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The crystal structure of 4-*tert*-butyl-*N'*-[(*E*)-(4-fluoro-3-methoxyphenyl)methylidene] benzohydrazide, C₁₉H₂₁F₁N₂O₂

Table 1: Data collection and handling.

Crystal:	Needle, colorless
Size:	0.48 × 0.20 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	STOE IPDS2T, ω -scans
$\theta_{\max}$, completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7545, 3151, 0.071
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2812
$N(\text{param})_{\text{refined}}$:	226
Programs:	Stoe programs [1], SHELX [2, 3], WinGX and ORTEP [4]

Source of materials

The title compound 4-*tert*-butyl-*N'*-[(*E*)-(4-fluoro-3-methoxyphenyl)methylidene] benzohydrazide was synthesized by condensing 1 mmol of 4-*tert*-butyl benzohydrazide with 1 mmol of 4-fluoro-3-methoxybenzaldehyde. Both reactants were dissolved in minimum amount of distilled and dried ethanol before mixing. A catalytic amount of acetic acid was added to the reaction mixture and the resulting mixture was refluxed for about 5 h. During the synthetic process the reaction progress was monitored by TLC. After completion of the reaction the reaction mixture was allowed to cool to room temperature. Transparent crystals were isolated from the solution by allowing it to stand for 6–12 h.

Experimental details

The absolute structure could not be determined crystallographically beyond doubt (non-centrosymmetric space group; the molecule itself does not bear a chiral center). Inverting the structure, however, did result in even less probable Flack parameter. The calculated Flack parameter was hence deleted from the cif-file. The C-bound hydrogen atoms were included in calculated positions and treated as riding: C–H = 0.93–0.98 Å with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl groups and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for all other C–H bonds. The hydrogen atom on N1 was located and refined without any restraints or constraints. The elongation of the ellipsoids of the ^tBu moiety suggests a rotational disorder of this group

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Abstract

C₁₉H₂₁F₁N₂O₂, monoclinic, *Cc* (no. 9), $a = 14.337(3)$ Å, $b = 15.549(3)$ Å, $c = 8.0212(16)$ Å, $\beta = 103.33(3)^\circ$, $V = 1740.0(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0796$, $wR_{\text{ref}}(F^2) = 0.2192$, $T = 170$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.9240(5)	0.7308(6)	0.9799(13)	0.091(3)
H1A	0.985578	0.738814	1.062102	0.136*
H1B	0.879713	0.776563	0.995082	0.136*
H1C	0.933890	0.733100	0.863041	0.136*
C2	0.9529(5)	0.5718(7)	1.0029(13)	0.098(3)
H2A	1.006669	0.575438	1.103304	0.146*
H2B	0.976811	0.577750	0.898420	0.146*
H2C	0.920983	0.516036	1.002165	0.146*
C3	0.8625(5)	0.6429(5)	1.1890(9)	0.0689(19)
H3A	0.835021	0.587341	1.209816	0.103*
H3B	0.817311	0.689001	1.198129	0.103*
H3C	0.922722	0.652061	1.274192	0.103*
C4	0.8819(4)	0.6435(4)	1.0101(9)	0.0603(17)
C5	0.7909(3)	0.6276(3)	0.8682(7)	0.0414(11)
C6	0.7009(3)	0.6228(3)	0.9027(7)	0.0393(10)
H6	0.693829	0.632516	1.016038	0.047*
C7	0.6207(3)	0.6039(3)	0.7739(6)	0.0347(9)
H7	0.559419	0.601157	0.800239	0.042*
C8	0.6287(3)	0.5890(3)	0.6087(6)	0.0318(9)
C9	0.7179(3)	0.5973(3)	0.5702(7)	0.0394(10)
H9	0.724407	0.589774	0.455821	0.047*
C10	0.7977(3)	0.6165(4)	0.7000(7)	0.0458(12)
H10	0.858448	0.622187	0.672688	0.055*
C11	0.5460(3)	0.5624(3)	0.4677(6)	0.0306(8)
C12	0.3670(3)	0.4107(3)	0.4470(6)	0.0356(9)
H12	0.388583	0.391257	0.561693	0.043*
C13	0.2837(3)	0.3689(3)	0.3344(6)	0.0361(10)
C14	0.2311(3)	0.3106(3)	0.4051(7)	0.0452(11)
H14	0.250188	0.296637	0.523361	0.054*
C15	0.1495(4)	0.2723(4)	0.3022(8)	0.0510(13)
H15	0.112960	0.231971	0.349342	0.061*
C16	0.1236(3)	0.2940(3)	0.1328(8)	0.0483(13)
C17	0.1762(3)	0.3501(4)	0.0563(7)	0.0457(11)
C18	0.2572(3)	0.3886(3)	0.1600(7)	0.0400(10)
H18	0.294264	0.428045	0.111870	0.048*
C19	0.1951(6)	0.4235(8)	−0.1910(10)	0.095(3)
H19A	0.185861	0.481102	−0.147780	0.143*
H19B	0.171174	0.422434	−0.315751	0.143*
H19C	0.263467	0.409166	−0.162069	0.143*
N1	0.4862(2)	0.5059(2)	0.5160(5)	0.0320(8)
N2	0.4107(2)	0.4723(2)	0.3936(4)	0.0320(8)
O1	0.5367(2)	0.5880(2)	0.3196(4)	0.0376(7)
O2	0.1439(3)	0.3625(3)	−0.1149(6)	0.0632(12)
F1	0.0448(2)	0.2578(2)	0.0320(5)	0.0654(10)
H1N	0.502(4)	0.479(3)	0.623(7)	0.031(12)*

