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#### Key indicators

Single-crystal X-ray study

$T = 100\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

$R$  factor = 0.058

w $R$  factor = 0.124

Data-to-parameter ratio = 12.1

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

## Diethyl *N,N'*-*m*-phenylenedioxamate

The title compound,  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_6$ , crystallizes in the monoclinic space group,  $C2/c$ .  $C_2$  symmetry is imposed on the molecule. The ethyl oxamate groups are twisted out of the aromatic ring plane by  $34.53(6)^\circ$  and both carbonyl groups are antiperiplanar. The intramolecular hydrogen-bonding pattern is depicted by a soft  $\text{C}-\text{H}\cdots\text{O}/\text{O}'$  three-centered hydrogen bond, and  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions which form an  $S(5)S(5)S(6)S(6)'S(5)'S(5)'$  motif. The molecules are linked into  $C(3)$  and  $C(4)$  chain motifs, forming supramolecular layers in the  $ac$  plane.

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#### Comment

The title compound, (I), forms monoclinic crystals ( $C2/c$ ,  $Z = 4$ ).  $C_2$  symmetry is crystallographically imposed on the molecule; thus only one half molecule is present in the asymmetric unit. The bond lengths and angles are in the standard ranges, with a mean  $\text{C}-\text{C}$  bond length of  $1.384(3)\text{ \AA}$  (Table 1). The ethyl oxamate  $-\text{N}(\text{H})-\text{C}(\text{O})-\text{C}(\text{O})-\text{OCH}_2\text{CH}_3$  group is almost planar, with an  $\text{N5}-\text{C5}-\text{C6}-\text{O7}$  torsion angle of  $170.2(2)^\circ$ . Both carbonyl groups are antiperiplanar, with an  $\text{O5}-\text{C5}-\text{C6}-\text{O6}$  torsion angle of  $170.8(2)^\circ$ . The  $\text{C5}-\text{C6}$  bond distance is almost exactly  $1.541(1)\text{ \AA}$  (Dewar & Schmeizing, 1968), the value usually assumed for a  $\text{Csp}^3-\text{Csp}^3$  single bond, while for the  $\text{Csp}^2-\text{Csp}^2$  single bond, the average value from the literature (Allen *et al.*, 1987) is  $1.478(12)\text{ \AA}$ . This may be indicative of the absence of conjugation, in spite of the planarity of the oxamate system, but can be justified by steric hindrance; at  $2.640(2)\text{ \AA}$ , the  $\text{O5}\cdots\text{O7}$  contact is markedly shorter than the sum of the van der Waals radii ( $3.04\text{ \AA}$ ; Bondi, 1964). The two ethyl oxamate groups are

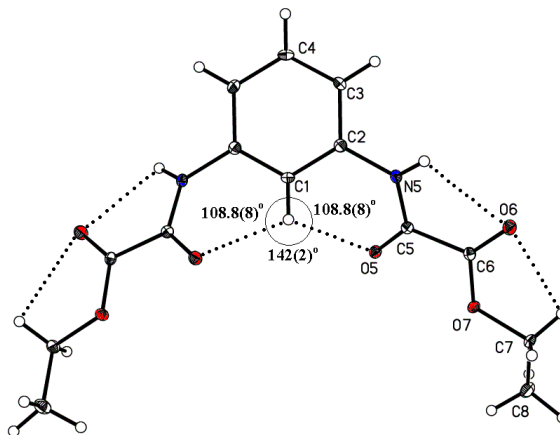
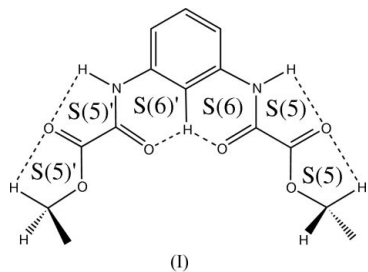


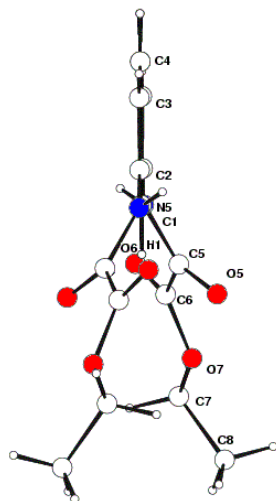
Figure 1

The molecular structure of the title compound, showing the atom-labelling scheme, the three-centered hydrogen-bonding interaction  $\text{C}-\text{H}\cdots\text{O}(\text{O}')$  and the  $\text{H5}\cdots\text{O6}\cdots\text{H7A}$  hydrogen-bonding interactions. Displacement ellipsoids are drawn at the 20% probability level.

