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Crystal structure of O-hexyl benzoylcarbamothioate, $C_{14}H_{19}NO_2S$

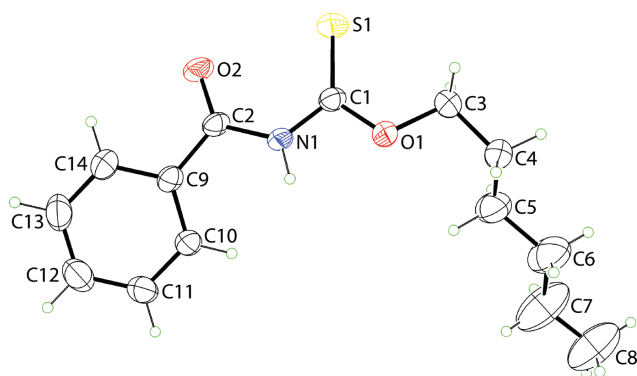


Table 1: Data collection and handling.

Crystal:	Yellow irregular
Size:	0.30 × 0.13 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.21 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{\max} , completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	44808, 3095, 0.060
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1838
$N(\text{param})_{\text{refined}}$:	167
Programs:	SHELX [1, 2], Bruker [3], SIR2014 [4], WinGX/ORTEP [5]

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Abstract

$C_{14}H_{19}NO_2S$, monoclinic, $P2_1/c$ (no. 14), $a = 8.6849(10)$ Å, $b = 18.740(2)$ Å, $c = 10.0465(12)$ Å, $\beta = 112.845(3)^\circ$, $V = 1506.9(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0685$, $wR_{\text{ref}}(F^2) = 0.2023$, $T = 293(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the 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	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.11624(17)	0.38660(6)	0.19203(11)	0.1009(5)
O1	0.1362(3)	0.35784(13)	-0.0561(2)	0.0774(7)
O2	0.3238(4)	0.26347(13)	0.3469(2)	0.0834(8)
N1	0.2573(3)	0.27733(14)	0.1066(2)	0.0590(7)
H1N	0.270(4)	0.2599(16)	0.032(2)	0.071*
C1	0.1709(4)	0.34067(17)	0.0810(3)	0.0594(8)
C2	0.3222(4)	0.23946(17)	0.2342(3)	0.0588(8)
C3	0.0388(6)	0.4221(2)	-0.1146(4)	0.0886(12)
H3A	0.100500	0.463951	-0.065618	0.106*
H3B	-0.065645	0.420393	-0.100794	0.106*
C4	0.0056(6)	0.4254(2)	-0.2707(4)	0.1014(15)
H4A	-0.052376	0.469685	-0.309502	0.122*
H4B	0.111689	0.426643	-0.281772	0.122*
C5	-0.0945(7)	0.3654(3)	-0.3567(5)	0.1186(17)
H5A	-0.196047	0.361206	-0.338742	0.142*
H5B	-0.031647	0.321535	-0.324734	0.142*
C6	-0.1411(8)	0.3740(4)	-0.5196(6)	0.160(3)
H6A	-0.209413	0.416485	-0.552025	0.192*
H6B	-0.039607	0.381486	-0.536339	0.192*
C7	-0.2306(9)	0.3141(6)	-0.6063(7)	0.216(4)
H7A	-0.157706	0.272763	-0.579756	0.259*
H7B	-0.325726	0.303690	-0.581659	0.259*
C8	-0.2876(9)	0.3228(5)	-0.7542(7)	0.208(4)
H8A	-0.350621	0.366285	-0.781458	0.313*
H8B	-0.357663	0.283218	-0.801407	0.313*
H8C	-0.194147	0.325008	-0.782623	0.313*
C9	0.3910(4)	0.16785(17)	0.2267(3)	0.0595(8)
C10	0.3545(5)	0.13003(18)	0.0991(4)	0.0693(9)
H10	0.289553	0.150868	0.011070	0.083*
C11	0.4143(6)	0.0618(2)	0.1029(5)	0.0908(12)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H11	0.387487	0.036348	0.017329	0.109*
C12	0.5128(6)	0.0310(3)	0.2313(6)	0.1048(15)
H12	0.553510	-0.015058	0.232688	0.126*
C13	0.5514(6)	0.0680(3)	0.3579(5)	0.1029(14)
H13	0.618969	0.047254	0.445186	0.123*
C14	0.4906(5)	0.1356(2)	0.3560(4)	0.0831(11)
H14	0.516390	0.160218	0.442349	0.100*

