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1-[4-(2-Aminoanilino)phenyl]-2,2,2-trifluoroethanone

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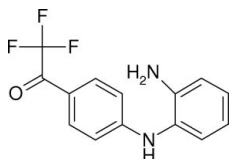
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.045; wR factor = 0.127; data-to-parameter ratio = 16.8.

In the title compound, $\text{C}_{14}\text{H}_{11}\text{F}_3\text{N}_2\text{O}$, the two aromatic rings are oriented at a dihedral angle of $70.84(8)^\circ$. The crystal structure displays intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{F}$ interactions.

Related literature

For 2,2,2-trifluoroacetophenones as intermediates for further Buchwald–Hartwig coupling, see: Colard *et al.* (1994); Schenck *et al.* (2004).



Experimental

Crystal data

 $\text{C}_{14}\text{H}_{11}\text{F}_3\text{N}_2\text{O}$ $M_r = 280.25$ Orthorhombic, $Pbca$ $a = 13.0385(13)$ Å $b = 8.7129(7)$ Å $c = 22.424(2)$ Å $V = 2547.4(4)$ Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.12$ mm⁻¹ $T = 173$ K $0.4 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART APEXII diffractometer
21134 measured reflections

3033 independent reflections
2498 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.127$ $S = 1.06$

3033 reflections

181 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.67$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N7}-\text{H7B}\cdots\text{F19}^{\text{i}}$	0.91	2.32	3.2077 (19)	166
$\text{N8}-\text{H8}\cdots\text{O16}^{\text{ii}}$	0.96	2.06	2.9757 (17)	159

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINTE* (Bruker, 2006); data reduction: *SAINTE*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5212).

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supplementary materials

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Comment

2,2,2-Trifluoroacetophenones are well known as building-blocks in the synthesis of therapeutic agents for example as acetylcholinesterase inhibitors (Colard *et al.*, 1994), as anticonvulsants (Schenck *et al.*, 2004) or as hPPAR agonists. The title compound was prepared in the course of our studies on acetophenone derivatives as potent p38 mitogen-activated protein (MAP) kinase inhibitors.

In the molecule (Fig. 1), rings A (C1—C6) and B (C10—C15) are, of course, planar and they are oriented at a dihedral angle of A/B = 70.84 (8)°. In the crystal structure, intermolecular N8—H8···O16 (2,06 Å) and N7—H7B···F19 (2,32 Å) interactions link the molecules into a three dimensional network. The N8—H8···O16 hydrogen bond forms a chain along the a-axis whereas the N7—H7B···F19 interaction connects two of this chains in direction parallel to the c-axis.

Experimental

For the preparation of the title compound a mixture of 501 mg (2.4 mmol) 1-(4-chlorophenyl)-2,2,2-trifluoroethanone, 332 mg (2.4 mmol) 2-nitroaniline, 1400 mg (4.3 mmol) Cs₂CO₃, 90 mg (0.19 mmol) 2-(dicyclohexylphosphino)-2', 4', 6'-triisopropylbiphenyl and 20 mg (0.09 mmol) Pd(OAc)₂ in 2 ml absolute *tert*-butanol and 8 ml absolute toluol was stirred for 2 h at 90 °C under an atmosphere of argon. The mixture was diluted with water then extracted with ethyl acetate. The extracts were combined, washed with saturated saline solution, and then dried over Na₂SO₄. The solvent was removed under vacuum and the crude product was dissolved in 10 ml ethanol, 840 mg (3.71 mmol) tin(II)chloride-dihydrate was added and stirred for 5 h at 348 K. After cooling down to room temperature the mixture was quenched with 20 ml ice-water and after alkalization with NaOH (20 %) extracted three-times with ethyl acetate. The combined organic layer was washed twice with water, dried (Na₂SO₄), and evaporated under reduced pressure. The residue was purified by flashchromatography (SiO₂ 60, hexane / ethyl acetate) (yield: 21.5 %). Crystals of the title compound were obtained by slow evaporation of a methanol *d*₆ solution at room temperature.

Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å (*sp*³ C-atom). Hydrogen atoms attached to N7 and N8 were located in difference Fourier maps. All H atoms were refined in the riding-model approximation with isotropic displacement parameters set at 1.2–1.5 times of the *U*_{eq} of the parent atom.

Figures

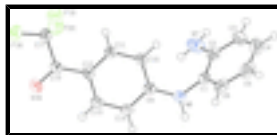


Fig. 1. View of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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Crystal data

$C_{14}H_{11}F_3N_2O$

$M_r = 280.25$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 13.0385$ (13) Å

$b = 8.7129$ (7) Å

$c = 22.424$ (2) Å

$V = 2547.4$ (4) Å³

$Z = 8$

$F(000) = 1152$

$D_x = 1.461$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7908 reflections

$\theta = 2.4$ – 27.7°

$\mu = 0.12$ mm⁻¹

$T = 173$ K

Block, brown

$0.4 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART APEXII
diffractometer

Radiation source: sealed Tube
graphite

CCD scan

21134 measured reflections

3033 independent reflections

2498 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 27.9^\circ$, $\theta_{min} = 1.8^\circ$

$h = -17 \rightarrow 17$

$k = -11 \rightarrow 8$

$l = -29 \rightarrow 29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.127$

$S = 1.06$

3033 reflections

181 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

$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 1.4118P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.67$ e Å⁻³

