Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Ethyl *N*-phenyloxamate

Efrén V. García-Báez,[a] Carlos Z. Gómez-Castro,[a] Herbert Höpfl,[b] Francisco J. Martínez-Martínez[a] and Itzia I. Padilla-Martínez[a]*

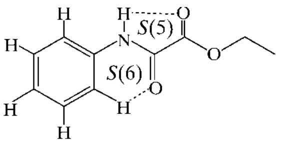
[a]Unidad Profesional Interdisciplinaria de Biotecnología, Instituto Politécnico Nacional, Avenida Acueducto s/n, Barrio La Laguna Ticomán, México DF 07340, Mexico, and [b]Centro de Investigaciones Químicas, Universidad Autónoma de Morelos, Cuernavaca Morelos, Mexico
Correspondence e-mail: ipadilla@acei.upibi.ipn.mx

Received 4 August 2003
Accepted 7 August 2003
Online 16 September 2003

The oxamate group in the title compound, $C_{10}H_{11}NO_3$, is almost coplanar with the phenyl ring because of intramolecular hydrogen-bonding interactions, and the structure can be described as an anilide single bonded to an ethyl carboxylate group. The supramolecular structure is achieved through intermolecular hard N—H···O and soft C—H···*X* (*X* = O and phenyl) hydrogen-bonding interactions.

Comment

Ethyl oxamates have been used as intermediates in the synthesis of oxamide compounds (Martínez-Martínez *et al.*, 1998) and more recently they have been used to design molecular clefts (Padilla-Martínez *et al.*, 2003). In spite of the growing importance of such compounds, there are few known examples of crystalline structures bearing aromatic oxamates, and those that are known are at least disubstituted. We analyse here the crystalline structure of the title compound, (I), which bears an ethyl oxamate group as the only substituent.



(I)

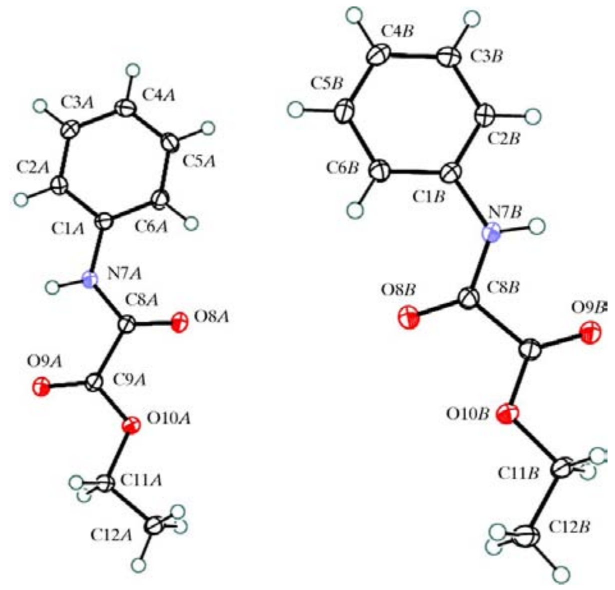


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. Two molecules are present in the asymmetric unit.

Compound (I) crystallizes in the triclinic system ($P\bar{1}$, $Z = 4$), and two independent molecules, which are labelled *A* and *B* (Fig. 1), are found in the asymmetric unit. These differ slightly, as evidenced by the O8—C8—C9—O9 torsion angles of −174.99 (13) and 171.89 (13)° for molecules *A* and *B*, respectively (Table 1). The two carbonyl groups are almost antiperiplanar, with a mean O8—C8—C9—O9 torsion angle of 173.3 (15)°, in agreement with the conformation most frequently adopted by open systems. The mean C6—C1—N7—C8 torsion angle is 15.0 (16)°, showing that the ethyl oxamate group is almost in the mean phenyl-ring plane, in contrast to the out-of-plane conformation adopted by 1,2-diphenyl (Martin *et al.*, 2002) and 1,3-diphenyl dioxamate (Padilla-Martínez *et al.*, 2003). In spite of the planarity exhibited by the oxamate group [mean O8—C8—C9—O9 = 175.5 (15)°], the mean CO—CO distance of 1.543 (3) Å is close to the value for a Csp^3—Csp^3 single bond (Dewar & Schmeizing, 1968), indicating the absence of conjugation.

