPPEE SARGOH SARGUN SATDIA SATHOK SAXKEH
SAXKIL SECFIP TAZIRP TFBIPH TFHCPY TFHPMN TFPIOC TFPTPM TFUPSN TOLCOB
TOPFCO TPFPCP VABXAX VACXEC VAFXOP VAJSII VAMLEA VAMTOS VASYAP VAVHEF
VAVVUJ VAWWUL VAXROB VAYHAE VEFMUO ZZZAOS ZZZAVM

Table II

Summary of Results of QUEST90 and GSTAT90 Search

	F...F/pm	C...F/pm
Mean	340.1	134.2
S.D.Sample	34.9	3.6
S.D.Mean	0.5	0.01
Minimum	257.7	122.1
Maximum	399.7	143.3
N_{obs}	4643	4643

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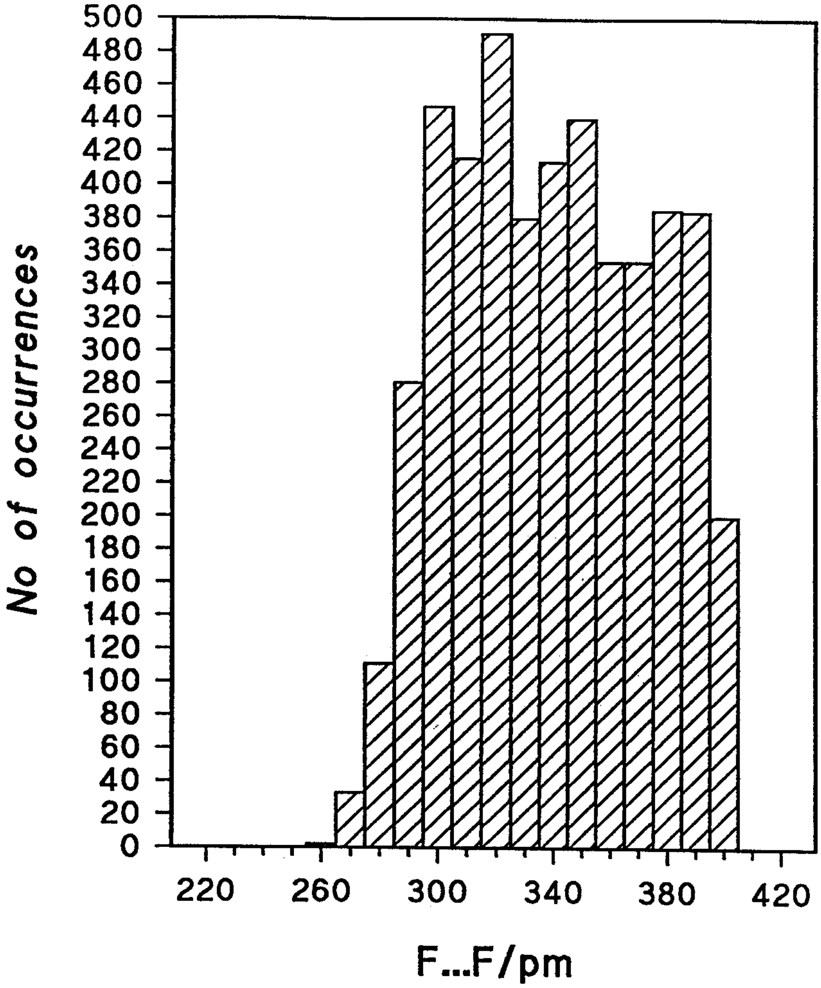
of volume changes, given the similarity of the van der Waals radii of F (135 pm) and H (120 pm). It is clear that the change in packing has to be associated with strong intermolecular interactions involving F.

For 4FDBCP, the bond centre to bond centre separation for centrosymmetric pairs, was found to be 430 pm, one of the longest separations for a reactive structure observed so far. pFDBCP shows a double bond to double bond separation of 412 pm, which is again favourable for topochemical reaction.

