The photoproduct ratios in the solid-state reactions do not differ very greatly from those in solution (Table 3), again indicating that the photoreactions are governed mainly by intramolecular forces. For H-Ad and Cl-Ad-*b*, the benzene solution and solid-state photoproduct ratios are virtually identical. The interpretation of the results for Cl-Ad-*b* is, however, somewhat ambiguous, as the crystals show clear evidence that the photolysis reaction is occurring at or near the surface (it was possible to remove the photolysed layer with a scalpel and expose the unreacted crystal interior); hence the reaction may not be a true (topochemically controlled) solid-state reaction for Cl-Ad-*b*. For Cl-Ad-*a*, the only solid-state photoproduct is the *trans*-OH cyclobutanol (% *cis*-OH = 0, Table 3).

Molecular models of the two possible types of photoproduct indicate that the *trans*-OH isomer is likely to be more stable, since the *cis*-OH isomer exhibits greater steric interactions between a pseudo-axial aryl substituent on the folded four-membered ring and the adamantyl grouping. This is in accord with the greater amount of *trans*-OH photoproduct, but does require large single-bond rotations of the reactant molecules to produce geometries suitable for cyclization. The reason for the decrease in the % *cis*-OH photoproduct for Cl-Ad-*a* is not clear, although various speculations can be made based on minor differences between Cl-Ad-*a* and Cl-Ad-*b* in torsion angles and angles between the biradical *p*-orbitals (Table 3) (Evans, Omkaram, Scheffer & Trotter, 1986).

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# Structure of Mixed Crystals of Benzoic Acid and *p*-Fluorobenzoic Acid, and their Energy Evaluation by Empirical Potential Functions

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## Abstract

'Solid-solution type' mixed crystals of benzoic acid and *p*-fluorobenzoic acid were obtained as phases that were completely different from either of the pure crystals of the two components. The structures of the mixed crystals for two different molar ratios were determined by the X-ray method, and stability of the new mixed crystalline phases was evaluated on the basis of empirical potential-energy calculations. $(C_7H_6O_2)_{0.268}.(C_7H_5FO_2)_{0.732}$, $M_r = 135·29$, monoclinic, $P2_1/c$, $a = 5·092\ (1)$, $b = 5·511\ (1)$, $c = 22·519\ (4)$ Å, $\beta = 94·86\ (1)°$, $V = 629·6$ Å$^3$, $Z = 4$, $D_x = 1·427$ Mg m$^{-3}$, $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 0·988$ mm$^{-1}$, $F(000) = 271·52$, $T = 293$ K, $R(F) = 0·051$ for 911 unique reflections. $(C_7H_6O_2)_{0.553}.(C_7H_5FO_2)_{0.447}$, $M_r = 130·09$, monoclinic, $P2_1/c$, $a = 5·184\ (1)$, $b = 5·474\ (1)$, $c = 22·086\ (2)$ Å, $\beta = 94·05\ (1)°$, $V = 625·2$ Å$^3$, $Z = 4$, $D_x = 1·382$ Mg m$^{-3}$, $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 0·835$ mm$^{-1}$, $F(000) = 261·0$, $T = 293$ K, $R(F) = 0·054$ for 838 unique reflections.

## Introduction

Mixed crystals of fluoride and non-fluoride compounds are thought to be good materials for the study of the differences and similarities between the properties of F and H atoms in organic compounds of biological and

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Table 1. *Unit-cell dimensions of BA, PFB and BPFB*

| | PFB[a] | BPFB[b] (1) | BPFB[b] (2) | BA[c] |
|---|---|---|---|---|
| BA (%) | 0 | 26·8 (5) | 55·7 (11) | 100 |
| PFB (%) | 100 | 73·2 (5) | 44·3 (11) | 0 |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| *a* (Å) | 3·820 (1) | 5·092 (1) | 5·184 (1) | 5·510 (5) |
| *b* (Å) | 6·382 (2) | 5·511 (1) | 5·474 (1) | 5·157 (6) |
| *c* (Å) | 26·588 (7) | 22·519 (4) | 22·086 (2) | 21·973 (8) |
| $\beta$ (°) | 93·81 (2) | 94·86 (2) | 94·05 (1) | 97·41 (8) |
| $V$ (Å$^3$) | 646·3 | 629·7 | 625·2 | 619·2 |
| $Z$ | 4 | 4 | 4 | 4 |

