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6-Benzyl-3-[4-(trifluoromethyl)phenyl]-1,2,4,5-tetrazine

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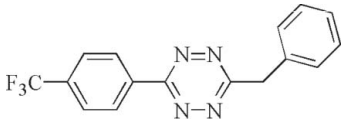
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; disorder in main residue; R factor = 0.073; wR factor = 0.261; data-to-parameter ratio = 14.5.

In the title compound, $C_{16}H_{11}F_3N_4$, the trifluoro-substituted benzene ring is almost coplanar with the central tetrazine ring, but the benzyl phenyl ring is twisted by an angle of 76.7 (2)°. There are no hydrogen bonds in the crystal structure. The F atoms are disordered over two sets of positions with refined site occupancy factors of 0.604 (9) and 0.396 (9).

Related literature

For related literature, see: Hu *et al.* (2004, 2005); Sauer (1996).



Experimental

Crystal data

$C_{16}H_{11}F_3N_4$
M_r = 316.29
Monoclinic, $P2_1/c$
a = 4.701 (2) Å
b = 30.810 (15) Å
c = 10.889 (5) Å
β = 109.490 (17)°
V = 1486.8 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 (2) K
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.967, T_{max} = 0.968
9146 measured reflections
3418 independent reflections
1315 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.073
$wR(F^2)$ = 0.261
S = 1.00
3418 reflections
236 parameters
51 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2362).

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supplementary materials

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6-Benzyl-3-[4-(trifluoromethyl)phenyl]-1,2,4,5-tetrazine

F. Xu and W.-X. Hu

Comment

1,2,4,5-Tetrazine derivatives have great potential for biological activity, possessing a wide spectrum of antiviral and antitumour properties. They have been widely used in pesticides and herbicides (Sauer, 1996). In continuation of our work on the structure–activity relationship of 1,2,4,5-tetrazine derivatives (Hu *et al.*, 2004, 2005), we present here the structure of the title compound, (I).

The molecule structure of (I) is illustrated in Fig. 1. The benzene (C7–C12) ring is almost coplanar with the the central tetrazine ring [dihedral angle 5.9 (2)°], but the benzylphenyl ring (C15–C20) is twisted by an angle of 76.7 (2)°. There are no hydrogen bonds in the crystal structure.

Experimental

With sulfur (1.0 g) as catalyst, 85% hydrazine hydrate (10 ml, 170 mmol) was added dropwise to an anhydrous ethanol solution (15 ml) of benzyl cyanide (50 mmol) and *p*-trifluoromethylbenzonitrile (50 mmol) at 295 K. After refluxing

for 3 h, the mixture was cooled to room temperature and the resulting solid product was filtered off. The solid product was then dissolved in diethyl ether

(15 ml), and oxidised by sodium nitrate (14 mmol) and acetic acid (14 mmol) over a period of 2 h to afford the product, which was purified by preparative thin-layer chromatography over silica gel PF254 (2 mm) (cyclohexane–dichloromethane, 1:1 v/v) to give red single crystals of (I). The solid product was dissolved in tetrahydrofuran and the solution evaporated gradually at room temperature to afford single crystals of (I) (m.p. 408–409 K).

Refinement

The trifluoromethyl group is disordered over two positions; their occupancy ratio was refined to 0.604 (9):0.396 (9). The six C—F bond distances were restrained to within 0.01 Å of each other and the displacement parameters of the disordered F atoms were restrained to approximately isotropic behaviour. H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å, and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$. Owing to the large number of weak high-angle reflections, the ratio of observed to unique reflections is low (38%).

Figures

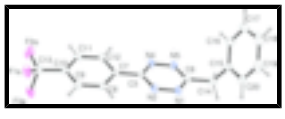


Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Only the major component of the disordered CF_3 group is shown.