Source of material

O-Hexyl benzoylcarbamothioate was prepared by reacting benzoyl chloride and potassium thiocyanate in acetone. The intermediate isothiocyanate obtained *in situ* was then reacted with hexan-1-ol to provide the desired thiocarbamate in 71% yield. Yellow solid. **M.pt** = 343–345 K, MeOH/H₂O (lit. [6] M.pt = 343 K, EtOH/H₂O). **IR** (KBr; cm⁻¹): 3259, 3217, 3062, 2954, 2924, 2854, 1697, 1601, 1527, 1489, 1296, 1184, 710. **¹H NMR** (300 MHz, CDCl₃, rotamers, 298 K, TMS): δ = 9.16 (br s, 1H), 7.82 (m, 2H), 7.59 (m, 1H), 7.48 (m, 2H), 4.58 (t, *J* = 6.6 Hz, 2H), 1.82 (m, 2H), 1.60–1.20 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H). **¹³C{¹H} NMR** (75 MHz, CDCl₃, rotamers, 298 K, TMS): δ = 189.3, 162.2, 132.8, 132.7, 128.7, 127.4, 73.6, 31.3, 28.0, 25.4, 22.4, 14.0. **MS (EI)**: *m/z* (rel. intensity) = 265(16) [M]⁺, 182(41), 123(32), 121(30), 105(100), 77(48), 56(24), 51(23). **HRMS** calcd. for C₁₄H₁₉NO₂S 265.11365, found 265.11493. Yellow crystals were obtained by dissolving the product in hot *n*-hexane and allowing the solution to slowly evaporate.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The N-bound H atom was refined with N–H = 0.86 ± 0.01 Å, and with $U_{iso}(H) = 1.2U_{eq}(N)$. Evidence for disorder is noted in the terminal ethyl residue but, this was not resolved.

Comment

The title compound, O-hexyl benzoylcarbamothioate, (I), is an example of a benzoylthiocarbamic acid ester, RC(=O)N(H)C(=S)OR', and has been reported in the literature [6, 7]. Herein, the hitherto unreported crystal structure of (I) is described. While the molecules themselves attract attention with respect to the relative conformation of the thione and carbonyl groups in the central C(=O)N(H)C(=S) chromophore [8], metal complexes of these molecules are comparatively rare. In this context, the characterisation of a binuclear bis (triphenylphosphane)copper species is noted [9].

The molecular structure of (I) is shown in the figure (25% displacement ellipsoids) and exhibits key geometric

parameters of C1–S1 [1.620(3) Å], C2–O2 [1.214(3) Å], C1–N1 [1.374(4) Å] and C2–N1 [1.379(4) Å], indicative of limited delocalisation of π-electron density over this residue. This is despite the observation this part of the molecule is almost planar as seen in the values of the C2–N1–C1–S1 and C1–N1–C2–O2 torsion angles of -2.4(5) and -8.0(5)°, respectively. The thione-S1 and carbonyl-O2 atoms are to a first approximation in a *syn* conformation. The conformation in (I) is also found in the PhC(=O)N(H)C(=S)OR' derivatives with R' = Me [10], Et [11] and *n*-Bu [12].

The most prominent feature of the molecular packing is the formation of amide-N–H···O(amide) [N1–H1n···O2ⁱ: H1n···O2ⁱ = 2.13(3) Å, N1···O2ⁱ = 2.983(3) Å with angle at H1n = 169(3)° for symmetry operation (i) *x*, 1/2 - *y*, -1/2 + *z*] hydrogen bonds which lead to zig-zag chains along the *c*-axis [glide symmetry]. As the chains pack without directional interactions between them, a further analysis of the molecular packing was conducted *via* the calculation of the Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots using Crystal Explorer 17 [13] and established methods [14].

The most notable feature of the fingerprint plots is the sharp spikes due to the N–H···O hydrogen bonding. Overall, H···O/O···H contacts contribute 11.0% to the Hirshfeld surface. Greater contributions are made by H···S/S···H [12.7%], H···C/C···H [18.4%] and, especially, H···H contacts [54.6%]. In common with (I), the crystals of the R' = Me [10], Et [11] and *n*-Bu [12] derivatives feature supramolecular zig-zag chains. Systematic variations in the contributions to the calculated surface contacts are noted with H···H decreasing with the decreasing size of the R' group [49.8, 39.1 and 35.0%, respectively] with concomitant increasing contributions by H···C/C···H, H···S/S···H and H···O/O···H of, for example, for R' = Me, 22.5, 17.1 and 15.9%, respectively.

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