$\Delta\rho_{min} = -0.28$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.18780 (11)	0.80106 (18)	0.63368 (7)	0.0277 (3)
C2	0.19637 (13)	0.7530 (2)	0.69312 (7)	0.0330 (4)
C3	0.11693 (16)	0.7953 (2)	0.73256 (8)	0.0479 (5)
H3	0.1203	0.7641	0.7731	0.057*
C4	0.03490 (16)	0.8806 (3)	0.71344 (11)	0.0580 (6)
H4	-0.0181	0.9060	0.7408	0.070*
C5	0.02813 (15)	0.9299 (3)	0.65535 (11)	0.0546 (6)
H5	-0.0282	0.9908	0.6427	0.065*
C6	0.10447 (13)	0.8895 (2)	0.61572 (8)	0.0381 (4)
H6	0.1000	0.9226	0.5754	0.046*
N7	0.27946 (14)	0.6728 (2)	0.71200 (7)	0.0486 (4)
H7A	0.3249	0.6275	0.6871	0.073*
H7B	0.2675	0.6308	0.7483	0.073*
N8	0.26108 (10)	0.75201 (16)	0.59059 (5)	0.0291 (3)
H8	0.2297	0.6912	0.5600	0.035*
C9	0.35838 (11)	0.80793 (18)	0.58519 (6)	0.0255 (3)
C10	0.39963 (12)	0.91396 (18)	0.62580 (6)	0.0271 (3)
H10	0.3594	0.9488	0.6584	0.033*
C11	0.49855 (12)	0.96782 (18)	0.61856 (6)	0.0272 (3)
H11	0.5256	1.0394	0.6464	0.033*
C12	0.55966 (11)	0.91856 (17)	0.57084 (6)	0.0253 (3)
C13	0.51717 (12)	0.81270 (19)	0.53022 (6)	0.0284 (3)
H13	0.5571	0.7789	0.4973	0.034*
C14	0.41990 (12)	0.75778 (19)	0.53712 (6)	0.0288 (3)
H14	0.3934	0.6854	0.5094	0.035*
C15	0.66340 (11)	0.97035 (18)	0.55983 (6)	0.0266 (3)
O16	0.71615 (9)	0.93617 (15)	0.51702 (5)	0.0362 (3)
C17	0.71528 (12)	1.0765 (2)	0.60606 (7)	0.0322 (3)
F18	0.81079 (8)	1.10979 (14)	0.59054 (5)	0.0480 (3)
F19	0.72009 (9)	1.00909 (14)	0.65988 (4)	0.0457 (3)
F20	0.66562 (9)	1.20895 (13)	0.61292 (6)	0.0490 (3)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0266 (7)	0.0279 (8)	0.0286 (7)	-0.0045 (6)	0.0007 (5)	-0.0050 (6)
C2	0.0395 (9)	0.0301 (8)	0.0294 (7)	-0.0087 (7)	0.0016 (6)	-0.0028 (6)
C3	0.0580 (12)	0.0506 (12)	0.0350 (9)	-0.0185 (9)	0.0134 (8)	-0.0102 (8)
C4	0.0368 (10)	0.0683 (15)	0.0690 (14)	-0.0087 (10)	0.0175 (9)	-0.0283 (12)
C5	0.0323 (9)	0.0582 (13)	0.0731 (15)	0.0060 (9)	-0.0043 (9)	-0.0257 (11)
C6	0.0323 (8)	0.0357 (9)	0.0461 (9)	-0.0009 (7)	-0.0083 (7)	-0.0099 (7)
N7	0.0645 (11)	0.0484 (10)	0.0328 (7)	0.0107 (8)	-0.0015 (7)	0.0043 (7)
N8	0.0285 (6)	0.0334 (7)	0.0254 (6)	-0.0031 (5)	-0.0012 (5)	-0.0067 (5)
C9	0.0268 (7)	0.0262 (7)	0.0235 (6)	0.0018 (6)	-0.0019 (5)	0.0023 (5)
C10	0.0291 (7)	0.0277 (8)	0.0246 (6)	0.0013 (6)	0.0031 (5)	-0.0041 (6)
C11	0.0300 (7)	0.0265 (8)	0.0252 (7)	-0.0009 (6)	0.0008 (5)	-0.0049 (6)
C12	0.0270 (7)	0.0265 (8)	0.0225 (6)	0.0027 (6)	0.0004 (5)	0.0005 (5)
C13	0.0315 (7)	0.0329 (8)	0.0208 (6)	0.0051 (6)	0.0011 (5)	-0.0029 (6)
C14	0.0334 (7)	0.0309 (8)	0.0221 (6)	0.0005 (6)	-0.0032 (6)	-0.0047 (6)
C15	0.0277 (7)	0.0272 (8)	0.0250 (7)	0.0041 (6)	0.0003 (5)	0.0019 (6)
O16	0.0313 (6)	0.0471 (7)	0.0302 (6)	0.0038 (5)	0.0073 (4)	-0.0043 (5)
C17	0.0301 (8)	0.0333 (9)	0.0331 (8)	-0.0041 (6)	0.0044 (6)	-0.0016 (6)
F18	0.0326 (5)	0.0561 (7)	0.0552 (7)	-0.0143 (5)	0.0085 (5)	-0.0073 (5)
F19	0.0530 (7)	0.0552 (7)	0.0289 (5)	-0.0147 (5)	-0.0056 (4)	-0.0012 (4)
F20	0.0485 (6)	0.0319 (6)	0.0667 (7)	-0.0023 (5)	0.0089 (5)	-0.0128 (5)

Geometric parameters (\AA , $^\circ$)

C1—C6	1.391 (2)	C9—C10	1.404 (2)
C1—C2	1.402 (2)	C9—C14	1.413 (2)
C1—N8	1.4244 (19)	C10—C11	1.382 (2)
C2—N7	1.357 (2)	C10—H10	0.9500
C2—C3	1.411 (2)	C11—C12	1.402 (2)
C3—C4	1.371 (3)	C11—H11	0.9500
C3—H3	0.9500	C12—C13	1.410 (2)
C4—C5	1.374 (4)	C12—C15	1.447 (2)
C4—H4	0.9500	C13—C14	1.364 (2)
C5—C6	1.380 (3)	C13—H13	0.9500
C5—H5	0.9500	C14—H14	0.9500
C6—H6	0.9500	C15—O16	1.2180 (18)
N7—H7A	0.9044	C15—C17	1.545 (2)
N7—H7B	0.9069	C17—F18	1.3251 (18)
N8—C9	1.364 (2)	C17—F20	1.332 (2)
N8—H8	0.9582	C17—F19	1.3437 (19)
C6—C1—C2	120.18 (15)	C10—C9—C14	118.74 (14)
C6—C1—N8	119.58 (15)	C11—C10—C9	120.30 (13)
C2—C1—N8	120.13 (14)	C11—C10—H10	119.8
N7—C2—C1	120.94 (15)	C9—C10—H10	119.8
N7—C2—C3	121.67 (16)	C10—C11—C12	121.08 (14)

