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Phenyl 3-Fluorobenzoate

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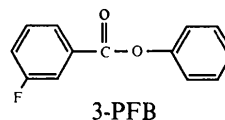
Abstract

Although the title compound, C₁₃H₉FO₂, differs from phenyl benzoate only in the presence of an F atom in the molecular structure, their molecular conformations and assemblies are quite different. It could be concluded that the change is due to the presence of the F atom.

Comment

During the past several years, molecular assembly has attracted special attention from various standpoints. The generation of an assembly with the

desired architectural features requires the design and/or modification of the starting component. This is because the assembling mode would depend on the interaction between components (Lehn, Mascal, Decian & Fischer, 1990). For the purpose of controlling the mode, hitherto components have generally been modified or designed by adding functional groups capable of hydrogen bonding, such as OH, NH₂, etc. One novel modification we have attempted is to add one F atom onto the starting material. The F atom has the highest electronegativity and, in addition, may form intermolecular hydrogen bonds in the solid state (Shibakami & Sekiya, 1992). Thus, the introduction of an F atom might be an effective modification method. Despite extensive studies of fluorine chemistry, however, there are few systematic studies of the F-atom effect on the assembling mode. Here we report the crystal structure of phenyl 3-fluorobenzoate (3-PFB) as the first example of our study, and compare it with the structure of phenyl benzoate (PB) (Adams & Morsi, 1976).



3-PFB was synthesized according to the conventional Schotten–Baumann method (Schotten, 1884) from 3-fluorobenzoic acid and phenol. The prismatic crystals of 3-PFB were grown from ethanol solution of the compound at room temperature. The crystal structure of 3-PFB is depicted in Fig. 1. As Table 2 shows, bond distances and angles are normal within experimental error. Inequality of the F(1)—C(5)—C(4) and F(1)—C(5)—C(6) angles is found. The angle between the planes of the two benzene rings in 3-PFB is 66.0°, while the corresponding angle in PB is 55.7°. In addition, the —COO group in 3-PFB is twisted by 8.7 and 74.5° with respect to the C(1)—C(6) and C(8)—C(13) rings, respectively; the angles in PB are 9.8 and 65.1°, respectively. These conformational differences are undoubtedly due to the effect of the F atom.

As shown in Fig. 1, it appears that the molecules are assembled through van der Waals interactions. The most striking structural feature is that the arrangement of the molecules differs notably from that of PB, which belongs to space group *P*2₁/*c* with *a* = 5.74 (1), *b* = 14.75 (2), *c* = 12.45 (2) Å, β = 101.0 (2)°. The arrangement of components along the axes as seen in the present structure was not observed in the PB structure. The shortest intermolecular distance is 2.39 Å from O(1) to H(9)(*x*, *y*, *z* - 1). This distance corresponds to a van der Waals contact. Further, it is noteworthy that the shortest

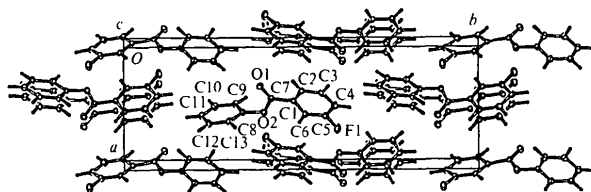


Fig. 1. ORTEP drawing (Johnson, 1976) of the crystal structure of 3-PFB as viewed along the *c* axis.

intermolecular contact involving the F atom is 2.50 Å from F(1) to H(5)($\frac{1}{2} - x, -y, \frac{1}{2} + z$). Since the van der Waals radii of F and H atoms are 1.47 and 1.00 Å, respectively (Bondi, 1964), it is obvious that the two atoms approach each other very closely.

In conclusion, our results show that introducing only one F atom into a particular position may lead to large differences in molecular conformation and assembly, although the size of the F atom is very close to that of an H atom.