but modeling did not improve the refinement and was abandoned.

Comment

Structural reports of synthetic 4-fluorobenzohydrazide derivatives have started to appear in the literature only as recently as 2004; reports of such single crystal structure

determinations continue to be released to date emphasizing their abiding relevance [5–15]. Hydrazide compounds and their role as ligands in complexes are studied due to widespread interest in their biological activities [16], for which the fluoro substituent is supposedly important for reasons of – *inter alia* – solubility, pharmaceutical application and in vivo monitoring. Hydrazides play further roles in the catalytic oxidation of alcohols [17], magnetic studies [18] and as chemosensors for pyrophosphate [19]. This contribution is part of our interest in phenylhydrazide compounds and their characteristics including solid state properties.

The title compound crystallized in the monoclinic space group *Cc* with one molecule in the asymmetric unit. All bond lengths and angles of the hydrazide moiety do fall into the expected ranges as found in related molecules [1–11]. The N1–N2 distance is 1.386(4) Å (range in literature 1.369–1.395 Å), the N1–C(11) distance is 1.344(5) Å (range 1.329–1.359 Å), the C11=O1 distance is 1.232(5) Å (range 1.216–1.245 Å) and the C16–F1 distance is 1.350(5) Å (range 1.345–1.365 Å); all apparently rather independent from further substitution on the phenyl rings adjacent to the hydrazide moiety (see top part of the figure). The angles between the two phenyl rings adjacent to the hydrazide moiety, on the other hand are rather distinct among this group of related compounds. This is apparently influenced by crystal packing effects and hydrogen bonding interactions. The angles range from almost coplanar (4.74°) to strongly out of plane (62.28°). In the title compound this value is 39.91°, i.e. on the larger side of the range. In the crystal lattice one medium strong hydrogen bonding interaction N1–H1N···O1 (*D*–*A* = 2.7886(6) Å) supported by a non-classical C12–H12···O1 (*D*–*A* = 3.3092(7) Å) hydrogen bonding interaction determines the crystal packing forming lines of molecules in a nearly zig-zag type arrangement of the molecule orientations along the crystallographic *c* axis (see bottom part of the figure; viewed along *b*). All molecules of the crystal are arranged in the same direction; i.e. the fluoro substituents of the molecules within the unit cell point roughly towards the origin of the coordinate system and the ^tBu substituents point away from it.

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