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(Cyclohexylideneamino)oxyacetic acid and [chloro(phenyl)methyleneamino]oxyacetic acid: hydrogen-bonded $R_2^2(8)$ dimers and aromatic π–π stacking interactions

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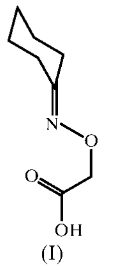
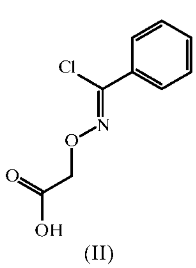
Molecules of (cyclohexylideneamino)oxyacetic acid, $C_8H_{13}NO_3$, (I), are linked into centrosymmetric dimers by pairs of O—H···O hydrogen bonds [H···O = 1.84 Å, O···O = 2.6782 (12) Å and O—H···O = 178°]. In [chloro(phenyl)methyleneamino]oxyacetic acid, $C_9H_8ClNO_3$, (II), the molecules are similarly linked into centrosymmetric dimers by pairs of O—H···O hydrogen bonds [H···O = 1.79 Å, O···O = 2.6329 (17) Å and O—H···O = 176°], and these dimers are weakly linked into chains by a single type of aromatic π–π stacking interaction.

Comment

Persulfate oxidation of iminooxyacetic acids, $R(R')C{=}NOCH_2COOH$, provides a useful route to iminyl radicals (Forrester *et al.*, 1979). The subsequent reactions of the iminyl radicals thus generated depend greatly on the substituents, and important species including nitrogen-containing heterocycles can result. We report here the molecular and supramolecular structures of two representative examples of such precursors, *viz.* (cyclohexylideneamino)oxyacetic acid, (I), and [chloro(phenyl)methyleneamino]oxyacetic acid, (II).



(I)



(II)

In both (I) and (II) (Figs. 1 and 2), the C—O distances in the carboxy groups (Tables 1 and 3) are consistent with the fully ordered locations of the carboxy H atoms as deduced from difference maps. In the side chains of (I) and (II), the corresponding distances show very similar values, apart from the O3—N4 distances, which are significantly different; for comparison, the mean value for the —O—N= bond in oximes is 1.416 Å (Allen *et al.*, 1987). The other distances are typical for bonds of their types.

The conformations of the side chains both exhibit near-planar fragments, *viz.* O1—C1—C2—O3 and C2—O3—N4—C*n* [$n = 11$ in (I) and $n = 5$ in (II); see Figs. 1 and 2], but while the intervening C1—C2—O3—N4 torsion angles have similar magnitudes in (I) and (II), they have opposite signs, and it is this difference that determines the different overall conformations of these two molecules. For the cyclohexylidene ring in (I), the ring-puckering parameters (Cremer & Pople, 1975) corresponding to the atom sequence C11–C16 [$\varphi = 174.0\ (2)^\circ$ and $\theta = 12\ (2)^\circ$] indicate a conformation close to the chair form (Evans & Boeyens, 1989), despite the planarity at atom C11.

In the structures of both (I) and (II), the molecules are linked into centrosymmetric $R_2^2(8)$ (Bernstein *et al.*, 1995) dimers (Figs. 3 and 4) by paired O—H···O hydrogen bonds, which are fairly short and effectively linear (Tables 2 and 4). In

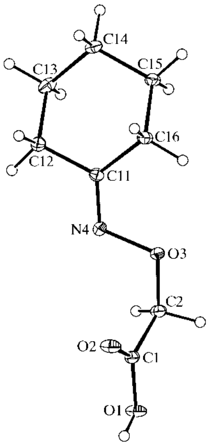


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

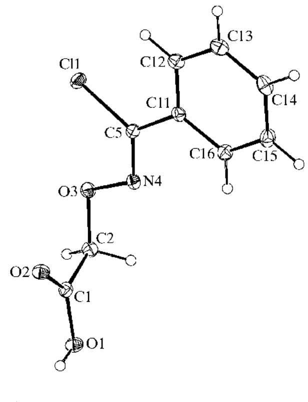


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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each structure, the reference molecule has been selected so that the hydrogen-bonded dimer in which this molecule participates is centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). In the structure of (I), there are no further direction-specific interactions between the molecules, but in (II), the $R_2^2(8)$ dimers are weakly linked into chains by a single aromatic π–π stacking interaction. The aryl rings in the molecules at (x, y, z) and ($2 - x, 1 - y, 2 - z$) are parallel, with an interplanar spacing of 3.422 (2) Å; the ring-centroid separation is 3.856 (2) Å, corresponding to a centroid offset of 1.777 (2) Å. The molecules at (x, y, z) and ($2 - x$, $1 - y$, $2 - z$) are components of hydrogen-bonded dimers centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and ($1, \frac{1}{2}, 1$), respectively, and propagation by inversion of the two intermolecular interactions generates a chain running parallel to the [101] direction (Fig. 5).

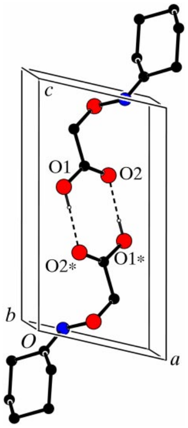

Figure 3
Part of the crystal structure of (I), showing the formation of an $R_2^2(8)$ dimer centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($1 - x, 1 - y, 1 - z$).

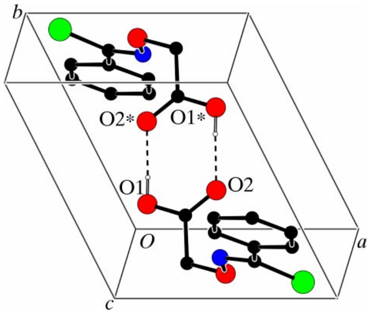

Figure 4
Part of the crystal structure of (II), showing the formation of an $R_2^2(8)$ dimer centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($1 - x, 1 - y, 1 - z$).