The mean N7—CO and N7—Ph distances of 1.348 (3) and 1.418 (3) Å are very similar to the values measured for acetanilide [1.354 (3) and 1.413 (3) Å, respectively; Brown & Corbridge, 1954; Brown, 1966]. Thus, (I) can be described as being composed of an anilide group single bonded to an ethyl carboxylate group, in accordance with the observed chemical

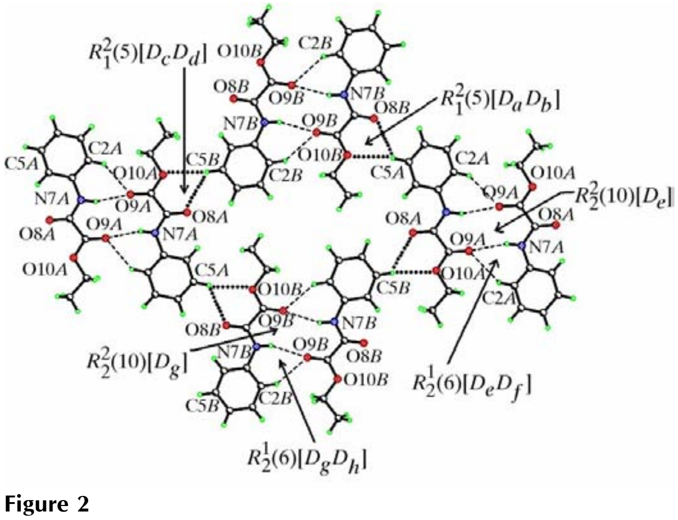


Figure 2
The supramolecular arrangement of (I), showing the hydrogen-bonding network along the [12$\bar{3}$] direction.

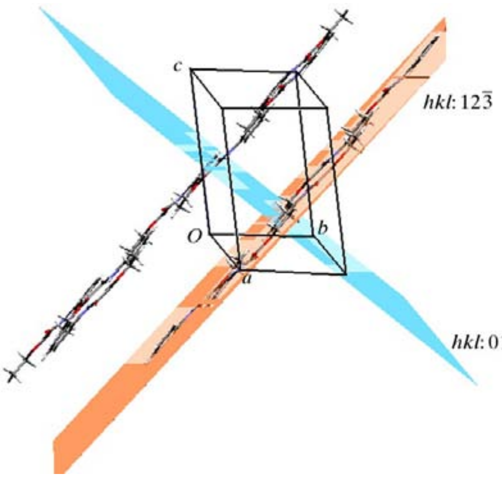


Figure 3
Assembly of parallel [12$\bar{3}$] layers along the [012] direction.

reactivity of these systems (Padilla-Martínez *et al.*, 2001). As a result of the lack of conjugation along the ethyl oxamate group, intramolecular hydrogen bonding should contribute to the planarity of the system, allowing the formation of the two adjacent $S(5)$ (N7—H7$\cdots$O9) and $S(6)$ (C6—H6$\cdots$O8) ring motifs (Bernstein *et al.*, 1995) indicated in the *Scheme*.

The hydrogen-bonding geometry is listed in Table 2. The two types of molecules can form $A\cdots B$ pairs through intermolecular three-centred O8$\cdots$H5$\cdots$O10 hydrogen bonds, thus forming $R_1^2(5)[D_aD_b]$ and $R_1^2(5)[D_cD_d]$ rings. Alternatively, two molecules of the same kind can form $A\cdots A'$ and $B\cdots B'$ pairs through intermolecular hydrogen bonding in the form of soft C2—H2$\cdots$O9 and hard N7—H7$\cdots$O9 (Desiraju, 1996) interactions, thus forming $R_2^1(6)[D_eD_f]$ and $R_2^1(6)[D_gD_h]$ ring motifs. By symmetry, the self-complementary $R_2^2(10)[D_e]$ and $R_2^2(10)[D_g]$ ring motifs appear (Fig. 2). The $R_2^1(6)$ ring motif seems to be the characteristic motif for these systems, since it has been found for other non-substituted aromatic oxamates (García-Báez *et al.*, 2003), whereas the $R_2^2(10)$ motif is typical for aliphatic oxamides (Nguyen *et al.*, 2001). The resulting parallel [12$\bar{3}$] layers are linked *via* C—H$\cdots\pi$(arene) interactions (Umezawa *et al.*, 1998). The CH_3 (molecule *A*) and CH_2 (molecule *B*) moieties are hydrogen bonded to the phenyl ring of molecule *A* (C12*A*—H12*B*$\cdots$*Cg*1 and C11*B*—H11*D*$\cdots$*Cg*1, respectively; *Cg*1 is the centroid of the C1*A*–C6*A* ring), thus forming a staircase motif that completes the three-dimensional structure along the (012) direction (Fig. 3).

Experimental

Compound (I) was prepared from aniline (9.8 ml, 0.1 mol) and ethyl chlorooxoacetate (12.0 ml, 0.1 mol) according to reported procedures (Martínez-Martínez *et al.*, 1998), yielding, after crystallization from hexane, a white solid (11.8 g; yield 60%; m.p. 347 K). IR (KBr, cm^{-1}): 3345 (NH), 1708 (CO); ^{1}H NMR (300.08 MHz, DMSO-d_6, p.p.m.): 7.86 (*d*, 2H), 7.48 (*t*, 2H), 7.26 (*t*, 1H), 4.40 (*q*, 2H), 1.43 (*t*, 3H); ^{13}C NMR (75.46 MHz, DMSO-d_6, p.p.m.): 161.4 (COO), 156.2 (CON), 138.2 (C_i), 129.5 (C_m), 125.4 (C_p), 121.2 (C_o), 63.0 (CH_2), 14.5 (CH_3). Crystals suitable for X-ray analysis were obtained by slow crystallization from toluene. The melting point was measured on an electrothermal IA 9100 apparatus and was left uncorrected. The IR spectrum was recorded using a Perkin–Elmer 16 F PC IR spectrophotometer, and the NMR spectra were recorded using a Varian Mercury 300 MHz instrument.