C1—C2—C3	117.36 (17)	C10—C11—H11	119.5
C4—C3—C2	121.20 (19)	C12—C11—H11	119.5
C4—C3—H3	119.4	C11—C12—C13	118.05 (14)
C2—C3—H3	119.4	C11—C12—C15	124.48 (14)
C3—C4—C5	121.06 (18)	C13—C12—C15	117.46 (13)
C3—C4—H4	119.5	C14—C13—C12	121.44 (13)
C5—C4—H4	119.5	C14—C13—H13	119.3
C4—C5—C6	119.0 (2)	C12—C13—H13	119.3
C4—C5—H5	120.5	C13—C14—C9	120.38 (14)
C6—C5—H5	120.5	C13—C14—H14	119.8
C5—C6—C1	121.21 (18)	C9—C14—H14	119.8
C5—C6—H6	119.4	O16—C15—C12	125.88 (14)
C1—C6—H6	119.4	O16—C15—C17	115.33 (14)
C2—N7—H7A	123.8	C12—C15—C17	118.78 (13)
C2—N7—H7B	110.6	F18—C17—F20	107.33 (14)
H7A—N7—H7B	119.4	F18—C17—F19	106.72 (14)
C9—N8—C1	125.23 (12)	F20—C17—F19	107.33 (13)
C9—N8—H8	122.1	F18—C17—C15	111.47 (13)
C1—N8—H8	111.3	F20—C17—C15	112.54 (13)
N8—C9—C10	122.24 (13)	F19—C17—C15	111.16 (13)
N8—C9—C14	119.02 (13)		
C6—C1—C2—N7	-176.94 (16)	C10—C11—C12—C13	0.2 (2)
N8—C1—C2—N7	6.8 (2)	C10—C11—C12—C15	179.43 (14)
C6—C1—C2—C3	1.2 (2)	C11—C12—C13—C14	-0.7 (2)
N8—C1—C2—C3	-175.01 (15)	C15—C12—C13—C14	-179.98 (14)
N7—C2—C3—C4	177.89 (19)	C12—C13—C14—C9	0.9 (2)
C1—C2—C3—C4	-0.3 (3)	N8—C9—C14—C13	179.40 (14)
C2—C3—C4—C5	-1.1 (3)	C10—C9—C14—C13	-0.5 (2)
C3—C4—C5—C6	1.4 (3)	C11—C12—C15—O16	-175.65 (16)
C4—C5—C6—C1	-0.4 (3)	C13—C12—C15—O16	3.6 (2)
C2—C1—C6—C5	-0.9 (3)	C11—C12—C15—C17	5.5 (2)
N8—C1—C6—C5	175.34 (17)	C13—C12—C15—C17	-175.33 (14)
C6—C1—N8—C9	107.87 (18)	O16—C15—C17—F18	-1.0 (2)
C2—C1—N8—C9	-75.9 (2)	C12—C15—C17—F18	178.04 (14)
C1—N8—C9—C10	5.3 (2)	O16—C15—C17—F20	119.68 (16)
C1—N8—C9—C14	-174.67 (15)	C12—C15—C17—F20	-61.32 (19)
N8—C9—C10—C11	-179.88 (14)	O16—C15—C17—F19	-119.90 (15)
C14—C9—C10—C11	0.1 (2)	C12—C15—C17—F19	59.11 (19)
C9—C10—C11—C12	0.1 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N7—H7B \cdots F19 ⁱ	0.91	2.32	3.2077 (19)	166
N8—H8 \cdots O16 ⁱⁱ	0.96	2.06	2.9757 (17)	159

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

Fig. 1

