

***N*-(4-Fluorophenyl)-4-nitrophthalimide: tripartite hydrogen-bonded sheets**Christopher Glidewell,^{a*} John N. Low,^b Janet M. S. Skakle^b and James L. Wardell^c^aSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland,^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cInstituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil

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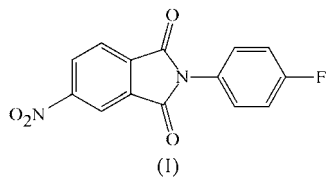
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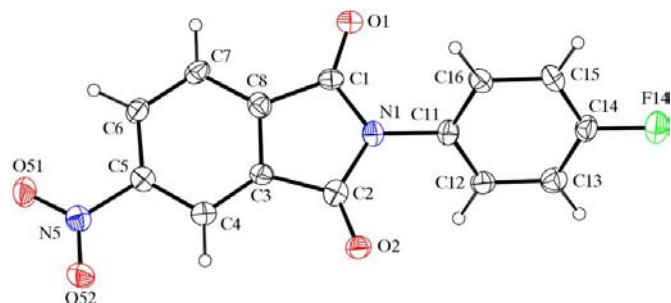
Molecules of the title compound, $C_{14}H_7FN_2O_4$, are linked by two $C-H \cdots O$ hydrogen bonds [$H \cdots O = 2.42$ and 2.44 Å, $C \cdots O = 3.173$ (9) and 3.313 (10) Å, and $C-H \cdots O = 134$ and 157°] into deep tripartite sheets, where the central layer is built from hydrogen-bonded $R_6^6(24)$ rings and where the F atoms all lie on the exterior surfaces of the sheets.

Comment

The title compound, (I), was synthesized as part of a study of supramolecular interactions in substituted phthalimides and related compounds. We present here its molecular and crystal structure.



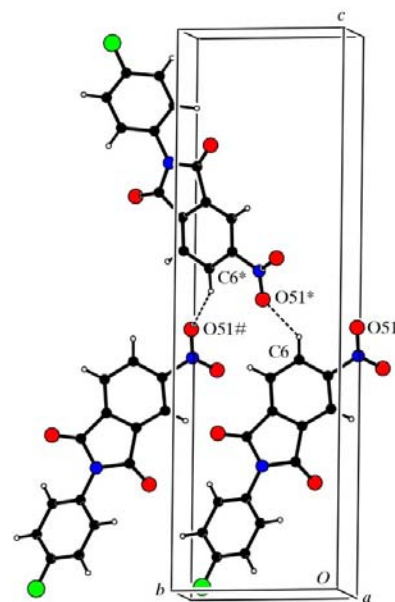
Within the molecule of (I) (Fig. 1), the dihedral angle between the planes of the heterocyclic rings and the fluorinated aryl ring is 50.5 (4) $^\circ$, while the dihedral angle between the $C-NO_2$ plane and the adjacent carbocyclic ring is 10.3 (4) $^\circ$. Consequently, the molecules of (I) have no internal symmetry in the solid state, and hence they are chiral in the solid state, although the bulk material in solution is racemic. Compound (I) crystallizes in the noncentrosymmetric space group $P2_1$. If the crystals form inversion twins, which is common in crystals having non-centrosymmetric space groups (Flack & Bernardinelli, 1999), then both enantiomers will be present in each such twinned crystal, although in the absence of such twinning, each crystal will contain only a single enantiomer, so that (I) would, in these circumstances, repre-

**Figure 1**

The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

sent an example of conglomerate crystallization associated with spontaneous resolution. The indeterminate nature of the Flack (1983) parameter in (I) prevents any decision between these possibilities. The bond lengths and angles in (I) present no unusual features.

The molecules of (I) are linked into thick sheets by means of two $C-H \cdots O$ hydrogen bonds (Table 1). Atom C6 in the molecule at (x, y, z) acts as hydrogen-bond donor to nitro atom O51 in the molecule at $(1-x, \frac{1}{2}+y, 1-z)$, so producing a zigzag $C(5)$ chain (Bernstein *et al.*, 1995) running parallel to the $[010]$ direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{2})$ (Fig. 2). At the same time, adjacent atom C7 in the molecule at (x, y, z) acts as hydrogen-bond donor to the other nitro O atom, O52, in the molecule at $(x-1, 1+y, z)$, so generating by translation a $C(6)$ chain running parallel to the $[\bar{1}10]$ direction (Fig. 3). The combination of these $[010]$ and $[\bar{1}10]$ chains generates a tripartite sheet occupying the entire

**Figure 2**

Part of the crystal structure of (I), showing the formation of a $C(5)$ chain along $[010]$. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1-x, y - \frac{1}{2}, 1-z)$ and $(x, 1+y, z)$, respectively.

