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2-Carbamoyl-3,4,5,6-tetrafluorobenzoic acid

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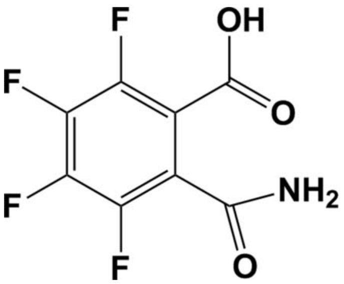
Key indicators: single-crystal X-ray study; T = 268 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.091; data-to-parameter ratio = 9.0.

In the title compound, $C_8H_3F_4NO_3$, the carboxy group lies nearly in the plane of the ring with a C—C—C—O torsion angle of −10.5 (4)°. The carbamoyl group is almost perpendicular to the benzene ring [C—C—C—O torsion angle = 82.2 (4) °]. In the crystal, molecules are linked *via* O—H⋯O and N—H⋯O hydrogen bonds involving the carbamoyl and carboxy groups.

Related literature

For general background to the title compound and its preparation, see: Xu *et al.* (2008); Li *et al.* (1999); Poshkus & Herweh (1957); Cai *et al.* (1992); Lee *et al.* (2005); Guo *et al.* (2011); Liao *et al.* (2011).



Experimental

Crystal data

$C_8H_3F_4NO_3$
M_r = 237.11
Monoclinic, $P2_1/c$
a = 14.5872 (6) Å
b = 6.9193 (3) Å
c = 8.6129 (4) Å
β = 100.086 (4)°
V = 855.89 (7) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.78 mm^{-1}
T = 268 K
0.42 × 0.31 × 0.17 mm

Data collection

Agilent Xcalibur Gemini ultra Sapphire-3 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{\min}$ = 0.643, $T_{\max}$ = 1.000
2346 measured reflections
1312 independent reflections
1240 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.091
S = 1.14
1312 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.23 e Å^{-3}
$\Delta\rho_{\min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O3$^{\rm i}$	0.82	1.78	2.5965 (18)	172
N1—H1A⋯O2$^{\rm ii}$	0.86	2.11	2.940 (2)	161

Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2367).

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2-Carbamoyl-3,4,5,6-tetrafluorobenzoic acid

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S1. Comment

The title compound, $C_8H_3F_4NO_3$ (Scheme 1, Fig. 1), as an intermediate in the synthesis of coupling reagent (Xu *et al.*, 2008; Li *et al.*, 1999; Poshkus & Herweh, 1957), was prepared by the reaction of 3,4,5,6-tetrafluorophthalic anhydride and ammonia gas at 268 K (Cai *et al.*, 1992; Lee *et al.*, 2005; Guo *et al.*, 2011; Liao *et al.*, 2011) with yield about 90%. The bond lengths and angles in the title molecule are unexceptional. The carboxyl group lies nearly in the plane of phenyl ring - torsion angle C6/C1/C8/O2 = -10.5 (4)°. The aminoacyl group is practically perpendicular to phenyl ring - torsion angle C1/C6/C7/O3 = 82.2 (4)°. In the crystal structure there are some intermolecular hydrogen bonds between the carbonyl- and amino-groups (Table 1) which form a network.

S2. Experimental

The 44.0 g 3,4,5,6-tetrafluorophthalic anhydride and 700 ml tetrahydrofuran were mixed to form a solution. After stirred solution was cooled to 268 K, ammonia gas was added at the pressure of 0.1 MPa for 1.5 h formed white solid. The white solid residue was dissolved in 350 ml distilled water, tetrahydrofuran was removed in vacuum at room temperature. Hydrochloric acid (2*N*) was added to adjust solution pH1 at 268 K, after the resulting the title product was obtained by filtration. The crude product was recrystallized from distilled water and methanol to give colourless crystals of the title product.

S3. Refinement

All H atoms were positioned geometrically and were included in the refinement in the riding-model approximation, with distances: 0.86Å (NH_2), 0.82Å (OH) with $U_{iso}(H) = 1.2U_{eq}(N)$ and $U_{iso}(H) = 1.5U_{eq}(O)$.

