

1-(2,6-Dimethylphenylamino)propane-1,2-dione

dioxime

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Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.056

wR factor = 0.189

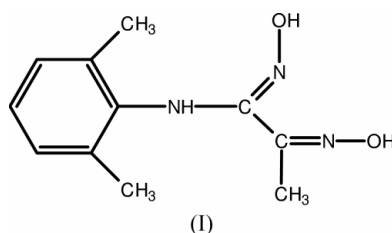
Data-to-parameter ratio = 14.0

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

The title compound, $\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_2$, consists of 2,6-dimethylphenyl and aminomethylglyoxime groups. The intermolecular $\text{O}-\text{H}\cdots\text{N}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds [$\text{O}\cdots\text{N}$ 2.742 (3) and 2.889 (3) \AA] are highly effective in forming the polymeric chains. The glyoxime group has an *E* configuration.

Comment

Intermolecular hydrogen bonding has received considerable attention among the directional noncovalent intermolecular interactions (Etter *et al.*, 1990); it combines moderate strength and directionality (Karle *et al.*, 1996) in linking molecules to form supramolecular structures.



The oxime ($-\text{C}=\text{N}-\text{OH}$) moiety, which is similar to carboxylic acid in that it contains one hydrogen-bond donor and two acceptor atoms, is a functional group that has not been extensively explored in crystal engineering. Structurally characterized oxime moieties are much less common than carboxylic acids and amides, but from a supramolecular perspective, this functionality does have some unique and desirable features (Aakeröy *et al.*, 2001).

Oxime groups possess stronger hydrogen-bonding capabilities than alcohols, phenols and carboxylic acids (Marsman *et al.*, 1999). The hydrogen-bond systems in the crystals of oximes have been analysed and a correlation between a pattern of hydrogen bonding and $\text{N}-\text{O}$ bond lengths has been suggested (Bertolasi *et al.*, 1982). The configurational and/or conformational isomers of glyoxime derivatives (dioximes) have also been analysed (Chertanova *et al.*, 1994).

The crystal structure determination of the title molecule, (I), was carried out in order to investigate the strength of the hydrogen bonding capabilities of the oxime groups.

As shown in Fig. 1, the title compound consists of aminomethylglyoxime and 2,6-dimethylphenyl moieties. The dihedral angles between the glyoxime planes *A* ($\text{O1}/\text{N2}/\text{C9}$), *B* ($\text{O2}/\text{N3}/\text{C10}$) and phenyl ring *C* ($\text{C1}-\text{C6}$) are $A/B = 45.3 (2)^\circ$, $A/C = 76.1 (1)^\circ$ and $B/C = 79.2 (1)^\circ$. In the glyoxime moiety, the $\text{O1}-\text{N2}$ [1.423 (3) \AA] bond length is longer than $\text{O2}-\text{N3}$ [1.396 (3) \AA], while the $\text{O2}-\text{N3}-\text{C10}$ [111.5 (2) $^\circ$] bond angle is larger than $\text{O1}-\text{N2}-\text{C9}$ [109.4 (2) $^\circ$], reflecting the types

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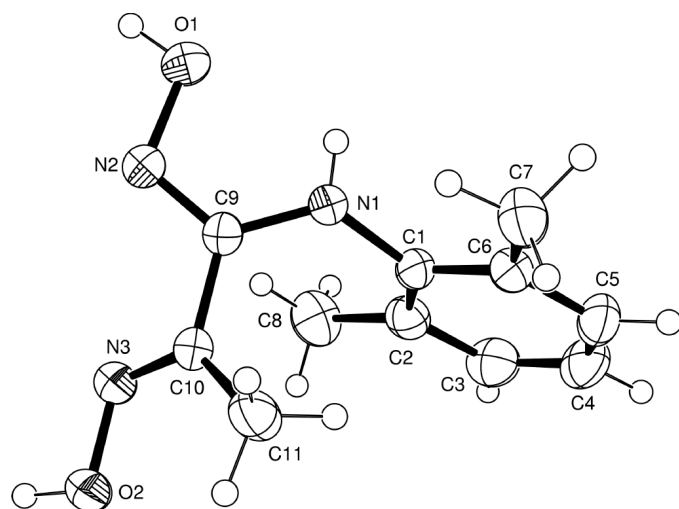


Figure 1
An ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

and electron-withdrawing or -donating properties of the substituents bonded to the C atoms of the glyoxime moiety. Comparing the bond lengths and angles of the aminomethylglyoxime moiety in the title compound, (I), with the corresponding ones in 2,3-dimethylquinoxaline-dimethylglyoxime (1/1), (II) (Hökelek *et al.*, 2001), the C9—C10 [1.489 (3) Å] bond length, and N3—C10—C9 [116.0 (2)°] and N3—C10—C11 [125.6 (2)°] bond angles are larger, while the C10—C11 [1.482 (3) Å] bond length, and C9—C10—C11 [119.4 (2)°] and C10—N3—O2 [111.5 (2)°] bond angles are smaller in (I) than the corresponding ones in (II). This may be partly due to the steric effect of the 2,6-dimethylphenyl group.