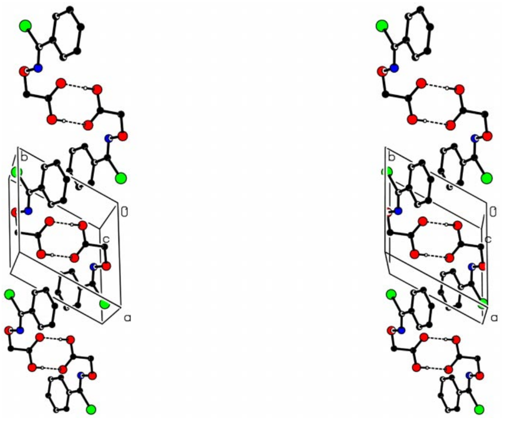

Figure 5
A stereoview of part of the crystal structure of (II), showing the formation of a π-stacked [101] chain of hydrogen-bonded dimers. For clarity, H atoms bonded to C atoms have been omitted.

In neither (I) nor (II) do atoms O3 and N4 act as acceptors of C—H$\cdots$$X$ (X = O or N) hydrogen bonds; there are no intermolecular H$\cdots$$X$ contact distances involving O3 or N4 that are less than 2.60 Å in (I), and none of less than 2.70 Å in (II).

Experimental

Benzhydroxamoyl chloride, Cl(Ph)C=NOH, was prepared from H(Ph)C=NOH according to the method of Baruah *et al.* (1988). Compounds (I) and (II) were prepared by reaction of chloroacetic acid with either cyclohexanone oxime [for (I)] or Cl(Ph)C=NOH [for (II)], using the following modification of the procedure of Forrester *et al.* (1979). A solution of the oxime (0.10 mol), chloroacetic acid (0.20 mol) and sodium hydroxide (0.40 mol) in a mixture of water (100 ml) and ethanol (50 ml) was heated under reflux overnight. The cooled solution was poured on to ice and acidified with dilute hydrochloric acid. The precipitate was collected, washed with water and dissolved in $NaHCO_3$ solution (100 ml of 1 mol dm^{-3}). This solution was extracted with diethyl ether and acidified with dilute hydrochloric acid. The resulting solid was collected, washed with water and recrystallized from ethanol, yielding crystals suitable for single-crystal X-ray diffraction; m.p: (I) 365–367 K, (II) 381–383 K.

Compound (I)

Crystal data

$C_8H_{13}NO_3$
$M_r = 171.19$
Triclinic, $P\overline{1}$
$a = 5.0776$ (1) Å
$b = 8.6533$ (3) Å
$c = 10.7804$ (3) Å
$\alpha = 111.2609$ (15)°
$\beta = 102.437$ (2)°
$\gamma = 93.597$ (2)°
$V = 425.88$ (2) Å^3

$Z = 2$
$D_x = 1.335$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1945 reflections
$\theta = 3.9$–27.5°
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.40 × 0.30 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.917$, $T_{\max} = 0.968$
9176 measured reflections
1945 independent reflections

1621 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 27.5°$
$h = -5 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.098$
$S = 1.04$
1945 reflections
110 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1199P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—O1	1.3186 (14)	O3—N4	1.4331 (12)
C1—O2	1.2134 (14)	N4—C11	1.2775 (15)
O1—C1—O2	124.23 (11)	C2—O3—N4	107.87 (8)
O1—C1—C2	111.52 (10)	O3—N4—C11	111.71 (9)
O2—C1—C2	124.24 (10)		
O1—C1—C2—O3	−177.14 (9)	C2—O3—N4—C11	−175.25 (9)
O2—C1—C2—O3	1.83 (17)	O3—N4—C11—C12	179.11 (9)
C1—C2—O3—N4	−83.62 (11)	O3—N4—C11—C16	1.24 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.84	1.84	2.6782 (12)	178

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

Table 3
Selected geometric parameters (Å, °) for (II).

C5—Cl1	1.738 (2)	O3—N4	1.405 (2)
C1—O1	1.311 (2)	N4—C5	1.273 (2)
C1—O2	1.226 (2)		
O1—C1—O2	124.64 (16)	C2—O3—N4	107.45 (13)
O1—C1—C2	112.36 (14)	O3—N4—C5	113.12 (14)
O2—C1—C2	123.00 (16)		
O1—C1—C2—O3	−171.61 (14)	C2—O3—N4—C5	−173.61 (14)
C1—C2—O3—N4	75.87 (17)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.84	1.79	2.6329 (17)	176

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

Compound (II)

Crystal data

$C_9H_8ClNO_3$
$M_r = 213.61$
Triclinic, $P\bar{1}$
$a = 6.7961$ (1) Å
$b = 7.3857$ (2) Å
$c = 10.8173$ (3) Å
$\alpha = 98.4852$ (9)°
$\beta = 93.4156$ (10)°
$\gamma = 117.0191$ (12)°
$V = 473.44$ (2) Å^3
$Z = 2$
$D_x = 1.498$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2133 reflections
$\theta = 3.2$–27.4°
$\mu = 0.38$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
0.28 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.922$, $T_{\max} = 0.981$
3988 measured reflections
2133 independent reflections
1980 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 27.4°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.141$
$S = 1.20$
2132 reflections
128 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0766P)^2 + 0.1738P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

Crystals of (I) and (II) are triclinic; space group $P\bar{1}$ was selected for each and confirmed in both cases by the subsequent analyses. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH_2), and O—H distances of 0.84 Å.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1209). Services for accessing these data are described at the back of the journal.

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