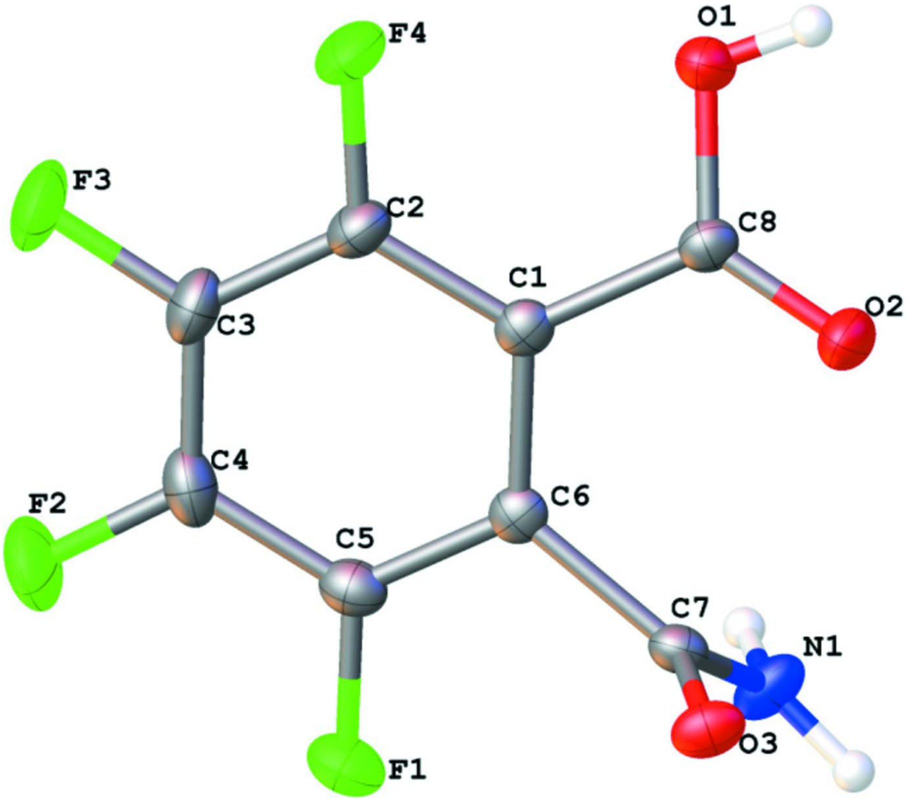

Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

(I)

Crystal data

$C_8H_3F_4NO_3$	$F(000) = 472$
$M_r = 237.11$	$D_x = 1.840$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
$a = 14.5872$ (6) Å	Cell parameters from 1702 reflections
$b = 6.9193$ (3) Å	$\theta = 5.2–62.6°$
$c = 8.6129$ (4) Å	$\mu = 1.78$ mm^{-1}
$\beta = 100.086$ (4)°	$T = 268$ K
$V = 855.89$ (7) Å^3	Block, colourless
$Z = 4$	0.42 × 0.31 × 0.17 mm

Data collection

Agilent Xcalibur Gemini ultra Sapphire-3 CCD diffractometer	$T_{\min} = 0.643$, $T_{\max} = 1.000$
	2346 measured reflections
Radiation source: Enhance Ultra (Cu) X-ray Source	1312 independent reflections
	1240 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{\text{int}} = 0.013$
Detector resolution: 16.0288 pixels mm^{-1}	$\theta_{\max} = 62.7°$, $\theta_{\min} = 7.1°$
ω scans	$h = -15 \rightarrow 16$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)	$k = -4 \rightarrow 7$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.091$
$S = 1.14$
1312 reflections
146 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.5536P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Experimental. Absorption correction: *CrysAlisPro* (Agilent Technologies, 2011); Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
F1	0.27285 (8)	0.04074 (16)	0.69216 (13)	0.0293 (3)
F4	0.11543 (8)	0.66145 (18)	0.36824 (14)	0.0328 (3)
F2	0.09507 (9)	0.02888 (19)	0.54379 (17)	0.0416 (4)
O3	0.39455 (9)	0.41810 (19)	0.84775 (14)	0.0219 (3)
F3	0.01714 (8)	0.3444 (2)	0.38240 (16)	0.0394 (4)
O1	0.27710 (9)	0.8186 (2)	0.40108 (15)	0.0253 (4)
H1	0.3157	0.9023	0.3929	0.038*
O2	0.39129 (9)	0.7021 (2)	0.58320 (16)	0.0280 (4)
N1	0.45248 (11)	0.2650 (2)	0.65574 (18)	0.0234 (4)
H1A	0.5059	0.2493	0.7150	0.028*
H1B	0.4431	0.2227	0.5604	0.028*
C1	0.25134 (12)	0.5238 (3)	0.5229 (2)	0.0182 (4)
C5	0.23637 (13)	0.1978 (3)	0.6119 (2)	0.0213 (4)
C6	0.29012 (12)	0.3598 (3)	0.6086 (2)	0.0173 (4)
C4	0.14478 (14)	0.1886 (3)	0.5367 (2)	0.0266 (5)
C3	0.10574 (13)	0.3486 (3)	0.4559 (2)	0.0259 (5)
C8	0.31341 (12)	0.6916 (3)	0.5074 (2)	0.0182 (4)
C2	0.15862 (13)	0.5134 (3)	0.4498 (2)	0.0223 (4)
C7	0.38555 (12)	0.3533 (3)	0.7106 (2)	0.0174 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0368 (7)	0.0204 (6)	0.0312 (6)	0.0008 (5)	0.0074 (5)	0.0066 (5)

