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Diethyl piperazine-1,4-diyldioxalate

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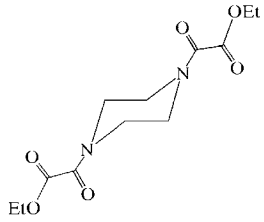
The ethyl oxamate group, N–C(O)–C(O)–OEt, in the title compound, alternatively called diethyl *N*,*N*′:*N*,*N*′-bis(ethylene)dioxamate, $C_{12}H_{18}N_2O_6$, can be considered as being composed of two singly bonded amide and ester functionalities. The ethyl oxamate group is not planar. The two carbonyl groups are almost perpendicular, with an oxalyl O=C—C=O torsion angle of −111.34 (17)°. The molecule is located on an inversion centre. Infinite supramolecular tapes, propagating along the *b* axis, are formed through soft C—H···O interactions which form a centrosymmetric $R_2^2(12)$ motif.

Comment

Alkyl oxamates have been used as intermediates in the synthesis of oxamides (Toda *et al.*, 1986) and oxamic acid derivatives which exhibit inhibitory protein tyrosine phosphatase activity (Andersen *et al.*, 2002). Recently, oxamates derived from primary amines have been used as molecular models for the study of three-centred hydrogen bonding (Martínez-Martínez *et al.*, 1998; Padilla-Martínez *et al.*, 2001) and in the design of molecular clefts (Martín *et al.*, 2002; Padilla-Martínez *et al.*, 2003). However, reports of oxamates derived from secondary amines are scarce in the literature (Cambridge Structural Database, April 2004 Version; Allen, 2002). In this context, the molecular and supramolecular structures of the title compound, (I), are reported.

Compound (I) forms monoclinic centrosymmetric crystals ($P2_1/c$, $Z = 2$). Thus, only one half of the molecule is found in the asymmetric unit and the other half is generated by symmetry. The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 1. Selected bond lengths and angles are listed in Table 1.

The piperazine ring exhibits a chair conformation, with bond lengths and angles in the standard ranges and a mean N—C bond length of 1.48 (2) Å. The angles around the N atom sum to almost 360° and the N1—C2 bond length is 1.3603 (19) Å, in accordance with Nsp^2—Csp^2 amide character [1.355 (14) Å; Allen *et al.*, 1987]. The oxalyl C2—C3 bond length is exactly 1.541 (2) Å, the value usually assumed for a Csp^3—Csp^3 single bond (Dewar & Schmeizing, 1968). Therefore, the ethyl oxamate moiety, –N–C(O)–C(O)–OEt, can be considered as composed of two singly bonded functionalities, an amide [–N1–C2(O2)] and an ester [–C3(O3)–O4–Et]. The ethyl oxamate group in (I) is not planar. The two carbonyl groups are almost perpendicular, with an O2—C2—C3—O3 torsion angle of −111.34 (17)°.



(I)

The steric hindrance between the amide carbonyl group and the ethoxy O atom is released by the adoption of the conformation exhibited by compound (I), in which the O2···O4 contact distance of 2.893 (2) Å is longer than the equivalent distance of 2.640 (2) Å observed in the antiperiplanar conformation (Padilla-Martínez *et al.*, 2003), but is nevertheless shorter than the sum of the van der Waals radii (3.04 Å; Bondi, 1964).

It is worth noting that the almost perpendicular conformation between the two carbonyl groups in (I) seems to be preferred in oxamates derived from secondary amines (Venkatramani *et al.*, 1994), in contrast with the antiperiplanar arrangement usually found in those derived from primary

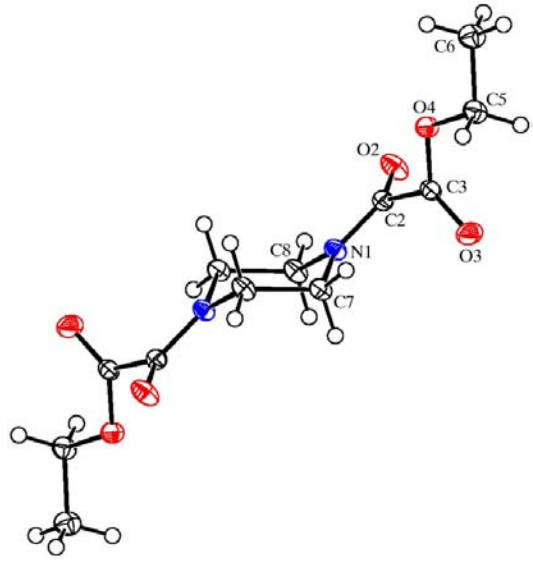


Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The molecule is located on an inversion centre.