References: (*a*) Colapietro *et al.* (1979); (*b*) this work; (*c*) Bruno & Randaccio (1980).

industrial interest. With respect to intermolecular interactions, an F atom has properties more similar to an H atom than to other halogen atoms. Owing to this similarity, for example, mono- or oligofluorinated bioreactants are often taken into the metabolic system in mistake for natural non-fluorinated substrates (Goldman, 1969). In relation to such biologically interesting phenomena, we have studied the mixed crystals of several simple organic compounds and their fluorides. This paper is concerned with mixed crystals of benzoic acid (BA) and *p*-fluorobenzoic acid (PFB). Energy calculations using the empirical potential function are one of the useful methods for evaluating crystal stability. In this paper the stability of mixed crystal (BPFB) structures determined by the X-ray method are evaluated by the intermolecular-interaction-energy calculation.

## Crystallization of BPFB

Transparent plate-like crystals were grown by supercooling and evaporating a mixed solution of BA and PFB in several solvents: water, ethanol and benzene. The crystal habits were very similar to that of PFB, but the Weissenberg photographs indicated completely different unit-cell parameters from those reported for the BA crystal (Bruno & Randaccio, 1980) and the PFB crystal (Colapietro, Domenicano & Ceccarani, 1979), as given in Table 1. The HPLC analysis of the molar ratios in the mixed crystals (using a Shimadzu LC-3A apparatus equipped with a SPD-2A UV detector) showed that each crystal always contained both BA and PFB and that the PFB content was larger than that in the mother solution. The phase diagram (crystallization temperature *vs* molar ratio of the solution) indicates the existence of three different crystalline states (Fig. 1). The crystallization temperature was measured for the aqueous solutions of the BA–PFB mixture with various molar ratios in 0·0286 mol l$^{-1}$ total molar concentration. The major phase in this phase diagram is in the range from about 20–70% PFB, but this range depends on the total molar concentration of the solution. The BPFB crystals containing 30–90% PFB from the more condensed solutions were used for the X-ray analysis. Plots of the unit-cell parameters *vs* the molar ratio are smooth lines (Fig. 2), but each of the unit-cell parameters extrapolated to 0 or 100% component does not agree with those of the BA and PFB crystals (Table 1). The BPFB mixed crystals are, therefore, a new type of crystal which differ from both BA and PFB. They are a 'solid-solution type' crystal, and are not stoichiometric molecular complexes as often observed in other mixed crystals of perfluorocarbons (Potenza & Mastropaolo, 1975; Dahl, 1979, 1981*a*,*b*). This type of mixed organic crystal has rarely been found. To our knowledge, the *p*-dibromobenzene–*p*-chloronitrobenzene mixed crystal is the only other example found hitherto (Kitaigorodsky, 1984).

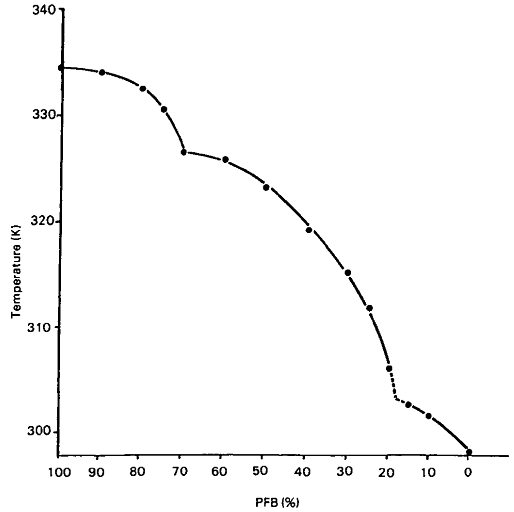

Fig. 1. Phase diagram for BA and PFB aqueous solutions. (Total molar concentration is 0·0286 mol l$^{-1}$.)

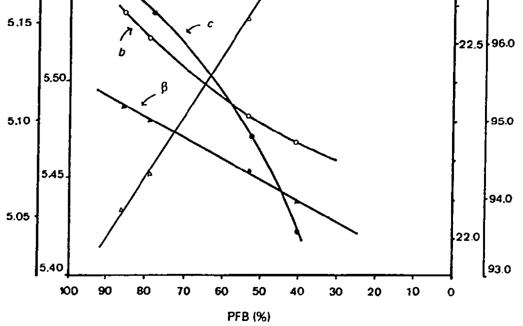

Fig. 2. The cell dimensions *a*, *b*, *c* and $\beta$ against the molar ratio of the crystal.