Experimental

Crystal data

$C_{13}H_9FO_2$
 $M_r = 216.21$
 Orthorhombic
 $P2_12_12_1$
 $a = 7.827(2) \text{ \AA}$
 $b = 23.364(2) \text{ \AA}$
 $c = 5.843(2) \text{ \AA}$
 $V = 1068.6(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.344 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 27.3\text{--}28.4^\circ$
 $\mu = 0.819 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Prismatic
 $0.10 \times 0.10 \times 0.10 \text{ mm}$
 Colourless

Data collection

Rigaku AFC-7R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 984 measured reflections
 984 independent reflections
 753 observed reflections
 $[I > 3\sigma(I)]$

$\theta_{\max} = 60.0^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 26$
 $l = 0 \rightarrow 7$
 3 standard reflections monitored every 150 reflections
 intensity variation: -5%

Refinement

Refinement on F
 $R = 0.043$
 $wR = 0.047$
 $S = 3.45$
 753 reflections
 146 parameters
 H-atom parameters not refined
 $w = 4F_o^2/\sigma^2(F_o^2)$
 $(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$
 Extinction coefficient: 5.448×10^{-8}
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
F(1)	0.3053 (4)	0.1001 (1)	0.1499 (6)	8.90 (9)
O(1)	0.6272 (4)	-0.1151 (1)	-0.1710 (6)	6.19 (9)
O(2)	0.4388 (4)	-0.1046 (1)	0.1175 (5)	5.84 (9)
C(1)	0.5058 (6)	-0.0233 (2)	-0.1015 (8)	4.7 (1)
C(2)	0.5756 (6)	0.0005 (2)	-0.2933 (9)	5.9 (1)
C(3)	0.5520 (7)	0.0583 (2)	-0.3348 (10)	6.7 (2)
C(4)	0.4627 (7)	0.0925 (2)	-0.1931 (10)	6.1 (1)
C(5)	0.3966 (7)	0.0674 (2)	-0.0019 (10)	6.4 (1)
C(6)	0.4131 (6)	0.0102 (2)	0.0554 (8)	5.3 (1)
C(7)	0.5337 (6)	-0.0856 (2)	-0.0608 (8)	4.9 (1)
C(8)	0.4402 (6)	-0.1643 (2)	0.1646 (8)	5.1 (1)
C(9)	0.3537 (7)	-0.2004 (2)	0.0187 (9)	6.4 (1)
C(10)	0.3460 (7)	-0.2577 (2)	0.0772 (10)	6.8 (2)
C(11)	0.4224 (7)	-0.2780 (2)	0.2692 (9)	6.0 (1)
C(12)	0.5088 (7)	-0.2409 (2)	0.4053 (8)	6.6 (2)
C(13)	0.5192 (6)	-0.1831 (2)	0.3539 (9)	6.1 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

F(1)—C(5)	1.371 (5)	C(4)—C(5)	1.365 (7)
O(1)—C(7)	1.194 (5)	C(5)—C(6)	1.383 (6)
O(2)—C(7)	1.354 (5)	C(8)—C(9)	1.377 (6)
O(2)—C(8)	1.422 (5)	C(8)—C(13)	1.340 (6)
C(1)—C(2)	1.366 (6)	C(9)—C(10)	1.382 (6)
C(1)—C(6)	1.407 (6)	C(10)—C(11)	1.357 (7)
C(1)—C(7)	1.491 (6)	C(11)—C(12)	1.358 (7)
C(2)—C(3)	1.385 (6)	C(12)—C(13)	1.386 (6)
C(3)—C(4)	1.345 (6)		
C(7)—O(2)—C(8)	117.8 (3)	O(1)—C(7)—O(2)	124.2 (4)
C(2)—C(1)—C(6)	120.9 (4)	O(1)—C(7)—C(11)	124.6 (5)
C(2)—C(1)—C(7)	118.1 (4)	O(2)—C(7)—C(11)	111.2 (4)
C(6)—C(1)—C(7)	121.0 (4)	O(2)—C(8)—C(9)	118.5 (4)
C(1)—C(2)—C(3)	119.2 (5)	O(2)—C(8)—C(13)	118.9 (4)
C(2)—C(3)—C(4)	122.7 (5)	C(9)—C(8)—C(13)	122.5 (4)
C(3)—C(4)—C(5)	116.5 (5)	C(8)—C(9)—C(10)	117.5 (5)
F(1)—C(5)—C(4)	119.2 (5)	C(9)—C(10)—C(11)	121.6 (5)
F(1)—C(5)—C(6)	115.5 (5)	C(10)—C(11)—C(12)	118.7 (5)
C(4)—C(5)—C(6)	125.3 (5)	C(11)—C(12)—C(13)	121.7 (5)
C(1)—C(6)—C(5)	115.3 (4)	C(8)—C(13)—C(12)	118.1 (5)

The structure was solved by direct methods using *SAPI91* (Fan, 1991) and expanded using *DIRDIF92* (Beurskens, Admiraal, Beurskens, Bosman, Garcia-Granda, Gould, Smits & Smykalla, 1992). H atoms were placed at calculated positions (C—H 1.02 Å). Displacement parameters of the H atoms were kept fixed at the isotropic values of the parent atoms. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms, contact distances and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71564 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1041]