6-Benzyl-3-[4-(trifluoromethyl)phenyl]-1,2,4,5-tetrazine

Crystal data

$C_{16}H_{11}F_3N_4$	F_{000} = 648
M_r = 316.29	D_x = 1.413 Mg m^{-3}
Monoclinic, $P2_1/C$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 1418 reflections
a = 4.701 (2) Å	θ = 2.4–21.5º
b = 30.810 (15) Å	μ = 0.11 mm^{-1}
c = 10.889 (5) Å	T = 296 (2) K
β = 109.490 (17)º	Prism, red
V = 1486.8 (12) Å^3	0.30 × 0.25 × 0.20 mm
Z = 4	

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	3418 independent reflections
Radiation source: fine-focus sealed tube	1315 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.043
T = 296(2) K	θ_{max} = 28.4º
φ and ω scans	θ_{min} = 1.3º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −6→3
T_{min} = 0.967, T_{max} = 0.968	k = −40→39
9146 measured reflections	l = −12→14

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.073	$w = 1/[\sigma^2(F_o^2) + (0.1289P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.261	$(\Delta/\sigma)_{max}$ = 0.005
S = 1.00	$\Delta\rho_{max}$ = 0.41 e Å^{-3}
3418 reflections	$\Delta\rho_{min}$ = −0.30 e Å^{-3}
236 parameters	Extinction correction: none
51 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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}	Occ. (<1)
F1A	0.5850 (10)	0.14622 (19)	0.6417 (8)	0.117 (3)	0.604 (9)
F2A	0.166 (3)	0.1461 (3)	0.4790 (6)	0.195 (5)	0.604 (9)
F3A	0.2082 (15)	0.17115 (14)	0.6674 (7)	0.121 (3)	0.604 (9)
F1B	0.416 (2)	0.1351 (3)	0.5049 (10)	0.128 (4)	0.396 (9)
F2B	0.0598 (18)	0.1627 (3)	0.5302 (13)	0.120 (4)	0.396 (9)
F3B	0.481 (4)	0.1634 (5)	0.6852 (11)	0.196 (6)	0.396 (9)
N1	0.0160 (7)	−0.07196 (11)	0.9373 (3)	0.0835 (10)	
N2	0.1103 (7)	−0.03635 (10)	0.8948 (3)	0.0780 (9)	
N4	−0.3120 (7)	−0.03970 (10)	0.7028 (3)	0.0809 (10)	
N5	−0.4068 (7)	−0.07520 (11)	0.7460 (3)	0.0843 (10)	
C3	−0.0555 (7)	−0.02094 (11)	0.7777 (3)	0.0601 (9)	
C6	−0.2405 (8)	−0.09063 (12)	0.8627 (4)	0.0704 (10)	
C7	0.0443 (7)	0.01888 (11)	0.7313 (3)	0.0578 (8)	
C8	0.2930 (8)	0.04200 (12)	0.8082 (3)	0.0672 (10)	
H8	0.4047	0.0314	0.8901	0.081*	
C9	0.3766 (8)	0.07991 (14)	0.7658 (4)	0.0758 (11)	
H9	0.5438	0.0950	0.8189	0.091*	
C10	0.2139 (8)	0.09624 (12)	0.6437 (3)	0.0684 (10)	
C11	−0.0269 (9)	0.07270 (13)	0.5642 (4)	0.0790 (11)	
H11	−0.1328	0.0828	0.4809	0.095*	
C12	−0.1110 (8)	0.03464 (12)	0.6068 (3)	0.0766 (11)	
H12	−0.2736	0.0191	0.5522	0.092*	
C13	0.2897 (10)	0.13876 (16)	0.6007 (4)	0.0953 (13)	
C14	−0.3392 (9)	−0.13095 (13)	0.9099 (4)	0.0843 (12)	
H14A	−0.5438	−0.1376	0.8550	0.101*	
H14B	−0.3410	−0.1263	0.9977	0.101*	
C15	−0.1404 (8)	−0.16889 (11)	0.9100 (4)	0.0679 (10)	
C16	−0.1595 (11)	−0.18897 (16)	0.7945 (4)	0.0984 (14)	
H16	−0.3000	−0.1794	0.7169	0.118*	
C17	0.0242 (17)	−0.2223 (2)	0.7936 (8)	0.137 (2)	
H17	0.0094	−0.2354	0.7146	0.165*	
C18	0.2330 (18)	−0.23762 (19)	0.9061 (11)	0.147 (3)	
H18	0.3573	−0.2609	0.9041	0.177*	

