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2-Formylthymol oxime

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.045
wR factor = 0.137
Data-to-parameter ratio = 19.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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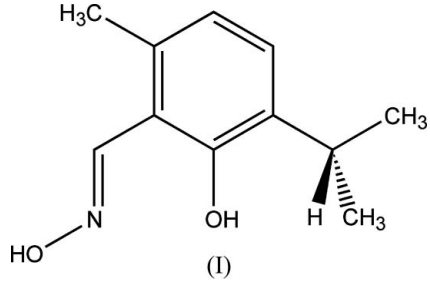
The structure of the title compound [systematic name: 2-hydroxy-6-methyl-3-(1-methylethyl)benzaldehyde oxime] $C_{11}H_{15}NO_2$, exhibits intra- as well as intermolecular hydrogen bonding, involving participation of the phenolic OH group in intramolecular hydrogen bonding and the hydroxyl group of the oxime in intermolecular hydrogen bonding. The H atom of the phenolic hydroxyl group forms a strong O—H···N intramolecular hydrogen bond with an O···N distance of 2.5788 (14) Å, which is in the middle of the expected range for such hydrogen bonds. The H atom of the hydroxyl group (in the oxime functionality) forms a weaker hydrogen bond with the phenolic hydroxyl group of a neighboring molecule [O···O = 2.8317 (14) Å], forming an extended chain, as expected for phenolic aldoximes which have bulky substituents on the aryl ring.

Comment

Thymol is a naturally occurring phenolic monoterpenoid. It possesses an ecological role and shows a broad spectrum of biological activities (Desai & Shah, 2003). In order to enhance the overall biological activity of thymol, derivatives such as nitroso, amino, azomethine, 4-thiazolidinones, 2-azetidinones and 4-imidazolinones have been prepared (Vashai *et al.*, 1995). On the other hand, derivatization of the hydroxyl group of thymol to ethers and esters has resulted in an increase in biological activities. A structure–activity correlation has also been established in this series of compounds and the overall activity has been found to depend on the nature and position of the functional groups. Thus, thymol was derivatized to 2-formyl thymol oxime, (I), to use it for the preparation of metal complexes, as a number of metal–oxime complexes are known to have biological significance (Chakravorty, 1974; Lumme *et al.*, 1984; Jayaraju & Kondapi, 2001). We present the structure of (I) here.



(I)

Compound (I) is a member of a general class of phenolic oximes (Smith *et al.*, 2003). These compounds have found extensive use in industry, mainly as extractants for copper

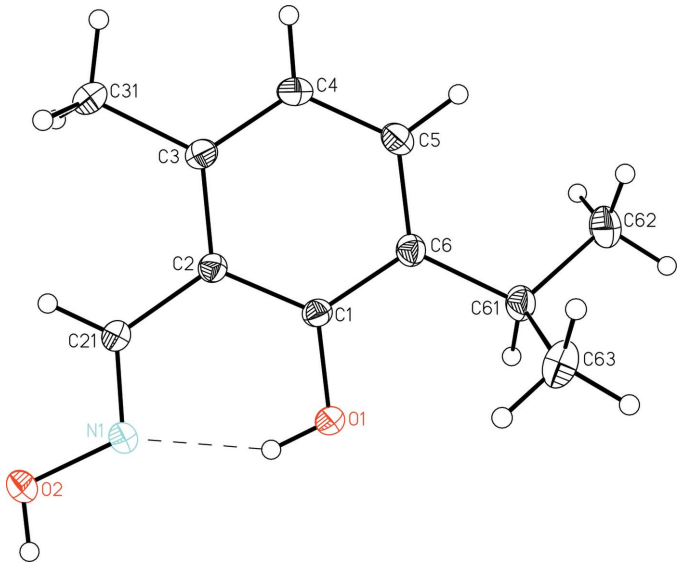


Figure 1
A view of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are represented by circles of arbitrary size. The dashed line indicates a hydrogen bond.

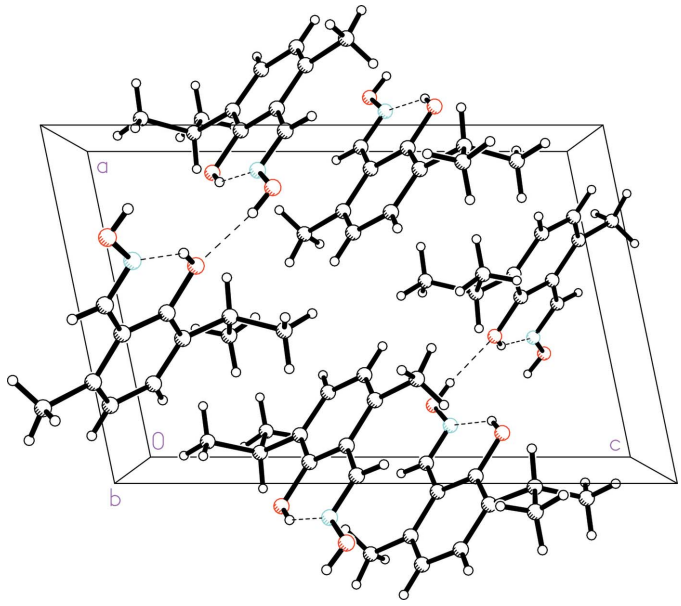


Figure 2
The molecular packing of the title compound, viewed along the *b* axis. Dashed lines indicate the hydrogen-bonding interactions.