Crystal data

$C_{10}H_{11}NO_3$
$M_r = 193.20$
Triclinic, $P\bar{1}$
$a = 7.8033$ (5) Å
$b = 10.6424$ (7) Å
$c = 13.2432$ (9) Å
$\alpha = 108.491$ (1)°
$\beta = 96.081$ (1)°
$\gamma = 110.165$ (1)°
$V = 950.03$ (11) Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 600 reflections
$\theta = 20$–25°
$\mu = 0.10$ mm^{-1}
$T = 100$ (2) K
Rhombohedral, colourless
0.50 × 0.47 × 0.43 mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.952$, $T_{max} = 0.967$
10 719 measured reflections
4107 independent reflections
3637 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.0$°
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$
100 standard reflections
frequency: 1 min
intensity decay: 5%

Table 1
Selected geometric parameters (Å, °).

O8*A*—C8*A*	1.2165 (16)	O8*B*—C8*B*	1.2116 (17)
O9*A*—C9*A*	1.2063 (16)	O9*B*—C9*B*	1.2078 (16)
O10*A*—C9*A*	1.3209 (16)	O10*B*—C9*B*	1.3161 (16)
O10*A*—C11*A*	1.4586 (16)	O10*B*—C11*B*	1.4639 (16)
N7*A*—C1*A*	1.4173 (17)	N7*B*—C1*B*	1.4193 (17)
N7*A*—C8*A*	1.3470 (17)	N7*B*—C8*B*	1.3488 (17)
C8*A*—C9*A*	1.5421 (19)	C8*B*—C9*B*	1.5436 (19)
O8*A*—C8*A*—C9*A*—O9*A*	−174.99 (13)	O8*B*—C8*B*—C9*B*—O9*B*	171.89 (13)
N7*A*—C1*A*—C2*A*—C3*A*	−178.05 (12)	N7*B*—C1*B*—C2*B*—C3*B*	179.44 (12)
C6*A*—C1*A*—N7*A*—C8*A*	−13.6 (2)	C6*B*—C1*B*—N7*B*—C8*B*	16.2 (2)
N7*A*—C1*A*—C6*A*—C5*A*	177.86 (12)	N7*B*—C1*B*—C6*B*—C5*B*	−179.07 (12)

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

*Cg*1 is the centroid of the C1*A*–C6*A* ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N7*A*—H7*A*$\cdots$O9*A*^{i}	0.88	2.24	3.0867 (17)	161
N7*B*—H7*B*$\cdots$O9*B*^{ii}	0.88	2.36	3.1410 (18)	148
N7*A*—H7*A*$\cdots$O9*A*	0.88	2.30	2.7168 (16)	109
N7*B*—H7*B*$\cdots$O9*B*	0.88	2.29	2.7059 (16)	109
C6*A*—H6*A*$\cdots$O8*A*	0.95	2.31	2.8974 (18)	120
C6*B*—H6*B*$\cdots$O8*B*	0.95	2.32	2.9004 (18)	119
C5*A*—H5*A*$\cdots$O8*B*^{iii}	0.95	2.67	3.294 (2)	124
C5*B*—H5*B*$\cdots$O8*A*^{iv}	0.95	2.70	3.3418 (18)	125
C5*A*—H5*A*$\cdots$O10*B*^{iii}	0.95	2.72	3.622 (2)	160
C5*B*—H5*B*$\cdots$O10*A*^{iv}	0.95	2.62	3.5669 (19)	175
C2*A*—H2*A*$\cdots$O9*A*^{i}	0.95	2.55	3.3309 (19)	140
C2*B*—H2*B*$\cdots$O9*B*^{ii}	0.95	2.51	3.3385 (19)	146
C11*B*—H11*D*$\cdots$*Cg*1^{v}	0.99	2.79	3.6719 (17)	149
C12*A*—H12*A*$\cdots$*Cg*1^{vi}	0.98	2.62	3.4703 (18)	146

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, 2-y, -z$; (iii) $x, y, 1+z$; (iv) $1+x, 1+y, z$; (v) $x-1, y, z-1$; (vi) $-x, -y, 1-z$.

o542 Efrén V. García-Báez et al. • $C_{10}H_{11}NO_3$ Acta Cryst. (2003). C59, o541–o543

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.114$
$S = 1.05$
4107 reflections
256 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.3757P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0054 (13)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

This work was supported by CGPI-IPN (grant No. 5201) and CONACYT–México (grant No. 33438-E).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1178). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2003). C**59**, o541–o543 Efrén V. García-Báez *et al.* • $C_{10}H_{11}NO_3$ **o543**