C19	0.2543 (12)	−0.2179 (2)	1.0217 (8)	0.125 (2)
H19	0.3949	−0.2277	1.0989	0.150*
C20	0.0700 (10)	−0.18376 (15)	1.0240 (4)	0.0879 (13)
H20	0.0862	−0.1705	1.1028	0.106*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1A	0.091 (4)	0.092 (3)	0.188 (7)	−0.015 (2)	0.075 (4)	0.002 (3)
F2A	0.257 (10)	0.187 (8)	0.110 (5)	−0.076 (7)	0.020 (6)	0.045 (5)
F3A	0.127 (4)	0.068 (3)	0.184 (6)	0.010 (3)	0.075 (4)	0.000 (3)
F1B	0.129 (7)	0.144 (6)	0.139 (8)	0.026 (5)	0.082 (6)	0.053 (5)
F2B	0.109 (6)	0.088 (5)	0.176 (10)	0.016 (4)	0.066 (6)	0.045 (5)
F3B	0.235 (11)	0.161 (9)	0.157 (8)	−0.064 (8)	0.017 (8)	0.015 (7)
N1	0.076 (2)	0.086 (2)	0.073 (2)	−0.0075 (18)	0.0043 (17)	0.0113 (17)
N2	0.068 (2)	0.081 (2)	0.067 (2)	−0.0071 (16)	−0.0018 (16)	0.0083 (16)
N4	0.070 (2)	0.073 (2)	0.075 (2)	−0.0102 (17)	−0.0084 (17)	−0.0023 (16)
N5	0.069 (2)	0.079 (2)	0.086 (2)	−0.0093 (17)	0.0016 (18)	−0.0017 (18)
C3	0.0501 (19)	0.067 (2)	0.051 (2)	0.0063 (16)	0.0009 (16)	−0.0095 (16)
C6	0.052 (2)	0.076 (2)	0.079 (3)	0.0016 (18)	0.016 (2)	−0.0034 (19)
C7	0.0501 (18)	0.061 (2)	0.052 (2)	0.0063 (15)	0.0028 (15)	−0.0084 (15)
C8	0.059 (2)	0.079 (2)	0.050 (2)	−0.0047 (18)	0.0001 (16)	−0.0023 (17)
C9	0.066 (2)	0.088 (3)	0.065 (2)	−0.010 (2)	0.011 (2)	−0.0100 (19)
C10	0.068 (2)	0.069 (2)	0.069 (2)	−0.0018 (18)	0.025 (2)	−0.0046 (18)
C11	0.081 (3)	0.079 (3)	0.063 (2)	0.005 (2)	0.006 (2)	0.0038 (19)
C12	0.071 (2)	0.074 (3)	0.061 (2)	−0.0037 (19)	−0.0088 (18)	−0.0064 (18)
C13	0.088 (3)	0.104 (4)	0.088 (3)	−0.013 (3)	0.021 (3)	0.001 (3)
C14	0.074 (3)	0.088 (3)	0.098 (3)	−0.007 (2)	0.037 (2)	0.001 (2)
C15	0.063 (2)	0.071 (2)	0.075 (2)	−0.0146 (19)	0.0291 (19)	0.000 (2)
C16	0.102 (3)	0.108 (3)	0.093 (3)	−0.021 (3)	0.042 (3)	−0.017 (3)
C17	0.158 (6)	0.104 (5)	0.186 (7)	−0.028 (4)	0.106 (5)	−0.054 (4)
C18	0.143 (6)	0.066 (3)	0.276 (11)	0.009 (3)	0.126 (7)	0.015 (5)
C19	0.097 (4)	0.101 (4)	0.179 (6)	0.017 (3)	0.051 (4)	0.057 (4)
C20	0.082 (3)	0.098 (3)	0.084 (3)	−0.011 (2)	0.028 (2)	0.014 (2)