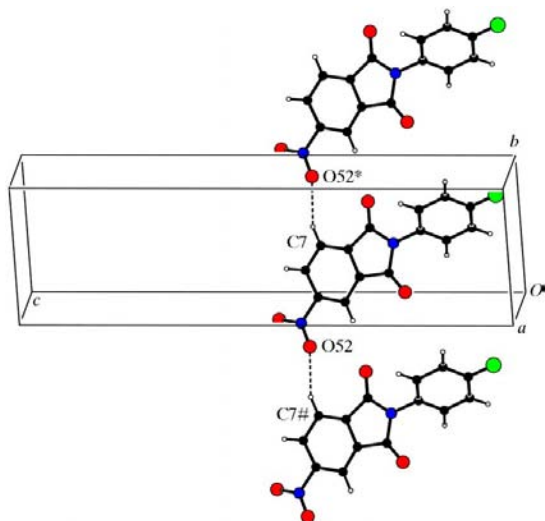


Figure 3
Part of the crystal structure of (I), showing the formation of a $C(6)$ chain along $[\bar{1}10]$. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x - 1, 1 + y, z)$ and $(1 + x, y - 1, z)$, respectively.

domain of z , in which a central hydrogen-bonded layer built from a single type of $R_6^6(24)$ ring lies between two outer layers of aryl rings, with the F substituents on the outside surfaces of the layer (Fig. 4).

There are neither $C-H \cdots \pi(\text{arene})$ hydrogen bonds nor aromatic $\pi-\pi$ stacking interactions in the structure of (I). The only possible direction-specific interaction between the sheets, involving a $C-H$ bond in one layer and an F substituent in the adjacent sheet, in fact, has an $H \cdots F$ distance (Table 1) far in excess of those associated with non-trivial interaction energies in $C-H \cdots F$ hydrogen bonds (Howard *et al.*, 1996). Accordingly, any possible structural significance of this $H \cdots F$ contact can be discounted, so that the hydrogen-bonded supramolecular structure of (I) is strictly two-dimensional.

The form of the supramolecular structure, as deep sheets partially coated with F, is reflected in the macroscopic behaviour of the crystals, which form very thin flakes which are highly hydrophobic and which when rubbed between the fingers leave a distinctly greasy coating.

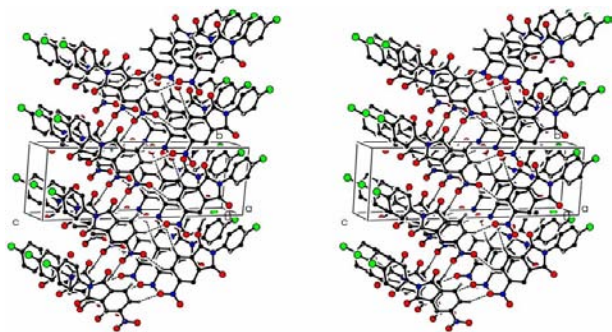


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of an (001) sheet built from $R_6^6(24)$ rings. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted.

Experimental

An equimolar mixture of very finely divided 4-fluoroaniline and 4-nitrophthalimide was heated on an electric hotplate, in the absence of solvent, until the evolution of water had ceased. The reaction product was cooled and dissolved in 1,2-dichloroethane. Activated charcoal was added, and the mixture was then filtered. Evaporation of the solvent gave compound (I). After repeated attempts to obtain crystals suitable for single-crystal X-ray diffraction, some very thin flakes of rather indifferent quality and markedly waxy consistency were finally obtained from ethanol. A number of these crystals were investigated before any satisfactory diffraction data were obtained.

Crystal data

$C_{14}H_7FN_2O_4$	$D_x = 1.582 \text{ Mg m}^{-3}$
$M_r = 286.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1099 reflections
$a = 3.7492 (13) \text{ \AA}$	$\theta = 3.5\text{--}25.0^\circ$
$b = 6.9376 (14) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$c = 23.099 (8) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 90.118 (11)^\circ$	Plate, yellow
$V = 600.8 (3) \text{ \AA}^3$	$0.15 \times 0.08 \times 0.02 \text{ mm}$
$Z = 2$	

Data collection

Nonius KappaCCD area-detector diffractometer	1099 independent reflections
φ and ω scans	757 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.114$
$T_{\text{min}} = 0.976, T_{\text{max}} = 0.997$	$\theta_{\text{max}} = 25.0^\circ$
4455 measured reflections	$h = -4 \rightarrow 4$
	$k = -7 \rightarrow 7$
	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2]$
$wR(F^2) = 0.154$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1099 reflections	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
190 parameters	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Table 1

Geometry of hydrogen bonds and short intermolecular contacts ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C6-H6 \cdots O51^i$	0.95	2.44	3.173 (9)	134
$C7-H7 \cdots O52^{ii}$	0.95	2.42	3.313 (10)	157
$C13-H13 \cdots F14^{iii}$	0.95	2.54	3.438 (9)	157

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, 1 - z$; (ii) $x - 1, 1 + y, z$; (iii) $1 - x, y - \frac{1}{2}, -z$.

The systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups; space group $P2_1$ was selected and confirmed by the subsequent structure analysis. All H atoms were located from difference maps and then treated as riding atoms, with $C-H$ distances of 0.95 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. In the absence of significant anomalous scattering, the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000). Accordingly, the Friedel-equivalent reflections were merged prior to the final refinement.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997);

program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1736). Services for accessing these data are described at the back of the journal.

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