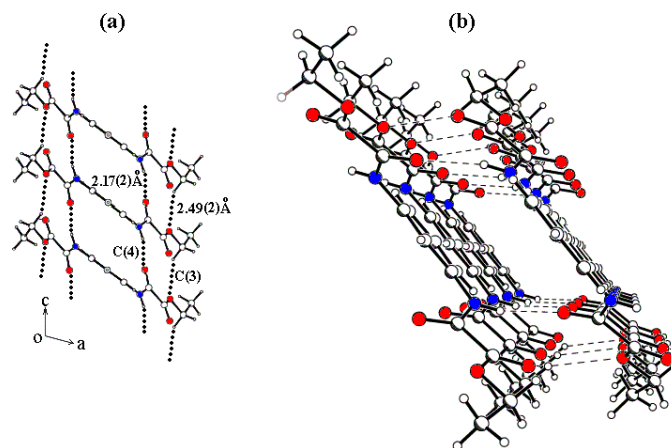
twisted by  $34.53(6)^\circ$  away from the aromatic ring mean plane (Fig. 2). These results contrast with those recently reported for the 1,2-isomer, *viz.* *N,N'*-*o*-phenylenedioxamate (Martin *et al.*, 2002). The analysis of this latter compound reveals a molecule with one ethyl oxamate group synperiplanar and the other antiperiplanar, both twisted with respect to the benzene ring as a result of steric interactions. The above-mentioned conformation allows the formation of the intramolecular three-centered hydrogen-bonding interaction (THB)  $C1-H \cdots O5(O5')$ . Selected bond distances and torsion angles are listed in Table 2.



According to graph-set notation (Bernstein *et al.*, 1995), two adjacent S(6) rings are formed. A particular feature of this interaction is the  $O5 \cdots H1 \cdots O5'$  angle of  $142(2)^\circ$ , and the sum of the angles at the donor is  $360^\circ$ , as required by the crystallographic symmetry (Fig. 1). The  $H1 \cdots O5$  distance [ $2.45(1) \text{ \AA}$ ] is shorter than the mean value reported for similar systems [ $2.553(4) \text{ \AA}$ ; Steiner, 2002]; however, it is larger than the values found for other intramolecular THB involving  $N-H$  as donor [ $2.09(2) \text{ \AA}$ ; Padilla-Martínez *et al.*, 2001]. These results reveal the relative weakness of the soft  $C-H \cdots O=C$  interaction (Vargas *et al.*, 2000), compared with the hard  $N-H \cdots O=C$  interaction (Desiraju, 1996) involving THB systems. The intramolecular hydrogen-bonding interactions  $N5-H5 \cdots O6$  and  $C7-H7A \cdots O6$  (Table 2) complete the overall hydrogen-bonding scheme, which can be depicted as a set of six hydrogen-bonded rings forming an  $S(5)S(5)S(6)S(6)S(5)S(5)$  motif. It is noteworthy that this last interaction should have some importance in determining



**Figure 2**  
Projection of the molecular structure, showing the twist.



**Figure 3**  
(a) Part of the packing of the title compound, showing the formation of C(3) and C(4) chain motifs along the [010] direction ( $R_2^2(11)[C(3)C(4)]$ ); (b) three-dimensional view of the supramolecular layers of the title compound.

the location of the ethyl group in the oxamate plane. Supramolecular layers of the title molecule are formed in the *ac* plane due to  $N5-H \cdots O5^i$  [ $2.17(2) \text{ \AA}$ ] and  $C7-H7B \cdots O7^{ii}$  [ $2.49(2) \text{ \AA}$ ] intermolecular hydrogen bonds (see Table 2 for symmetry codes), which lead to C(4) and C(3) chains motifs, respectively (Fig. 3a), whose topological motif corresponds to a ring graph-set descriptor  $R_2^2(11)[C(3)C(4)]$  (Bernstein *et al.*, 1995). These parallel chains are generated by translation along the [010] direction (Fig. 3b) and are formed because of the close proximity of alternate acceptors. There are no hydrogen bonds between these layers.