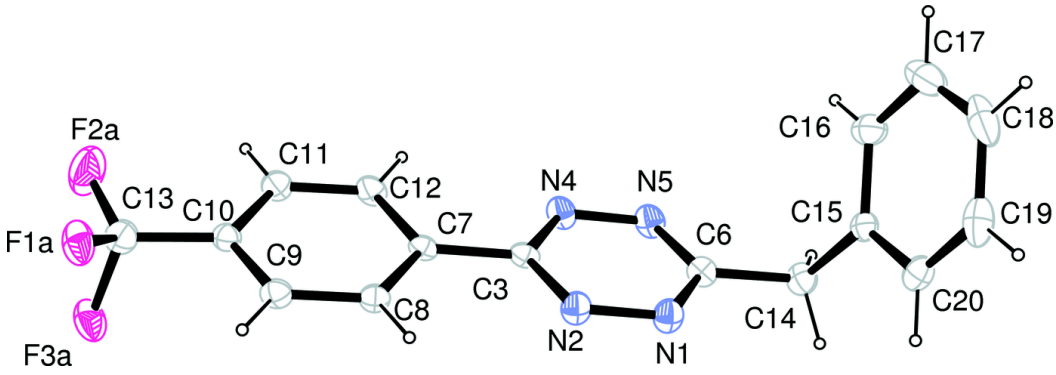
Geometric parameters (Å, °)

F1A—C13	1.329 (6)	C10—C11	1.380 (5)
F2A—C13	1.278 (6)	C10—C13	1.474 (6)
F3A—C13	1.362 (6)	C11—C12	1.367 (5)
F1B—C13	1.368 (7)	C11—H11	0.93
F2B—C13	1.322 (7)	C12—H12	0.93
F3B—C13	1.295 (7)	C14—C15	1.496 (5)
N1—N2	1.323 (4)	C14—H14A	0.97
N1—C6	1.338 (4)	C14—H14B	0.97
N2—C3	1.340 (4)	C15—C16	1.377 (6)
N4—N5	1.325 (4)	C15—C20	1.383 (5)
N4—C3	1.340 (4)	C16—C17	1.345 (8)
N5—C6	1.337 (5)	C16—H16	0.93

C3—C7	1.462 (5)	C17—C18	1.373 (9)
C6—C14	1.477 (5)	C17—H17	0.93
C7—C8	1.386 (4)	C18—C19	1.371 (9)
C7—C12	1.395 (4)	C18—H18	0.93
C8—C9	1.361 (5)	C19—C20	1.368 (7)
C8—H8	0.93	C19—H19	0.93
C9—C10	1.388 (5)	C20—H20	0.93
C9—H9	0.93		
N2—N1—C6	118.9 (3)	F1A—C13—F3A	98.2 (5)
N1—N2—C3	118.0 (3)	F2A—C13—F1B	52.2 (6)
N5—N4—C3	118.7 (3)	F3B—C13—F1B	102.4 (10)
N4—N5—C6	118.1 (3)	F2B—C13—F1B	94.7 (7)
N4—C3—N2	123.1 (3)	F1A—C13—F1B	66.3 (6)
N4—C3—C7	118.6 (3)	F3A—C13—F1B	137.6 (6)
N2—C3—C7	118.3 (3)	F2A—C13—C10	114.4 (5)
N5—C6—N1	123.1 (3)	F3B—C13—C10	118.6 (7)
N5—C6—C14	118.5 (3)	F2B—C13—C10	116.3 (5)
N1—C6—C14	118.3 (4)	F1A—C13—C10	112.5 (4)
C8—C7—C12	118.0 (3)	F3A—C13—C10	109.9 (4)
C8—C7—C3	121.7 (3)	F1B—C13—C10	112.4 (5)
C12—C7—C3	120.2 (3)	C6—C14—C15	112.9 (3)
C9—C8—C7	121.1 (3)	C6—C14—H14A	109.0
C9—C8—H8	119.4	C15—C14—H14A	109.0
C7—C8—H8	119.4	C6—C14—H14B	109.0
C8—C9—C10	120.4 (3)	C15—C14—H14B	109.0
C8—C9—H9	119.8	H14A—C14—H14B	107.8
C10—C9—H9	119.8	C16—C15—C20	118.7 (4)
C11—C10—C9	119.0 (4)	C16—C15—C14	120.0 (4)
C11—C10—C13	120.2 (4)	C20—C15—C14	121.2 (4)
C9—C10—C13	120.8 (3)	C17—C16—C15	120.3 (5)
C12—C11—C10	120.5 (3)	C17—C16—H16	119.9
C12—C11—H11	119.8	C15—C16—H16	119.9
C10—C11—H11	119.8	C16—C17—C18	121.6 (6)
C11—C12—C7	120.8 (3)	C16—C17—H17	119.2
C11—C12—H12	119.6	C18—C17—H17	119.2
C7—C12—H12	119.6	C19—C18—C17	118.6 (6)
F2A—C13—F3B	126.9 (8)	C19—C18—H18	120.7
F2A—C13—F2B	45.3 (6)	C17—C18—H18	120.7
F3B—C13—F2B	109.0 (10)	C20—C19—C18	120.4 (6)
F2A—C13—F1A	112.4 (7)	C20—C19—H19	119.8
F3B—C13—F1A	42.4 (9)	C18—C19—H19	119.8
F2B—C13—F1A	131.2 (6)	C19—C20—C15	120.4 (5)
F2A—C13—F3A	108.1 (8)	C19—C20—H20	119.8
F3B—C13—F3A	56.2 (10)	C15—C20—H20	119.8
F2B—C13—F3A	65.2 (6)		
C6—N1—N2—C3	−0.7 (5)	C11—C10—C13—F2A	−15.3 (10)
C3—N4—N5—C6	−0.1 (5)	C9—C10—C13—F2A	166.7 (9)
N5—N4—C3—N2	−0.1 (5)	C11—C10—C13—F3B	168.1 (13)