QUEST90 was used to scan the Cambridge crystallographic database for structures containing a fluorobenzene moiety, and 692 such structures were identified, several containing more than one target moiety. GSTAT90 was used to identify those structures which contained intermolecular F...F contacts in the range 200 to 550 pm. Such contacts were present in 317 structures, giving 4695 F...F contacts, of which 4643 were less than 400pm. Table I contains the refcodes for these 317 structures. Only those structures with an agreement factor less than 0.095 and which were error free were used in the calculations. The variation in C---F bond lengths for these 317 structures was also examined. The results of the GSTAT90 calculations are shown in Table II, together with other results from the geometric calculations. A scattergram was obtained between the values for the F...F distances and the C---F bond lengths, which showed no correlation. It was assumed that the C---F bond length would be a measure of the polarisation of the bond, and thus the charge on the fluoro atom.

Closest intermolecular F...F contacts were found to be 338 pm for 4FDBCP, 393 pm for pFDBCP, and for BpFBCP, in excess of 500 pm. These distances are well in excess of 270 pm, which is 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. It can thus be said that short F...F intermolecular contacts are unfavourable, unlike chloro substitutions where short Cl...Cl contacts are often observed, especially where

Fig. 1 F...F Distances Distribution



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dichloro substituents are present in the benzene ring. Short dichloro non-bonded intermolecular contacts have often been used in crystal engineering, to steer molecules to lie parallel to each other. The fact that short F...F contacts are avoided, is corroborated by an examination of Fig. 1. It can be seen that very few structures show intermolecular F...F contacts less or equal to 270 pm, with most contacts falling within the range 290 to 395 pm.

It appears that the steering effect of F...F interactions is to achieve a packing where the non-bonded distances are maximised, consistent with efficient packing. However, the strong electron withdrawing effect of the fluoro substituent induces $\delta+$ charges on the phenolic carbons attached to them; whereas the substituent will have a $\delta-$ charge associated with it. Thus, close intermolecular contacts between phenolic carbon atoms and fluoro substituents should be energetically favourable. In the case of planar molecules, such as pFDBCP and 4FDBCP, these contacts are maximised for molecules related by a centre of symmetry. Since the number of F...$C^{\delta-}$ contacts is superior to the F...F contacts, the former hold sway. Thus, the centrosymmetric packing motif would be favoured, in spite of a relatively short contact for 4FDBCP. The effect of different motifs of fluoro substitution on the packing of dibenzylidenes can be best assessed by comparing the packing of the archetype DBCP (see Fig. 2) with those for pFDBCP and 4FDBCP in Fig. 3 and Fig. 4 respectively.

In the case of BpFBCP (Fig. 5), however, a centrosymmetric packing motif would bring the fluoro group in proximity to the benzyl group, which is unsubstituted. To obtain favourable contacts with the fluorinated benzylidene phenyl ring, one needs to pack two BpFBCP molecules parallel to each other. Since these molecules are not planar, such a motif would be highly inefficient, in addition to resulting in a short F...F contact. In general, the presence of only one fluorinated ring per molecule would result in fewer favourable F...$C^{\delta-}$ short conacts. A large number of such contacts can be achieved by forcing the molecule in a non-reactive motif, where

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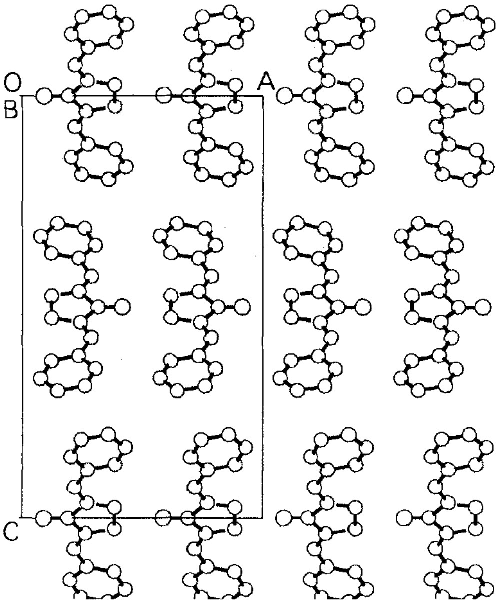