## Experimental

The compound was prepared from 2.3 ml (20.4 mmol) of ethyl chlorooxacetate and 1.0 g (9.3 mmol) of 1,3-diaminobenzene, according to reported procedures (Martínez-Martínez *et al.*, 1998), to yield 20.0 g (70%) of a pale yellow solid (m.p. 425–427 K). IR (KBr,  $\text{cm}^{-1}$ ): 3349 (NH), 1699 (CO);  $^1\text{H}$  NMR (300.08 MHz, DMSO- $d_6$ , p.p.m.): 10.8 (s, 2H, NH), 8.2 (s, 1H), 7.5 (d, 2H), 7.3 (t, 1H), 4.3 (q, 4H,  $\text{CH}_2$ ), 1.3 (t, 6H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75.46 MHz, DMSO- $d_6$ , p.p.m.): 161.3 (COO), 156.4 (CON), 138.3 ( $C_i$ ), 129.6 ( $C_m$ ), 117.7 ( $2C_o$ ), 113.5 ( $C_o$ ), 63.0 ( $\text{CH}_2$ ), 14.5 ( $\text{CH}_3$ ). Crystals suitable for X-ray analysis were obtained after slow crystallization from acetone.

### Crystal data

$C_{14}H_{16}N_2O_6$   
 $M_r = 308.29$   
Monoclinic,  $C2/c$   
 $a = 25.086(5) \text{ \AA}$   
 $b = 7.1225(14) \text{ \AA}$   
 $c = 8.2529(17) \text{ \AA}$   
 $\beta = 104.870(3)^\circ$   
 $V = 1425.2(5) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.437 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 600 reflections  
 $\theta = 20.0\text{--}1.0^\circ$   
 $\mu = 0.11 \text{ mm}^{-1}$   
 $T = 100(2) \text{ K}$   
Prism, colourless  
 $0.32 \times 0.21 \times 0.20 \text{ mm}$

### Data collection

Bruker SMART area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
5869 measured reflections  
1607 independent reflections  
1464 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -31 \rightarrow 32$   
 $k = -8 \rightarrow 9$   
 $l = -10 \rightarrow 10$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.124$   
 $S = 1.22$   
 1607 reflections  
 133 parameters  
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 2.0276P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C1—C2	1.385 (2)	C5—C6	1.543 (3)
C2—C3	1.386 (3)	C6—O6	1.204 (2)
C2—N5	1.425 (2)	C6—O7	1.325 (2)
C3—C4	1.382 (3)	C7—O7	1.468 (2)
C5—O5	1.223 (2)	C7—C8	1.499 (3)
C5—N5	1.343 (2)		
C1—C2—C3—C4	−0.4 (3)	C6—C5—N5—C2	−175.42 (16)
N5—C2—C3—C4	−179.55 (18)	C1—C2—N5—C5	37.0 (3)
O5—C5—C6—O6	170.82 (19)	C3—C2—N5—C5	−143.9 (2)
N5—C5—C6—O6	−9.6 (3)	O6—C6—O7—C7	4.6 (3)
O5—C5—C6—O7	−9.3 (2)	C5—C6—O7—C7	−175.28 (15)
N5—C5—C6—O7	170.22 (15)	C8—C7—O7—C6	−169.18 (17)
O5—C5—N5—C2	4.1 (3)		

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 $\cdots$ O5	0.94 (4)	2.450 (12)	2.896 (2)	108.8 (8)
N5—H5 $\cdots$ O6	0.85 (2)	2.35 (2)	2.734 (2)	108 (2)
C7—H7A $\cdots$ O6	0.95 (2)	2.49 (2)	2.717 (3)	93 (1)
N5—H5 $\cdots$ O5 <sup>i</sup>	0.85 (2)	2.17 (2)	3.001 (2)	165 (2)
C7—H7B $\cdots$ O7 <sup>ii</sup>	0.97 (2)	2.49 (2)	3.361 (3)	149 (2)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

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## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bruker (2000). *SMART*, *SAINTE* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
- Dewar, M. J. S. & Schmeizing, H. N. (1968). *Tetrahedron*, **11**, 96–120.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Martin, S., Beitia, J., Ugalde, M., Vitoria, P. & Cortes, R. (2002). *Acta Cryst.* **E58**, o913–o915.
- Martínez-Martínez, F. J., Padilla-Martínez, I. I., Brito, M. A., Geniz, E. D., Rojas, R. C., Saavedra, J. B. R., Höpfl, H., Tlahuex, M. & Contreras, R. (1998). *J. Chem. Soc. Perkin Trans. 2*, pp. 401–406.
- Padilla-Martínez, I. I., Martínez-Martínez, F. J., García-Báez, E. V., Torres-Valencia, J. M., Rojas-Lima, S. & Höpfl, H. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 1817–1823.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Steiner, T. (2002). *Angew. Chem. Int. Ed. Engl.* **41**, 48–76.
- Vargas, R., Garza, J., Dixon, D. A. & Hay, B. P. (2000). *J. Am. Chem. Soc.* **122**, 4750–4755.