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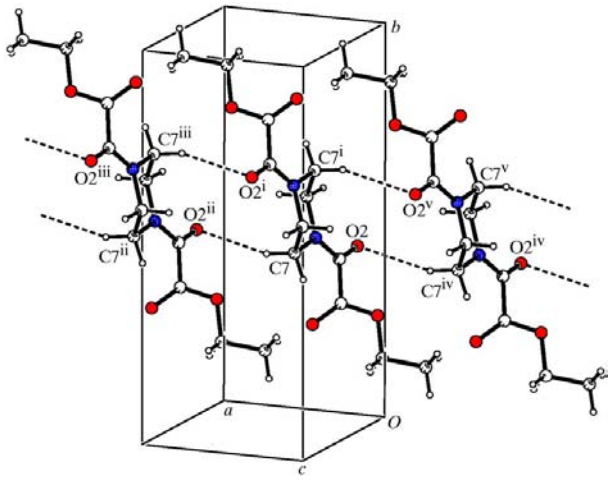

Figure 2
The supramolecular arrangement of (I), showing the tapes formed by the $R_2^2(12)$ motif along the *a* direction [symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1+x, y, z$; (iii) $2-x, 1-y, -z$; (iv) $x-1, y, z$; (v) $-x, 1-y, -z$].

amines, probably due to its stabilization by strong intramolecular hydrogen-bonding interactions (Padilla-Martínez *et al.*, 2001; García-Báez *et al.*, 2003).

An soft intramolecular C—H···O hydrogen-bonding interaction (Desiraju, 1996) exists between C8—H8*B* and the amidic carbonyl O2 atom [C8···O2 = 2.842 (2) Å and C8—H8*B*···O2 = 106°], forming an *S*(5) ring motif, according to graph-set notation (Bernstein *et al.*, 1995). The hydrogen-bonding geometry is listed in Table 2. Infinite supramolecular tapes, which propagate along the *b* direction (Fig. 2), are formed through a second soft hydrogen-bonding interaction along C7—H7*B*···O2^{ii} [C7···O2 = 3.425 (2) Å and C7—H7*B*···O2 = 156°; symmetry code: (ii) $1+x, y, z$], which forms a 12-membered ring described by the graph-set descriptor $R_2^2(12)$. The rotation energy barrier around the oxalyl C2—C3 bond should be low enough that these two hydrogen bonds fix the molecule of (I) in a symmetrical conformation in the solid state. On the other hand, the four C atoms of the piperazine ring are observed as four different signals, at 45.5, 44.7, 40.7 and 40.0 p.p.m. in the ^{13}C NMR spectrum, revealing the predominance of a non-symmetrical conformation in solution.

Experimental

The title compound was prepared from a solution of piperazine (0.5 g, 5.8 mmol) and ethyl chlorooxoacetate (1.3 ml, 11.6 mmol) in tetrahydrofuran in the presence of triethylamine (1.6 ml, 11.6 mmol). After filtering, evaporation of the solvent, several washings with distilled water and drying, compound (I) was obtained as a colourless solid (1.33 g, 80% yield; m.p. 393–394 K). IR spectroscopy (neat solid, ν, cm^{-1}): 3286 (NH), 1780 (CO); ^{1}H NMR (300.08 MHz, DMSO-d_6, p.p.m.): 4.29, 4.28 (*q*, 2H each, $2CH_2$), 3.55, 3.42 (*m*, 4H each, $4NCH_2$), 1.26 (*t*, 6H, $2CH_3$); ^{13}C NMR (75.46 MHz, DMSO-d_6, p.p.m.): 162.4, 159.8 (4CO), 62.0 ($2CH_2$), 45.5, 44.7, 40.7, 40.0 ($4NCH_2$), 13.8 ($2CH_3$). Crystals of (I) suitable for X-ray analysis were obtained after slow crystallization from a solution in ethanol.

Crystal data

$C_{12}H_{18}N_2O_6$
M_r = 286.28
Monoclinic, $P2_1/c$
a = 6.2258 (15) Å
b = 13.660 (3) Å
c = 8.656 (2) Å
β = 99.807 (4)°
V = 725.4 (3) Å^3
Z = 2
D_x = 1.311 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 600 reflections
θ = 20–25°
μ = 0.11 mm^{-1}
T = 293 (2) K
Block, colourless
0.42 × 0.36 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
7773 measured reflections
1581 independent reflections
1473 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.2°
$h = -7 \rightarrow 7$
$k = -17 \rightarrow 17$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.118
S = 1.11
1581 reflections
91 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.4689P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—C2	1.2474 (18)	N1—C7	1.490 (2)
O3—C3	1.211 (2)	N1—C8	1.471 (2)
O4—C3	1.3350 (18)	C2—C3	1.541 (2)
O4—C5	1.4756 (19)	C5—C6	1.514 (3)
N1—C2	1.3603 (19)	C7—C8^{i}	1.556 (2)
C2—N1—C7	126.33 (12)	O3—C3—C2	122.26 (13)
C2—N1—C8	119.86 (13)	O4—C3—C2	111.72 (12)
C7—N1—C8	113.70 (13)	O4—C5—C6	107.34 (13)
O2—C2—N1	126.11 (14)	N1—C7—C8^{i}	111.39 (13)
O2—C2—C3	117.49 (12)	N1—C8—C7^{i}	110.12 (13)
N1—C2—C3	116.18 (12)		
C7—N1—C2—O2	−178.94 (15)	N1—C2—C3—O3	63.5 (2)
O2—C2—C3—O3	−111.34 (17)		

Symmetry code: (i) $1-x, 1-y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7*B*···O2^{i}	0.97	2.52	3.425 (2)	156
C8—H8*B*···O2	0.97	2.42	2.842 (2)	106

Symmetry code: (ii) $1+x, y, z$.

All H atoms were refined as riding on their parent atoms, with C—H distances in the range 0.96–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; 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*2003 (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1752). Services for accessing these data are described at the back of the journal.

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