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received matching attention. As part of a detailed investigation (Mehta, Padma, Pattabhi, Pramanik & Chandrasekhar, 1990), we have studied the cycloaddition of several dienes to the novel dienophile tricyclo[6.2.1.0^{2,7}]undeca-2(7),4,9-triene-3,6-dione (1) (Cookson, Hill & Hudec, 1964; Mehta *et al.*, 1989), whose two faces are distinguishable by the presence of methano and etheno bridges, respectively. It was essential to establish unambiguously the stereochemistry of the cycloaddition products of (1); here we describe the molecular structure of the products (I) and (II), obtained by cycloadditions of tricyclo[5.2.1.0^{2,16}]deca-2,5,8-triene (2) and cyclooctatetraene (3), respectively.

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Cycloaddition Products of Tricyclo[6.2.1.0^{2,7}]undeca-2(7),4,9-triene-3,6-dione

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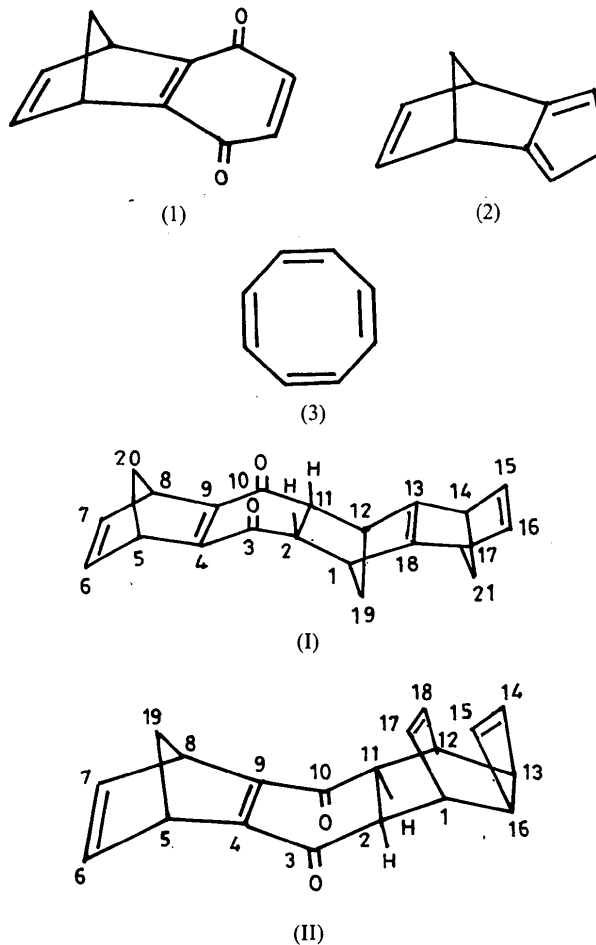
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Abstract

The crystal structures of *endo,anti,syn*-heptacyclo[10.6.1.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]henicosa-4(9),-6,13(18),15-tetraene-3,10-dione, C₂₁H₁₈O₂ (I), and *exo,syn,syn*-hexacyclo[10.4.2.1^{5,8}.0^{2,11}.0^{4,9}.0^{13,16}]nonadeca-4(9),6,14,17-tetraene-3,10-dione, C₁₉H₁₆O₂ (II), are reported. The packing of the molecules in both structures is stabilized by van der Waal's forces.

Comment

Stereoelectronic effects which influence the stereochemical outcome of the Diels–Alder reaction have been investigated extensively in recent years. In this context, facially perturbed diene or dienophile constituents are particularly incisive probes for evaluating the relative contributions of steric and electronic factors. While cycloadditions to facially perturbed dienes have been explored widely, the complementary response of facially perturbed dienophiles in Diels–Alder cycloadditions has not



The average e.s.d.'s for the bond lengths and angles are 0.006 Å and 0.4°, respectively, in (I), and 0.003 Å and 0.2°, respectively, in (II). The bond lengths and angles in the two structures are comparable and normal. C(3)—C(4) and C(15)—C(16) in (I) and C(3)—C(4) and C(11)—C(12) in (II) exhibit partial double-bond character. The C(5)—C(6) bond in both compounds is significantly elongated, which may be due to overcrowding of the atoms at C(6).

† DCB contribution No. 821.