## Structure determination and refinement

Two single crystals, (1) 0·2 × 0·3 × 0·4 mm and (2) 0·1 × 0·2 × 0·2 mm, with different mixing ratios of BA and PFB molecules were chosen for the X-ray structure determination. Each was mounted on a Rigaku AFC-5RU four-circle diffractometer and the cell dimensions were refined by the use of 24 reflections measured in the range $50 < 2\theta < 60°$. Intensities were measured using the $2\theta$–$\omega$ scan with $2\theta < 120°$; $h0\to5$, $k0\to6$, $l-24\to24$; scan width $\Delta(\omega) = 0{\cdot}8° + 0{\cdot}5°\tan\theta$; no significant intensity variation for three standard reflections. 911 [for (1)] and 838 [for (2)] independent reflections with $F_o > 3\sigma(F_o)$ were used; Lorentz and polarization factors were corrected; no absorption correction was applied.

Table 1 lists crystal data of (1) and (2). The molar ratio of BA and PFB molecules for each crystal was determined by interpolation of their cell dimensions (Fig. 2).

The structure was solved with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the full-matrix least-squares method using the modified version of *ORFLS* (Busing, Martin & Levy, 1963). The quantity minimized was $\sum w(F_o - kF_c)^2$, where $w$ was $[\sigma(F_o)]^{-1}$. The refined parameters were coordinates and anisotropic thermal parameters for C, O and F atoms. H atoms were located in difference Fourier maps and their coordinates and isotropic thermal parameters were refined. The H and F atoms at the *para* position of BA and PFB molecules respectively were refined independently as disordered atoms with the fixed occupancies listed in Table 1. The other constituent atoms were assumed not to be affected by the disorder. At the final stage, $R$, $wR$, $S$ and $(\Delta/\sigma)_{\max}$ were 0·051, 0·046, 0·49 and 0·75 for (1), and 0·054, 0·048, 0·51 and 1·0 for (2); $(\Delta\rho)_{\max} = 0{\cdot}21$ e Å$^{-3}$ for (1) and (2). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All computations were performed by the use of *KPPXRAY* (Taga, Higashi & Iizuka, 1985).

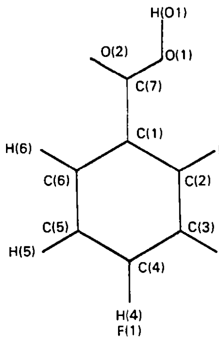

Fig. 3. Atomic numbering of the molecule.

Table 2. *Atomic parameters and their e.s.d.'s for BPFB (1) and (2) crystals*

$B_{eq}$ is the isotropic equivalent of the anisotropic thermal parameter in Å$^2$. $B_{iso} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| (1) | | | | |
| F(1) | 0·9493 (12) | 0·1800 (11) | 0·2772 (3) | 7·32 (20) |
| C(1) | 0·4360 (5) | 0·3611 (4) | 0·3994 (1) | 4·18 (7) |
| C(2) | 0·4552 (6) | 0·5046 (5) | 0·3495 (1) | 4·96 (15) |
| C(3) | 0·6291 (6) | 0·4449 (5) | 0·3083 (1) | 5·57 (16) |
| C(4) | 0·7800 (6) | 0·2422 (5) | 0·3172 (1) | 5·34 (16) |
| C(5) | 0·7662 (6) | 0·0962 (5) | 0·3658 (1) | 5·70 (16) |
| C(6) | 0·5916 (6) | 0·1560 (4) | 0·4068 (1) | 5·18 (15) |
| C(7) | 0·2501 (5) | 0·4236 (4) | 0·4438 (1) | 4·55 (14) |
| O(1) | 0·1143 (5) | 0·6168 (4) | 0·4353 (1) | 5·60 (14) |
| O(2) | 0·2320 (4) | 0·2869 (3) | 0·4882 (1) | 5·75 (6) |
| (2) | | | | |
| F(1) | 0·9535 (9) | 0·1953 (10) | 0·2755 (2) | 7·92 (25) |
| C(1) | 0·4405 (6) | 0·3664 (6) | 0·3983 (1) | 4·61 (15) |
| C(2) | 0·4602 (6) | 0·5123 (6) | 0·3475 (2) | 5·46 (17) |
| C(3) | 0·6355 (7) | 0·4560 (7) | 0·3058 (2) | 6·05 (19) |
| C(4) | 0·7894 (7) | 0·2530 (7) | 0·3151 (2) | 5·95 (18) |
| C(5) | 0·7731 (7) | 0·1067 (7) | 0·3650 (2) | 6·11 (18) |
| C(6) | 0·5972 (7) | 0·1622 (6) | 0·4063 (2) | 5·52 (18) |
| C(7) | 0·2529 (6) | 0·4259 (6) | 0·4434 (1) | 4·97 (16) |
| O(1) | 0·1206 (4) | 0·6198 (4) | 0·4344 (1) | 6·25 (14) |
| O(2) | 0·2315 (4) | 0·2875 (4) | 0·4883 (1) | 6·16 (15) |