(Kordosky, 2002), but also as anticorrosives in protective coatings (Thorpe *et al.*, 1999). Another feature of the phenolic oxime ligands is their propensity (Chaudhuri *et al.*, 1993; Bill *et al.*, 1997) to form polynuclear complexes in which both the oxime and phenolate functions can act as bridging units.

Elemental analysis for (I) gave a satisfactory fit to the formula $C_{11}H_{15}NO_2$. Table 1 contains selected bond lengths and angles. A view of the molecule and unit-cell contents are shown in Figs. 1 and 2, respectively. The average length of the benzene ring bonds is 1.396 (12) Å, which is in good agreement with generally accepted values.

Hydrogen bonding is a major feature of the structures of phenolic oximes. This results from the high density of hydrogen-bonding donors and acceptors per molecule. Invariably, the phenolic H atom forms an intramolecular hydrogen bond to the N atom of the oxime group, giving a six-membered ring. Since the phenolic H atom is often not found in Fourier difference maps, this interaction is usually characterized in terms of the phenolic O to oxime N separation. This distance varies little between structures, with a maximum value of 2.65 Å and a minimum of 2.51 Å. However, a general trend is that aldoximes have a greater phenolic O···N distance than the ketoximes (Smith *et al.*, 2003). In all of the free ligand structures, the molecules associate *via* intermolecular hydrogen bonding. These structures fall into two categories. Dimers result from the interaction of the oxime H atom with an adjacent phenolic O atom to produce a pseudomacrocyclic ligand with a 14-membered inner ring. This structure is seen only for aldoximes with no substituents or only monoatomic substituents on the aromatic ring (Smith *et al.*, 2003).

The introduction of groups which remove planarity in the molecule appears to stop efficient packing of dimeric units in the crystal structure and, instead, a polymeric structure, $[(H_2sal)_n]$, is observed. This is true for all phenolic ketoximes and for phenolic aldoximes which have bulky substituents on the aryl ring (Smith *et al.*, 2003).

The title compound exhibits intra- as well as intermolecular hydrogen bonding (Table 2), involving participation of the phenolic OH group in intramolecular hydrogen bonding and the hydroxyl group of the oxime in intermolecular hydrogen bonding, as indicated above. The H atom of the phenolic hydroxyl group forms a strong O1—H···N1 intramolecular hydrogen bond with an O1···N1 distance of 2.5788 (14) Å, which is in the middle of the expected range for such hydrogen bonds (Smith *et al.*, 2003).

The H atom of the hydroxyl group (in the oxime functionality) attached to atom N1 forms a weaker hydrogen bond with the phenolic hydroxyl group of a neighboring molecule [O2···O1 = 2.8317 (14) Å], forming an extended chain, as expected for phenolic aldoximes which have bulky substituents on the aryl ring (Smith *et al.*, 2003).

Experimental

The title compound was prepared by the condensation of 2-formylthymol (obtained by *ortho*-formylation of thymol) (3.56 g, 20 mmol) with hydroxylamine hydrochloride (1.4 g, 20 mmol) in ethanol (150 ml). Yellow crystals of (I) suitable for X-ray diffraction were obtained upon slow evaporation of the reaction mixture.

Crystal data

$C_{11}H_{15}NO_2$
M_r = 193.24
Monoclinic, $P2_1/n$
a = 8.8517 (7) Å
b = 9.0145 (7) Å
c = 13.5956 (10) Å
β = 101.698 (2)°
V = 1062.31 (14) Å^3
Z = 4
D_x = 1.208 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4359 reflections
θ = 2.5–28.2°
μ = 0.08 mm^{-1}
T = 293 (2) K
Irregular fragment, pale yellow
0.55 × 0.45 × 0.32 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer	2592 independent reflections
φ and ω scans	1897 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)	$R_{int} = 0.026$
$T_{min} = 0.716$, $T_{max} = 0.928$	$\theta_{max} = 28.3^\circ$
8098 measured reflections	$h = -10 \rightarrow 11$
	$k = -10 \rightarrow 11$
	$l = -17 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.1206P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$(\Delta/\sigma)_{max} = 0.007$
$wR(F^2) = 0.137$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
2592 reflections	
132 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3710 (14)	N1—C21	1.2743 (16)
O2—N1	1.3982 (14)		
C21—N1—O2	112.32 (11)	O1—C1—C2	120.36 (11)
O1—C1—C6	117.15 (11)	N1—C21—C2	121.68 (11)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N1	0.82	1.85	2.5788 (14)	148
O2—H2O···O1^{i}	0.82	2.02	2.8317 (14)	169

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

H atoms were positioned geometrically and constrained to ride on their parent atoms. For methyl H atoms, C—H = 0.96 Å and U_{iso}(H) = $1.5U_{eq}$(C); each group was allowed to rotate freely about its C—C bond. For other H atoms, O—H = 0.82 Å, aromatic C—H = 0.93 Å and methine C—H = 0.98 Å, and U_{iso}(H) = $1.2U_{eq}$(C,O).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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