The glyoxime moiety has an *E* configuration [C10—C9—N2—O1 179.6(2)° and C9—C10—N3—O2 −177.4(2)°] (Chertanova *et al.*, 1994). In this configuration, both oxime

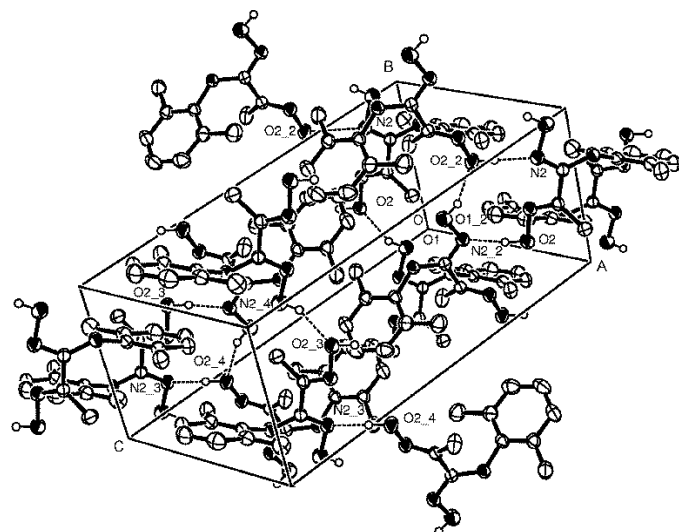


Figure 2
Packing diagram for (I). Hydrogen bonds are shown as dotted lines.

groups are involved as donors in intermolecular hydrogen bonds (Table 2). There is also an N1—H1···O1 intramolecular hydrogen bond. As can be seen from the packing diagram (Fig. 2), the crystal structure is stabilized by the intermolecular hydrogen bonds, which are highly effective in forming the polymeric chains approximately parallel to (101) plane.

Experimental

A mixture of chloromethylglyoxime (2.73 g, 20.0 mmol) and 2,6-dimethylaniline (2.44 g, 20.0 mmol) in ethanol (55 ml) was stirred at 263 K for 20 h and then diluted with water (120 ml). It was allowed to stand overnight at 273 K. The precipitated product was filtered off, washed with water and then recrystallized from CCl₄.

Crystal data

C ₁₁ H ₁₅ N ₃ O ₂	$D_x = 1.328 \text{ Mg m}^{-3}$
$M_r = 221.26$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 8.404 (2) \text{ \AA}$	$\theta = 10\text{--}18^\circ$
$b = 7.672 (2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 17.592 (3) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 102.620 (19)^\circ$	Prism, colorless
$V = 1106.8 (4) \text{ \AA}^3$	$0.35 \times 0.15 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Enraf-Nonius Turbo-CAD-4 diffractometer	1769 reflections with $I > 2\sigma(I)$
Non-profiled ω scans	$\theta_{\text{max}} = 26.3^\circ$
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.968$, $T_{\text{max}} = 0.986$	$k = 0 \rightarrow 9$
2198 measured reflections	$l = 0 \rightarrow 21$
2198 independent reflections	3 standard reflections
	frequency: 120 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0973P)^2 + 0.6954P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.189$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.13$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
2198 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
157 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

O2—N3	1.396 (3)	N1—C9	1.358 (3)
N3—C10	1.282 (3)	N1—C1	1.438 (3)
O1—N2	1.423 (3)	C9—C10	1.489 (3)
N2—C9	1.290 (3)	C10—C11	1.482 (3)
C10—N3—O2	111.52 (19)	N1—C9—C10	119.29 (19)
C9—N2—O1	109.37 (18)	N3—C10—C11	125.6 (2)
C9—N1—C1	127.5 (2)	N3—C10—C9	115.0 (2)
N2—C9—N1	123.8 (2)	C11—C10—C9	119.4 (2)
N2—C9—C10	116.59 (19)		
O1—N2—C9—N1	6.4 (3)	O2—N3—C10—C11	0.2 (3)
O1—N2—C9—C10	179.61 (19)	O2—N3—C10—C9	−177.37 (18)
C1—N1—C9—N2	−154.7 (2)	C8—C2—C3—C4	178.7 (3)
C1—N1—C9—C10	32.3 (4)	C7—C6—C5—C4	178.2 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1' \cdots O2^i$	0.86 (4)	2.09 (4)	2.889 (3)	154 (3)
$O2-H2' \cdots N2^{ii}$	0.94 (3)	1.81 (5)	2.742 (3)	174 (4)
$N1-H1 \cdots O1$	0.80 (3)	2.13 (3)	2.53 (3)	111 (3)

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

The OH and NH H atoms were located from a difference map and refined isotropically; the positions of the remaining H atoms were calculated geometrically at distances of 0.98 (CH₃) and 0.95 Å (CH) from the corresponding C atoms, and a riding model was used during the refinement process.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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