

N-(2,4,5-Trichlorophenyl)maleamic acid

B. Thimme Gowda,^{a*} Miroslav Tokarčík,^b Jozef Kožíšek,^b
K. Shakuntala^a and Hartmut Fuess^c

^aDepartment of Chemistry, Mangalore University, Mangalagangothri 574 199, Mangalore, India, ^bFaculty of Chemical and Food Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovak Republic, and ^cInstitute of Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany

Correspondence e-mail: gowdabt@yahoo.com

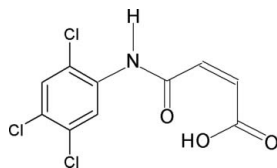
Received 26 November 2009; accepted 7 December 2009

Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.028; wR factor = 0.079; data-to-parameter ratio = 14.0.

The title compound, $\text{C}_{10}\text{H}_6\text{Cl}_3\text{NO}_3$, crystallizes with two independent molecules in the asymmetric unit. The molecular structure is stabilized by a short intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond within the maleamic unit. In the crystal, each molecule self-associates *via* $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds into chains, each running along the b axis. Two short intermolecular $\text{Cl}\cdots\text{O}$ contacts [3.1267 (15) and 3.0523 (12) Å] and $\text{C}-\text{H}\cdots\text{O}$ interactions interconnect these chains into a three-dimensional network.

Related literature

For studies on the effect of ring- and side-chain substitutions on the crystal structures of amides, see: Gowda *et al.* (2009, 2010); Lo & Ng (2009); Prasad *et al.* (2002); Shakuntala *et al.* (2009). For the concept of orthogonality of halogen and hydrogen bonds, see: Voth *et al.* (2009). For a review on short halogen–oxygen contacts, see: Fourmigué (2009); Kubicki (2004).



Experimental

Crystal data

$\text{C}_{10}\text{H}_6\text{Cl}_3\text{NO}_3$

$M_r = 294.51$

Monoclinic, $P2_1/c$

$a = 10.8979$ (2) Å

$b = 11.0225$ (2) Å

$c = 19.4739$ (3) Å

$\beta = 95.4761$ (9)°

$V = 2328.57$ (7) Å³

$Z = 8$

Mo $K\alpha$ radiation

$\mu = 0.78$ mm⁻¹

$T = 295$ K

$0.34 \times 0.25 \times 0.22$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby Gemini detector
Absorption correction: analytical (*CrysAlis PRO*; Oxford

Diffraction, 2009)
 $T_{\min} = 0.794$, $T_{\max} = 0.852$
49446 measured reflections
4424 independent reflections
3825 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.079$

$S = 1.06$

4424 reflections

315 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.28$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}2-\text{H}2A\cdots\text{O}1$	0.82	1.69	2.5080 (15)	175
$\text{O}5-\text{H}5A\cdots\text{O}4$	0.82	1.72	2.5332 (17)	175
$\text{N}1-\text{H}1N\cdots\text{O}3^i$	0.77 (2)	2.30 (2)	3.0356 (18)	161.2 (19)
$\text{N}2-\text{H}2N\cdots\text{O}6^{ii}$	0.81 (2)	2.481 (19)	3.0775 (19)	131.3 (16)
$\text{N}1-\text{H}1N\cdots\text{Cl}1$	0.77 (2)	2.56 (2)	2.9628 (14)	114.2 (17)
$\text{N}2-\text{H}2N\cdots\text{Cl}4$	0.81 (2)	2.519 (18)	2.9476 (14)	114.3 (15)
$\text{C}2-\text{H}2\cdots\text{O}3^i$	0.93	2.29	3.123 (2)	149
$\text{C}12-\text{H}12\cdots\text{O}2$	0.93	2.47	3.330 (2)	154

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 2

Halogen-bond geometry (Å, °).

$\text{C}-\text{Cl}\cdots\text{O}$	$\text{Cl}\cdots\text{O}$	$\text{C}-\text{Cl}\cdots\text{O}$
$\text{C}9-\text{Cl}3\cdots\text{O}6^{iii}$	3.1267 (15)	158.99 (6)
$\text{C}16-\text{Cl}4\cdots\text{O}1$	3.0523 (12)	159.62 (7)

Symmetry code: (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2009) and *WinGX* (Farrugia, 1999).