N5—N4—C3—C7	−178.4 (3)	C9—C10—C13—F3B	−9.9 (14)
N1—N2—C3—N4	0.6 (5)	C11—C10—C13—F2B	35.1 (9)
N1—N2—C3—C7	178.8 (3)	C9—C10—C13—F2B	−142.9 (8)
N4—N5—C6—N1	0.0 (6)	C11—C10—C13—F1A	−145.2 (5)
N4—N5—C6—C14	−178.1 (3)	C9—C10—C13—F1A	36.8 (7)
N2—N1—C6—N5	0.4 (6)	C11—C10—C13—F3A	106.5 (5)
N2—N1—C6—C14	178.5 (3)	C9—C10—C13—F3A	−71.5 (6)
N4—C3—C7—C8	174.5 (3)	C11—C10—C13—F1B	−72.6 (8)
N2—C3—C7—C8	−3.8 (5)	C9—C10—C13—F1B	109.4 (7)
N4—C3—C7—C12	−5.6 (5)	N5—C6—C14—C15	108.7 (4)
N2—C3—C7—C12	176.1 (3)	N1—C6—C14—C15	−69.5 (5)
C12—C7—C8—C9	2.6 (5)	C6—C14—C15—C16	−75.4 (5)
C3—C7—C8—C9	−177.4 (3)	C6—C14—C15—C20	102.9 (4)
C7—C8—C9—C10	−0.2 (6)	C20—C15—C16—C17	−0.1 (6)
C8—C9—C10—C11	−2.3 (5)	C14—C15—C16—C17	178.2 (4)
C8—C9—C10—C13	175.7 (4)	C15—C16—C17—C18	0.5 (8)
C9—C10—C11—C12	2.4 (6)	C16—C17—C18—C19	−0.5 (9)
C13—C10—C11—C12	−175.6 (4)	C17—C18—C19—C20	0.2 (9)
C10—C11—C12—C7	0.1 (6)	C18—C19—C20—C15	0.2 (7)
C8—C7—C12—C11	−2.6 (5)	C16—C15—C20—C19	−0.2 (6)
C3—C7—C12—C11	177.5 (3)	C14—C15—C20—C19	−178.5 (4)

Fig. 1


F2a
C13
C10
C11
C12
C7
N4
N5
C6
C15
C16
C17
C18
C19
C20
F1a
C9
C8
C3
N2
N1
C14
F3a