Table 3. *Bond lengths* (Å) *and bond angles* (°)

| | (1) | (2) | | (1) | (2) |
|---|---|---|---|---|---|
| F(1)–C(4) | 1·343 (7) | 1·301 (6) | C(1)–C(2) | 1·384 (3) | 1·387 (5) |
| C(1)–C(6) | 1·382 (3) | 1·386 (5) | C(1)–C(7) | 1·475 (4) | 1·477 (4) |
| O(1)–C(7) | 1·275 (3) | 1·272 (4) | C(2)–C(3) | 1·376 (4) | 1·374 (6) |
| O(2)–C(7) | 1·261 (3) | 1·259 (3) | C(3)–C(4) | 1·361 (4) | 1·375 (5) |
| C(4)–C(5) | 1·365 (3) | 1·370 (6) | C(5)–C(6) | 1·375 (4) | 1·369 (6) |
| C(2)–C(1)–C(6) | 119·1 (2) | 119·5 (3) | C(2)–C(1)–C(7) | 120·7 (2) | 120·6 (3) |
| C(6)–C(1)–C(7) | 120·2 (2) | 120·0 (3) | C(1)–C(2)–C(3) | 120·3 (3) | 120·2 (3) |
| C(2)–C(3)–C(4) | 119·0 (2) | 119·0 (4) | F(1)–C(4)–C(3) | 119·8 (3) | 119·7 (4) |
| F(1)–C(4)–C(5) | 117·8 (4) | 118·6 (4) | C(3)–C(4)–C(5) | 122·4 (3) | 121·6 (4) |
| C(4)–C(5)–C(6) | 118·5 (3) | 119·2 (4) | C(1)–C(6)–C(5) | 120·8 (2) | 120·4 (4) |
| C(1)–C(7)–O(1) | 117·7 (2) | 116·9 (2) | C(1)–C(7)–O(2) | 119·5 (2) | 119·8 (3) |
| O(1)–C(7)–O(2) | 122·9 (2) | 123·3 (3) | | | |

## Crystal structure of BPFB

Fig. 3 shows the atomic numbering of BA and PFB molecules. Table 2 shows the atomic coordinates and the thermal parameters for the non-H atoms.* Table 3 lists bond lengths and bond angles. Crystals (1) and (2) have the same type of molecular packing. All bond lengths and bond angles of (1) except for F(1)–C(4) agree with the corresponding bond lengths and bond angles of (2) within 3$\sigma$. On comparison of these bond lengths and angles with those of BA and PFB crystals, the F(1)–C(4) bond length 1·301 (6) Å of (2) is shorter than the 1·364 (3) Å of PFB by 10$\sigma$, and the F(1)–C(4)–C(3) bond angles

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* Lists of structure factors, phase angles, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51403 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

119·8 (3)° of (1) and 119·7 (4)° of (2) are larger than the 117·9 (2)° of PFB by 6$\sigma$ and 5$\sigma$, respectively. However, all the other bond lengths and bond angles of (1) and (2) are in good agreement with those of BA and PFB crystals.

Fig. 4 shows the three crystal structures BA, BPFB and PFB. Each crystal structure consists of hydrogen-bonded dimers, and these dimers have similar van der Waals contacts across the $(xy\frac{1}{4})$ plane. In view of the stability of the BPFB crystal, this $(xy\frac{1}{4})$ plane is of particular importance, since the disordered H and F atoms are close to one another across this plane. The intermolecular distances [2·4 Å for F(4)···H(3), 3·2 Å for F(4)···F(4) and 3·8 Å for F(4)···C(4)] are shorter than the corresponding distances in the PFB crystal, but these short distances are deceptive because of the disorder of the H and F atoms. The intermolecular interactions across this $(xy\frac{1}{4})$ plane will be described later through the energy evaluation by the use of the empirical potential function.