MT and JK thank the Grant Agency of the Slovak Republic (VEGA 1/0817/08) and Structural Funds, Interreg IIIA, for financial support in purchasing the diffractometer. KS thanks the University Grants Commission, Government of India, New Delhi, for the award of a research fellowship under its faculty improvement programme

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2591).

References

- Brandenburg, K. (2002). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fourmigué, M. (2009). *Curr. Opin. Solid State Mater. Sci.* **13**, 36–45.
- Gowda, B. T., Tokarčík, M., Kožíšek, J., Shakunthala, K. & Fuess, H. (2009). *Acta Cryst.* **E65**, o2945.
- Gowda, B. T., Tokarčík, M., Kožíšek, J., Shakunthala, K. & Fuess, H. (2010). *Acta Cryst.* **E66**, o51.
- Kubicki, M. (2004). *J. Mol. Struct.* **698**, 67–73.
- Lo, K. M. & Ng, S. W. (2009). *Acta Cryst.* **E65**, o1101.
- Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
- Prasad, S. M., Sinha, R. B. P., Mandal, D. K. & Rani, A. (2002). *Acta Cryst.* **E58**, o1296–o1297.
- Shakuntala, K., Gowda, B. T., Tokarčík, M. & Kožíšek, J. (2009). *Acta Cryst.* **E65**, o3119.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Voth, A. R., Khuu, P., Oishi, K. & Ho, P. S. (2009). *Nat. Chem.* **1**, 74–79.

supplementary materials

Acta Cryst. (2010). E66, o182-o183 [doi:10.1107/S1600536809052520]

N-(2,4,5-Trichlorophenyl)maleamic acid

B. T. Gowda, M. Tokarcík, J. Kozísek, K. Shakuntala and H. Fues

Comment

In the present work, as a part of studying the effect of ring- and side-chain substitutions on the crystal structures of biologically significant amides (Gowda *et al.*, 2009, 2010; Shakuntala *et al.*, 2009; Prasad *et al.*, 2002), the crystal structure of *N*-(2,4,5-trichlorophenyl)-maleamic acid (I) has been determined. The asymmetric unit of (I) contains two independent molecules (Fig. 1).

The conformations of the N—H and C=O bonds in the amide segment of the structure are *anti* to each other, and the amide-O atom and the carbonyl-O atom of the acid segment are also *anti* to each other. Further, the amide-O atom is *anti* to the H atom attached to the adjacent C atom, while the carbonyl-O atom is *syn* to the H atom attached to its adjacent C atom (Fig.1). In the structure, a rare *anti* conformation of the C=O and O—H bonds of the acid group has been observed, similar to that observed in *N*-phenylmaleamic acid (Lo & Ng, 2009), *N*-(2,5-dichlorophenyl)maleamic acid (Shakuntala *et al.*, 2009), *N*-(3,5-dichlorophenyl)maleamic acid (Gowda *et al.*, 2010) and *N*-(2,4,6-dimethylphenyl)maleamic acid (Gowda *et al.*, 2009). Further, the conformation of the N—H bond is *syn* to the 2-Cl in the phenyl ring, while it is *anti* to the 5-Cl in the ring. Each maleamic unit includes a short intramolecular hydrogen O—H \cdots O bond (Table 1). The bond lengths of C2—C3 and C12—C13 (i.e. 1.329 (2) and 1.328 (2) Å) clearly indicate double bond character.

In both the molecules, the dihedral angle between the amido group —NHCO— and the tri-substituted phenyl ring is 6.1 (3)°. The two N—H \cdots O hydrogen bonds have quite different geometry, as seen in the N—H \cdots O angles (Table 1). Remarkably small N2—H2N \cdots O6ⁱⁱ angle of 131.3 (16)° can be attributed to the competing effect of the neighbouring C9—Cl3 \cdots O6ⁱⁱⁱ halogen bond. The angle Cl3 \cdots O6ⁱⁱⁱ \cdots H2N = 78.24 (6)° is close to 90° and can be interpreted within the concept of orthogonality of halogen and hydrogen bonds (Voth *et al.*, 2009). The N1—H1N \cdots O3ⁱ hydrogen bond with the angle of 161.2 (19)° is much less influenced by the near C6—Cl1 \cdots O3ⁱ halogen bond, which is weaker as indicated by the Cl1 \cdots O3ⁱ contact of 3.2372 (13) Å. [Symmetry codes: (i) $-x + 1, y + 1/2, -z + 3/2$; (ii) $-x, y + 1/2, -z + 3/2$; (iii) $x, -y + 1/2, z - 1/2$.]