Fig. 2 Packing diagram for DBCP

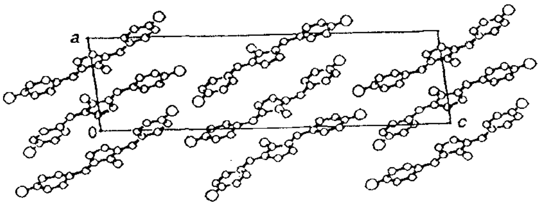

Fig. 3 The packing diagram of fluorinated enone pFDBCP

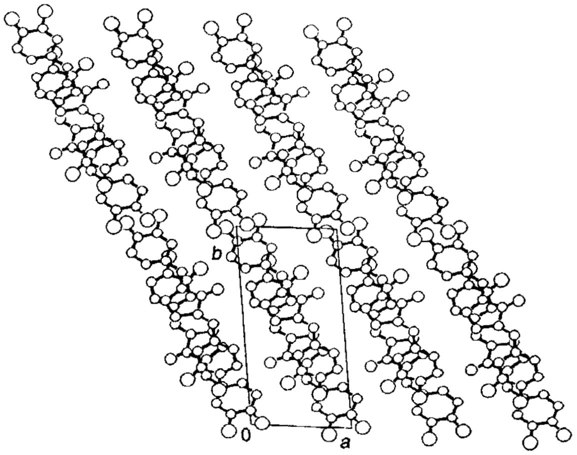

Fig. 4 The packing diagram of fluorinated enone 4FDBCP

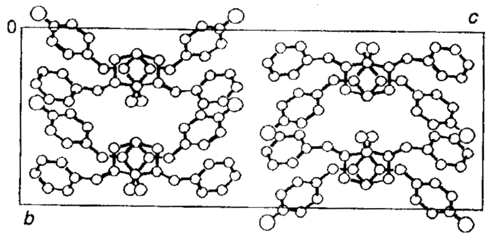

Fig. 5 The packing diagram of fluorinated enone BpFBCP

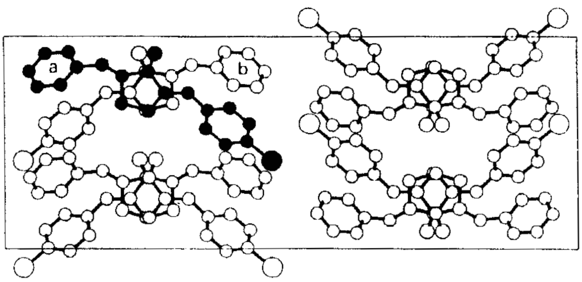

Fig. 6 Packing diagram for BpClBCP

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they are related with a glide plane, which would also result in long F...F distances. Thus, whereas 4FDBCP and pFDBCP have contacts only slightly lower than the mean calculated by GSTAT90, BpFBCP showed a significantly longer contact. The BpFBCP packing motif, is thus very similar to that of its chloro analogue BpClBCP, which is shown in Fig. 6.

Fluoro substitution appears to result in novel packing motifs for the DBCP family of molecules; this augurs well for the employment of fluoro substitution in a crystal engineering strategy, alongside di-chloro substitution. The relatively easier access to fluorinated compounds than hitherto, and the increasing knowledge of the organic chemist in the use of these compounds in synthesis, is an added bonus.

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REFERENCES

(1) J.M. Thomas, Nature, 289, 633, (1981)
(2) C.R. Theocharis, in (Eds. S. Patai and Z. Rappoport) "The Chemistry of Enones", J. Wiley and Sons, 1133-1176 (1989)
(3) J.M. Thomas, Pure Appl. Chem., 51, 1996, (1979)
(4) C.R. Theocharis and W. Jones, in (Ed. G.R. Desiraju) "Organic Solid State Chemistry", Elsevier Press: Amsterdam, pp 47-68, (1987)
(5) A.I. Kitaigorodskii, "Molecular Crystals and Molecules", Academic Press, (1973)
(6) S.E. Hopkin, M. Muir and C.R. Theocharis, J. Chem. Soc. Perkin Trans II, 1131-1135, (1991)
(7) W. Jones, H. Nakanishi, C.R. Theocharis and J.M. Thomas, J. Chem. Soc. Chem. Comm., 610, (1980)
(8) C.R. Theocharis, W. Jones, J.M. Thomas, M. Motevalli and M.B. Hursthouse, J. Chem. Soc. Perkin Trans II, 71, (1984)
(9) F.H. Allen, O. Kennard, and R. Taylor, Acc. Chem. Res., 16, 145, (1983)