

Diethyl *N,N'*-*o*-phenylenedioxamate

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## Key indicators

Single-crystal X-ray study

*T* = 293 K

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

*R* factor = 0.058

w*R* factor = 0.155

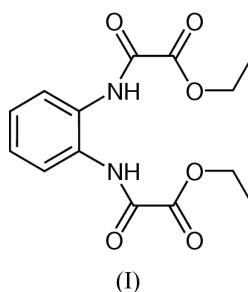
Data-to-parameter ratio = 19.6

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

The crystal structure analysis of the title compound,  $\text{C}_6\text{H}_4(\text{NHC}_2\text{O}_3\text{C}_2\text{H}_5)_2$  or  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_6$ , reveals a molecule with both oxamate groups twisted with respect to the benzene ring, as a result of steric interactions and the presence of three strong  $\text{N}-\text{H}\cdots\text{O}$  and one weak  $\text{C}-\text{H}\cdots\text{O}$  intramolecular hydrogen bonds. Centrosymmetrically related molecules form dimers connected by two  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Comment

Although the *N,N'*-*o*-phenylenedioxamate anion (opba) is a well known ligand present in many mono- and polymetallic systems, where it acts as a bridge transmitting, antiferro-, ferri- and ferromagnetic interactions between nearest-neighbour magnetic centers (Stumpf, Ouahab *et al.*, 1993; Stumpf, Pei, Ouahab *et al.*, 1993; Stumpf, Pei, Kahn *et al.*, 1993; Stumpf *et al.*, 1994; Turner *et al.*, 1995; Oushoorn *et al.*, 1996; Unamuno *et al.*, 1998; Daigebonne *et al.*, 2001), the crystal structure of this ligand has never been described. In the present paper, we report the crystal structure of the diethyl ester of *N,N'*-*o*-phenylenedioxamic acid [(I),  $\text{Et}_2\text{H}_2\text{opba}$ ].



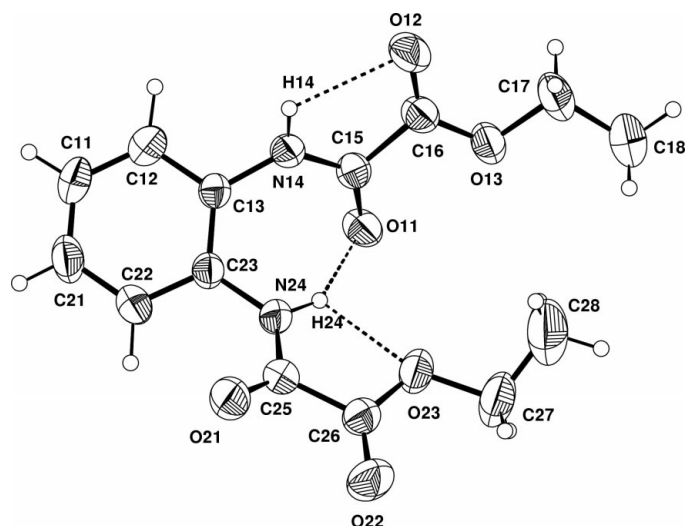
The asymmetric unit of (I) (Fig. 1) contains one  $\text{Et}_2\text{H}_2\text{opba}$  molecule, in which two oxamic acid ethyl ester groups are connected to the benzene ring in *ortho* positions. For steric reasons, the two substituents adopt a non-planar arrangement with respect to the phenyl ring. Thus, the oxamate groups (described by the mean planes through atoms  $\text{O11}/\text{C15}/\text{N14}/\text{O13}/\text{C16}/\text{O12}$  and  $\text{O21}/\text{C25}/\text{N24}/\text{O23}/\text{C26}/\text{O22}$ ) are twisted by  $39.8(1)$  and  $29.4(1)^\circ$ , respectively, with respect to the plane defined by the aromatic ring.

The two oxamate moieties adopt opposite conformations, *s-trans* and *s-cis* for the one bonded to the benzene atoms C13 and C23, respectively. Both are nearly planar, and stabilized by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds [ $\text{N14}-\text{H14}\cdots\text{O12}$   $2.694(3) \text{ \AA}$  and  $\text{N24}-\text{H24}\cdots\text{O23}$   $2.612(2) \text{ \AA}$ ]. There is another intramolecular hydrogen bond [ $\text{N24}-\text{H24}\cdots\text{O11}$   $2.722(3) \text{ \AA}$ ], connecting both oxamate groups.

Received 8 July 2002

Accepted 16 July 2002

Online 25 July 2002



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids for the non-H atoms. H atoms are drawn as circles of arbitrary radii.