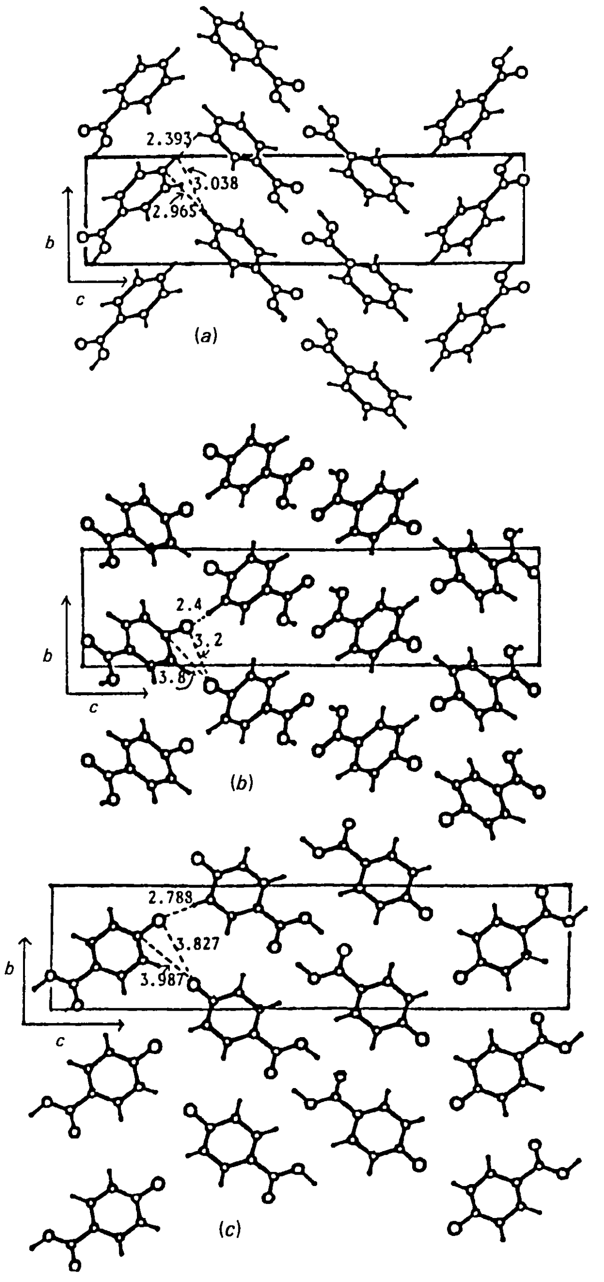

Fig. 4. Projections of the structures along the *a* axis. (*a*) BA (Bruno & Randaccio, 1980). (*b*) BPFB (this work). (*c*) PFB (Colapietro *et al.*, 1979). Distances in Å.

Table 4. *Interatomic potential coefficients used* ($10^{-18}$ J, Å)

| | *A* | *B* | *C* |
|---|---|---|---|
| C···C[a] | 517·30 | 3·600 | 3·7170 |
| O···O[a] | 670·41 | 4·330 | 2·4593 |
| H···H[a] | 27·79 | 3·740 | 0·2500 |
| C···O[a] | 588·90 | 3·965 | 3·0234 |
| C···H[a] | 65·38 | 3·670 | 0·9657 |
| O···H[a] | 136·50 | 4·035 | 0·7841 |
| F···F[b] | 473·43 | 3·900 | 1·5797 |
| F···C[b] | 475·69 | 3·650 | 2·4180 |
| F···O(–H)[b] | 369·31 | 4·166 | 1·1950 |
| F···O(=C)[b] | 504·06 | 4·155 | 1·4758 |
| F···H[b] | 45·94 | 4·400 | 0·2614 |

References: (*a*) Kim *et al.* (1985); (*b*) this work.

## Empirical potential function for the calculation of the intermolecular-interaction energy

The intermolecular-interaction energy of the mixed crystals was evaluated by the use of a Buckingham exp—6 type potential and a Coulomb potential, which is expressed by

$$E_{\text{total}} = \sum_{i,j}{}' \, [A_{ij}\exp(-B_{ij}r_{ij}) - C_{ij}r_{ij}^{-6} + e_ie_j/r_{ij}]$$

where $r_{ij}$ is the interatomic distance between atoms *i* and *j*, and $e_i$ and $e_j$ are the atomic charges. The coefficients $A_{ij}$, $B_{ij}$ and $C_{ij}$ depend on the kind of atoms *i* and *j*.