F4	0.0216 (6)	0.0325 (7)	0.0399 (7)	0.0031 (5)	−0.0069 (5)	0.0090 (5)
F2	0.0326 (7)	0.0308 (7)	0.0608 (9)	−0.0166 (6)	0.0066 (6)	0.0017 (6)
O3	0.0257 (7)	0.0245 (7)	0.0145 (7)	0.0056 (6)	0.0007 (5)	−0.0019 (5)
F3	0.0163 (6)	0.0463 (8)	0.0514 (8)	−0.0076 (5)	−0.0056 (5)	−0.0016 (6)
O1	0.0235 (7)	0.0248 (8)	0.0254 (7)	−0.0043 (6)	−0.0017 (6)	0.0084 (6)
O2	0.0205 (7)	0.0282 (8)	0.0318 (8)	−0.0053 (6)	−0.0053 (6)	0.0070 (6)
N1	0.0191 (8)	0.0329 (10)	0.0168 (8)	0.0069 (7)	−0.0009 (6)	−0.0051 (7)
C1	0.0191 (9)	0.0204 (10)	0.0153 (9)	0.0009 (7)	0.0036 (7)	−0.0015 (7)
C5	0.0257 (10)	0.0190 (10)	0.0203 (9)	0.0030 (8)	0.0068 (8)	0.0016 (7)
C6	0.0186 (9)	0.0200 (10)	0.0140 (8)	0.0013 (7)	0.0052 (7)	−0.0020 (7)
C4	0.0237 (10)	0.0265 (11)	0.0312 (11)	−0.0084 (8)	0.0090 (8)	−0.0043 (9)
C3	0.0153 (9)	0.0326 (12)	0.0288 (10)	−0.0020 (8)	0.0013 (8)	−0.0046 (9)
C8	0.0191 (9)	0.0198 (10)	0.0150 (9)	0.0012 (7)	0.0015 (7)	−0.0004 (7)
C2	0.0187 (9)	0.0262 (11)	0.0208 (9)	0.0036 (8)	0.0004 (7)	0.0014 (8)
C7	0.0213 (9)	0.0157 (9)	0.0153 (9)	0.0004 (7)	0.0032 (7)	0.0023 (7)

Geometric parameters (Å, º)

F1—C5	1.346 (2)	N1—C7	1.308 (2)
F4—C2	1.336 (2)	C1—C6	1.416 (3)
F2—C4	1.329 (2)	C1—C8	1.493 (3)
O3—C7	1.249 (2)	C1—C2	1.390 (3)
F3—C3	1.336 (2)	C5—C6	1.371 (3)
O1—H1	0.8200	C5—C4	1.380 (3)
O1—C8	1.312 (2)	C6—C7	1.511 (2)
O2—C8	1.209 (2)	C4—C3	1.377 (3)
N1—H1A	0.8600	C3—C2	1.383 (3)
N1—H1B	0.8600		
C8—O1—H1	109.5	F2—C4—C3	120.74 (17)
H1A—N1—H1B	120.0	C3—C4—C5	118.76 (18)
C7—N1—H1A	120.0	F3—C3—C4	120.14 (18)
C7—N1—H1B	120.0	F3—C3—C2	119.97 (18)
C6—C1—C8	118.48 (16)	C4—C3—C2	119.88 (17)
C2—C1—C6	117.56 (17)	O1—C8—C1	113.98 (15)
C2—C1—C8	123.83 (17)	O2—C8—O1	124.27 (17)
F1—C5—C6	119.64 (16)	O2—C8—C1	121.69 (16)
F1—C5—C4	117.84 (17)	F4—C2—C1	122.02 (17)
C6—C5—C4	122.52 (18)	F4—C2—C3	115.95 (16)
C1—C6—C7	124.76 (16)	C3—C2—C1	122.02 (18)
C5—C6—C1	119.22 (16)	O3—C7—N1	123.22 (17)
C5—C6—C7	115.81 (16)	O3—C7—C6	118.21 (15)
F2—C4—C5	120.50 (18)	N1—C7—C6	118.29 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3$^{\rm i}$	0.82	1.78	2.5965 (18)	172

N1—H1*A*···O3^{ii}	0.86	2.82	3.281 (2)	116
N1—H1*A*···O2^{ii}	0.86	2.11	2.940 (2)	161

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2; (ii) −*x*+1, *y*−1/2, −*z*+3/2.