In the crystal of (I), the intermolecular N—H \cdots O hydrogen bonds link the molecules, which self-associate, into infinite chains running along the *b* axis. These chains are connected through relatively short Cl \cdots O contacts: Cl4 \cdots O1 = 3.0523 (12), Cl3 \cdots O6(iii) = 3.1267 (15) Å. [Symmetry codes: (iii) $x, -y + 1/2, z - 1/2$].(iii) $x, -y + 1/2, z - 1/2$] as well as C—H \cdots O contacts to consolidate the crystal packing. Fig. 2 outlines part of the crystal structure of (I) with the N—H \cdots O hydrogen bonding and Cl \cdots O contacts highlighted. The data for the C—Cl \cdots O halogen bonds are in agreement with others (Kubicki, 2004; Fourmigué, 2009).

Experimental

The solution of maleic anhydride (0.025 mol) in toluene (25 ml) was treated drop-wise with the solution of 2,4,5-trichloroaniline (0.025 mol) also in toluene (20 ml) with constant stirring. The resulting mixture was warmed with stirring for over 30 min and set aside for an additional 30 min at room temperature for completion of the reaction. The mixture

supplementary materials

was then treated with dilute hydrochloric acid to remove the unreacted 2,4,5-trichloroaniline. The resultant solid *N*-(2,4,5-trichlorophenyl)maleamic acid was filtered under suction and washed thoroughly with water to remove the unreacted maleic anhydride and maleic acid. It was recrystallized to constant melting point from ethanol. The purity of the compound was checked by elemental analysis and characterized by its infrared spectra. Colourless single crystals used in X-ray diffraction studies were grown in an ethanol solution by slow evaporation at room temperature.

Refinement

H atoms were visible in difference maps. In the final cycles of refinement, the amido-H atoms were refined freely, while the C,*O*-bound H atoms were placed in calculated positions and refined using the riding model with C–H = 0.93 Å and O–H = 0.82 Å. The $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C},\text{O})$.

Figures

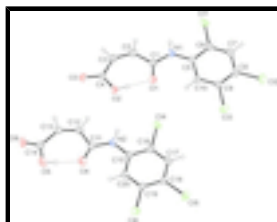


Fig. 1. Molecular structure of the two independent molecules comprising the asymmetric unit in (I) showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

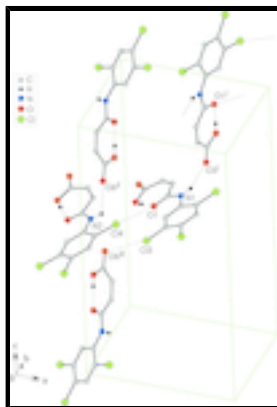


Fig. 2. Part of crystal structure of (I) showing the main intermolecular interactions: N–H \cdots O hydrogen bonds and short Cl \cdots O contacts (all represented by dashed lines). Symmetry codes: (i) $-x + 1, y + 1/2, -z + 3/2$; (ii) $-x, y + 1/2, -z + 3/2$; (iii) $x, -y + 1/2, z - 1/2$.

N-(2,4,5-Trichlorophenyl)maleamic acid

Crystal data

$\text{C}_{10}\text{H}_6\text{Cl}_3\text{NO}_3$

$M_r = 294.51$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 10.8979\ (2)\ \text{\AA}$

$b = 11.0225\ (2)\ \text{\AA}$

$c = 19.4739\ (3)\ \text{\AA}$

$\beta = 95.4761\ (9)^\circ$

$F(000) = 1184$

$D_x = 1.68\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 30027 reflections

$\theta = 1.8\text{--}29.5^\circ$

$\mu = 0.78\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Block, colourless