Table 4 lists the potential coefficients, *A*, *B* and *C*, that were used. The coefficients for C···C, O···O, H···H, C···O, C···H and O···H were taken from the set reported by Kim, Machida, Taga & Osaki (1985). The F···F, F···C and F···H coefficients were originally determined by the method of optimizing the intermolecular force for several fluorohydrocarbon crystals (Williams, 1970). The F···O(–H) and F···O(=C) coefficients were obtained from the geometric average of F···F and O···O (Momany, Carruthers, McGuire & Sheraga, 1974). These coefficients were examined for the PFB crystal structure by the method reported by Machida & Kuroda (1981). The lattice energy of the PFB structure was successfully converged to a minimum by changing the translation and rotation parameters of the rigid dimer and the unit-cell parameters *a*, *b*,

Table 5. *Atomic charges used* ($e \times 10^4$)

| | BA | PFB |
|---|---|---|
| F(1) | | −2285 |
| C(1) | −0364 | −0579 |
| C(2) | 0266 | 0593 |
| C(3) | 0182 | −0811 |
| C(4) | 0324 | 3062 |
| C(5) | 0233 | −0819 |
| C(6) | 0336 | 0617 |
| C(7) | 4856 | 4217 |
| O(1) | −4019 | −3938 |
| O(2) | −3152 | −2383 |
| H(C2) | 0103 | 0120 |
| H(C3) | −0246 | 0400 |
| H(C4) | −0073 | |
| H(C5) | −0243 | 0250 |
| H(C6) | −0019 | −0050 |
| H(O1) | 1845 | 1600 |

Table 6. *Observed and calculated structural parameters for the PFB crystal*

| | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (°) |
|---|---|---|---|---|
| Observed | 3·820 | 6·382 | 26·588 | 94·43 |
| Calculated | 3·865 | 5·686 | 26·289 | 90·91 |
| $\Delta$ | 0·045 | −0·696 | −0·199 | −3·52 |
| (%) | 1·18 | −10·91 | −0·75 | |

| $\Delta$ of molecular translation (Å) | $\Delta$ of molecular rotation (°) | | |
|---|---|---|---|
| | $\theta_1$ | $\theta_2$ | $\theta_3$ |
| 1·360 | 5·68 | 6·13 | 4·53 |

$c$ and $\beta$. The atomic charges used are given in Table 5. The final structure parameters are listed in Table 6.

## Mixed crystal models for the intermolecular-energy calculation

The intermolecular-interaction energies were calculated for nine models of the mixed crystals. Three of the models were the observed BPFB structures in which the PFB/BA molar ratios were 86·5/13·5 [crystal (3), unpublished], 73·2/26·8 [crystal (1)] and 55·7/44·3 [crystal (2)]. Three other models were solid-solution models having the BA structure, in which BA molecules were replaced with PFB molecules in the PFB/BA molar ratios 0/100, 10/90 and 20/80. The other three models were constructed with the PFB structure, in which PFB molecules were replaced with BA molecules in the PFB/BA molar ratios 0/100, 50/50 and 100/0. For all nine models, the C—F distance of a PFB molecule was fixed to 1·364 Å and the C—H distance of the H atom at the *para* position of a BA molecule was fixed to 1·0 Å. The atomic charges were assigned as given in Table 5. The rigid hydrogen-bonded dimer was assumed because the O—H···O hydrogen bonds between the carboxylic acid groups of the two molecules are strong; the hydrogen-bond energy is estimated at about 25 kJ mol$^{-1}$ (Coulson, 1957).

## Lattice energy and ($xy\frac{1}{4}$) surface energy

The lattice energies and the ($xy\frac{1}{4}$) surface energies for the nine models were calculated by the use of the potential functions mentioned above. Fig. 5 shows plots of the lattice energy *vs* the molar ratio for the three types of models, BPFB, BA and PFB. The lattice energy of BPFB, about 30–90% PFB, is lower than those of BA and PFB. The energy of BPFB has a minimum at about 70% PFB, whereas the energy curve of PFB has no minimum, and the energy of BA rapidly increases with increasing PFB content because of an increase in the Coulomb repulsion. These lattice-energy curves, therefore, justify stability of the BPFB mixed crystal in the range 30–90% PFB. The calculated BPFB range coincides approximately with the observed range described previously. Fig. 5 seems to suggest the existence of a new PFB phase in the range of about 15–30% PFB, but such a phase was not found in the phase diagram in Fig. 1. This disagreement may be caused by ignorance of the change in entropy in the energy evaluation.