Two  $\text{Et}_2\text{H}_2\text{opba}$  units related by a centre of symmetry form dimers bonded through two  $\text{N14}\cdots\text{H14}\cdots\text{O21}^i$  [symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ ] hydrogen bonds (Fig. 2). The aromatic rings of each component of the dimer are parallel stacked, at a distance of  $3.55(5) \text{ \AA}$ , with the centres of the rings laterally displaced.

These dimeric units form zigzag chains along the crystallographic [001] direction, forming layers parallel to the crystallographic (100) plane at  $x = 0.25$  and  $x = 0.75$ . The interaction between the dimeric units takes place through hydrogen bonds of type  $\text{C}-\text{H}\cdots\text{O}$ .

## Experimental

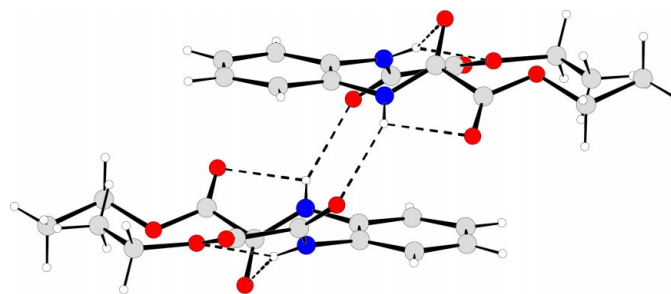
The title compound has been obtained as a polycrystalline powder, according to a literature method (Stumpf, Pei, Kahn *et al.*, 1993). To a suspension of this powder in an ethanol–water mixture (1/1), an NaOH solution was added until an almost clear solution was obtained (pH 7). After any insoluble material was filtered off, the resulting solution was allowed to stand at room temperature, whereupon prismatic colourless crystals of (I) were formed.

### Crystal data

$\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_6$	$D_x = 1.35 \text{ Mg m}^{-3}$
$M_r = 308.29$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25 reflections
$a = 17.756(4) \text{ \AA}$	$\theta = 8.1\text{--}13.3^\circ$
$b = 15.986(2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 11.924(2) \text{ \AA}$	$T = 293(2) \text{ K}$
$\beta = 116.31(2)^\circ$	Prism, colourless
$V = 3034.0(9) \text{ \AA}^3$	$0.50 \times 0.45 \times 0.40 \text{ mm}$
$Z = 8$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 30.0^\circ$
$\omega/2\theta$ scans	$h = -24 \rightarrow 22$
Absorption correction: none	$k = 0 \rightarrow 22$
4616 measured reflections	$l = 0 \rightarrow 16$
4419 independent reflections	2 standard reflections every 100 reflections
1870 reflections with $I > 2\sigma(I)$	intensity decay: <2%
$R_{\text{int}} = 0.033$	



**Figure 2**  
View of the dimer of (I).

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.155$   
 $S = 0.88$   
 4419 reflections  
 225 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0787P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

**Table 1**

Selected interatomic distances ( $\text{\AA}$ ).

O11–C15	1.219 (3)	O23–C27	1.467 (3)
O12–C16	1.193 (3)	N14–C13	1.424 (3)
O13–C16	1.313 (3)	N14–C15	1.338 (3)
O13–C17	1.458 (4)	N24–C23	1.414 (3)
O21–C25	1.214 (3)	N24–C25	1.351 (3)
O22–C26	1.188 (3)	C15–C16	1.528 (3)
O23–C26	1.315 (3)	C25–C26	1.535 (3)

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{N14--H14}\cdots\text{O12}$	0.81 (3)	2.28 (2)	2.694 (3)	112.2 (19)
$\text{N24--H24}\cdots\text{O11}$	0.90 (2)	1.93 (2)	2.722 (3)	145 (2)
$\text{N24--H24}\cdots\text{O23}$	0.90 (2)	2.21 (2)	2.612 (2)	106.5 (17)
$\text{C22--H22}\cdots\text{O21}$	1.02 (3)	2.44 (2)	2.927 (3)	108.5 (16)
$\text{N14--H14}\cdots\text{O21}^i$	0.81 (3)	2.37 (2)	3.115 (3)	153 (2)
$\text{C17--H17}^2\cdots\text{O12}^{ii}$	0.9700	2.5237	3.109 (4)	118.82
$\text{C21--H21}\cdots\text{O11}^{iii}$	0.93 (3)	2.49 (3)	3.248 (3)	140 (2)
$\text{C12--H12}\cdots\text{O21}^{iv}$	1.03 (3)	2.52 (3)	3.428 (3)	146.9 (18)

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

The phenyl and amino H atoms were located in difference Fourier maps and refined freely. Because of the relatively strong thermal motion of the ethyl groups, their H atoms were located in calculated positions and refined as riding atoms.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms, 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) and *PLATON* (Spek, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by UPV/EHU (grant No. 169.310-EA8057/2000)

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