$V = 2328.57 (7) \text{ \AA}^3$
 $Z = 8$ $0.34 \times 0.25 \times 0.22 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby Gemini detector graphite	4424 independent reflections 3825 reflections with $I > 2\sigma(I)$
Detector resolution: $10.434 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.022$
ω scans	$\theta_{\text{max}} = 25.7^\circ$, $\theta_{\text{min}} = 1.9^\circ$
Absorption correction: analytical (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.794$, $T_{\text{max}} = 0.852$	$k = -13 \rightarrow 13$
49446 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.079$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.5233P]$
4424 reflections	where $P = (F_o^2 + 2F_c^2)/3$
315 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.44390 (14)	0.49367 (14)	0.63260 (8)	0.0359 (3)
C2	0.49027 (16)	0.44723 (15)	0.70185 (8)	0.0435 (4)
H2	0.5531	0.4921	0.7254	0.052*

supplementary materials

C3	0.45354 (16)	0.34984 (16)	0.73449 (8)	0.0437 (4)
H3	0.4945	0.3395	0.7782	0.052*
C4	0.36034 (14)	0.25383 (14)	0.71553 (8)	0.0353 (3)
C5	0.47664 (14)	0.65859 (13)	0.55063 (8)	0.0338 (3)
C6	0.55197 (15)	0.75667 (14)	0.53696 (8)	0.0390 (4)
C7	0.52840 (17)	0.82580 (15)	0.47808 (9)	0.0447 (4)
H7	0.5787	0.8917	0.4705	0.054*
C8	0.43056 (16)	0.79770 (15)	0.43042 (8)	0.0418 (4)
C9	0.35753 (15)	0.69853 (15)	0.44191 (8)	0.0385 (4)
C10	0.37961 (15)	0.63019 (14)	0.50161 (8)	0.0374 (3)
H10	0.3289	0.5645	0.5090	0.045*
N1	0.50133 (13)	0.59440 (12)	0.61283 (7)	0.0364 (3)
H1N	0.5504 (19)	0.6210 (18)	0.6398 (10)	0.047 (6)*
O1	0.36099 (12)	0.44379 (11)	0.59559 (6)	0.0524 (3)
O2	0.29633 (10)	0.25568 (10)	0.65501 (6)	0.0440 (3)
H2A	0.3156	0.3154	0.6334	0.053*
O3	0.34614 (11)	0.17281 (10)	0.75610 (6)	0.0439 (3)
Cl1	0.67690 (5)	0.79432 (5)	0.59434 (2)	0.06029 (15)
Cl2	0.40225 (5)	0.88690 (4)	0.35759 (3)	0.06031 (15)
Cl3	0.23559 (4)	0.65766 (5)	0.38355 (2)	0.05600 (14)
C11	-0.01578 (14)	0.08037 (14)	0.62405 (8)	0.0356 (3)
C12	0.05760 (15)	0.08711 (15)	0.69170 (8)	0.0405 (4)
H12	0.1200	0.1450	0.6953	0.049*
C13	0.04666 (15)	0.02176 (16)	0.74809 (8)	0.0429 (4)
H13	0.1058	0.0398	0.7843	0.051*
C14	-0.04107 (16)	-0.07430 (17)	0.76485 (9)	0.0468 (4)
C15	-0.04415 (14)	0.19115 (14)	0.51309 (7)	0.0348 (3)
C16	-0.00319 (16)	0.29029 (15)	0.47665 (8)	0.0393 (4)
C17	-0.05759 (17)	0.32085 (16)	0.41215 (8)	0.0450 (4)
H17	-0.0298	0.3880	0.3892	0.054*
C18	-0.15340 (16)	0.25164 (15)	0.38159 (8)	0.0410 (4)
C19	-0.19375 (15)	0.15206 (15)	0.41656 (8)	0.0374 (3)
C20	-0.14062 (15)	0.12225 (14)	0.48168 (8)	0.0380 (4)
H20	-0.1696	0.0557	0.5046	0.046*
N2	0.01228 (14)	0.16733 (13)	0.57959 (7)	0.0393 (3)
H2N	0.0613 (18)	0.2172 (17)	0.5962 (9)	0.044 (5)*
O4	-0.09307 (13)	0.00116 (12)	0.60847 (6)	0.0572 (4)
O5	-0.12126 (16)	-0.11735 (15)	0.71730 (7)	0.0818 (5)
H5A	-0.1146	-0.0818	0.6808	0.098*
O6	-0.03687 (14)	-0.11161 (13)	0.82354 (7)	0.0629 (4)
Cl4	0.11807 (5)	0.37788 (4)	0.51289 (2)	0.05662 (14)
Cl5	-0.22020 (5)	0.29035 (5)	0.30038 (2)	0.06325 (15)
Cl6	-0.31341 (4)	0.06298 (4)	0.38018 (2)	0.05475 (14)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0387 (8)	0.0346 (8)	0.0336 (8)	-0.0062 (6)	-0.0006 (6)	-0.0020 (6)