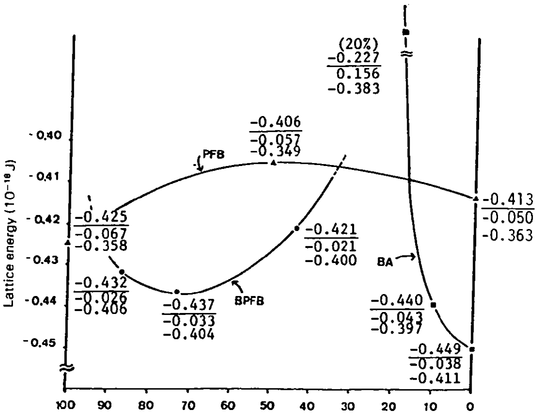

Fig. 5. Lattice energy against the molar ratio. From top to bottom in a column are total energy, Coulomb energy and dispersion energy.

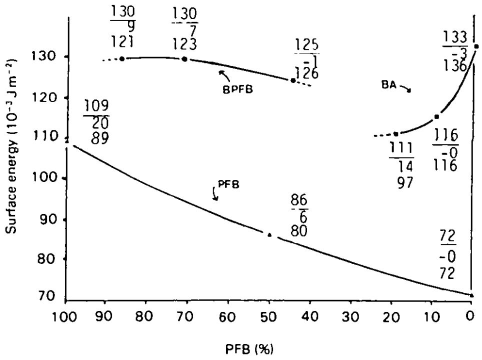

Fig. 6. The ($xy\frac{1}{4}$) surface energy against the molar ratio. From top to bottom in a column are total energy, Coulomb energy and dispersion energy.

The evaluation of the $(xy\frac{1}{4})$ surface energies also indicates stability of the BPFB mixed crystal. In this paper the surface energy means the energy necessary to cleave the crystal along the given plane (namely to make two surfaces). Fig. 6 shows plots of the $(xy\frac{1}{4})$ surface energy *vs* molar ratio. The surface energy of BPFB does not significantly vary in the range 44–87% PFB, whereas the surface energies for BA and PFB structures are reduced by mixing a small amount of PFB or BA into the pure crystal. An increase of PFB in the BPFB crystal decreases the dispersion energy and increases the Coulomb energy. Since the Coulomb energy compensates the dispersion energy, the total surface energy keeps approximately the same value. The unchangeable surface energy of BPFB reflects the random disorder of BA and PFB acceptable for the intermolecular interactions across the $(xy\frac{1}{4})$ plane. Hence the surface energy also supports stability of the BPFB structure.

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# Pitfalls of a Disordered Structure: Distinguishing the Compound Present, 4-Iodomethyl-1,7,7-trimethyl-3-oxabicyclo[2.2.1]heptan-2-one, from 5-Iodomethyl-1,2,2-trimethyl-4-oxabicyclo[3.2.0]heptan-3-one

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## Abstract

4-Iodomethyl-1,7,7-trimethyl-3-oxabicyclo[2.2.1]-heptan-2-one, $C_{10}H_{15}IO_2$, $M_r = 294{\cdot}13$, orthorhombic, *Pnma*, $a = 18{\cdot}768\,(2)$, $b = 8{\cdot}029\,(1)$, $c = 7{\cdot}467\,(2)$ Å, $V = 1125{\cdot}2$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}736$ g cm$^{-3}$, Mo $K\alpha$ radiation (graphite-monochromated), $\lambda = 0{\cdot}70926$ Å, $\mu = 26{\cdot}15$ cm$^{-1}$, $F(000) = 576$, $T = 295$ K, 1054 unique reflections, 766 with $I \geq 2\sigma(I)$, final $R = 0{\cdot}030$. The molecule sits on and is disordered about a crystallographic mirror plane. It is possible, by interchanging three atoms with their mirror-related partners, to generate a different compound, 5-iodomethyl-1,2,2-trimethyl-4-oxabicyclo[3.2.0]heptan-3-one, but it is unlikely that this is the species present, since refinement of this compound produced several

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