C2	0.0481 (10)	0.0433 (9)	0.0364 (8)	-0.0128 (7)	-0.0103 (7)	-0.0004 (7)
C3	0.0486 (10)	0.0459 (9)	0.0335 (8)	-0.0075 (8)	-0.0123 (7)	0.0040 (7)
C4	0.0341 (8)	0.0345 (8)	0.0363 (8)	0.0035 (6)	-0.0014 (6)	0.0018 (7)
C5	0.0366 (8)	0.0325 (8)	0.0326 (7)	-0.0023 (6)	0.0044 (6)	-0.0035 (6)
C6	0.0420 (9)	0.0372 (8)	0.0376 (8)	-0.0096 (7)	0.0035 (7)	-0.0066 (7)
C7	0.0546 (10)	0.0372 (9)	0.0435 (9)	-0.0113 (7)	0.0107 (8)	-0.0004 (7)
C8	0.0498 (10)	0.0393 (9)	0.0372 (8)	0.0034 (7)	0.0095 (7)	0.0047 (7)
C9	0.0371 (8)	0.0426 (9)	0.0354 (8)	0.0011 (7)	0.0007 (7)	-0.0016 (7)
C10	0.0367 (8)	0.0378 (8)	0.0373 (8)	-0.0074 (7)	0.0012 (7)	0.0012 (7)
N1	0.0387 (7)	0.0359 (7)	0.0331 (7)	-0.0101 (6)	-0.0049 (6)	-0.0018 (6)
O1	0.0594 (8)	0.0510 (7)	0.0427 (6)	-0.0255 (6)	-0.0165 (6)	0.0126 (5)
O2	0.0467 (7)	0.0429 (6)	0.0398 (6)	-0.0156 (5)	-0.0099 (5)	0.0095 (5)
O3	0.0487 (7)	0.0372 (6)	0.0441 (6)	-0.0003 (5)	-0.0035 (5)	0.0105 (5)
C11	0.0609 (3)	0.0657 (3)	0.0520 (3)	-0.0323 (2)	-0.0066 (2)	-0.0027 (2)
C12	0.0741 (3)	0.0548 (3)	0.0516 (3)	0.0010 (2)	0.0036 (2)	0.0191 (2)
C13	0.0502 (3)	0.0696 (3)	0.0451 (2)	-0.0060 (2)	-0.01197 (19)	0.0054 (2)
C11	0.0355 (8)	0.0389 (8)	0.0320 (8)	-0.0030 (7)	0.0002 (6)	0.0020 (6)
C12	0.0358 (8)	0.0466 (9)	0.0377 (8)	-0.0102 (7)	-0.0041 (7)	0.0043 (7)
C13	0.0402 (9)	0.0516 (10)	0.0347 (8)	-0.0073 (7)	-0.0081 (7)	0.0046 (7)
C14	0.0491 (10)	0.0495 (10)	0.0403 (9)	-0.0074 (8)	-0.0043 (8)	0.0098 (8)
C15	0.0392 (8)	0.0366 (8)	0.0278 (7)	-0.0015 (6)	-0.0002 (6)	-0.0009 (6)
C16	0.0424 (9)	0.0405 (9)	0.0341 (8)	-0.0096 (7)	-0.0008 (7)	-0.0007 (7)
C17	0.0541 (10)	0.0454 (9)	0.0346 (8)	-0.0102 (8)	-0.0006 (7)	0.0069 (7)
C18	0.0465 (9)	0.0473 (9)	0.0282 (7)	-0.0003 (7)	-0.0024 (7)	0.0022 (7)
C19	0.0386 (8)	0.0404 (9)	0.0325 (8)	-0.0033 (7)	-0.0006 (6)	-0.0039 (6)
C20	0.0419 (9)	0.0375 (8)	0.0339 (8)	-0.0056 (7)	0.0006 (7)	0.0010 (6)
N2	0.0435 (8)	0.0411 (8)	0.0316 (7)	-0.0117 (6)	-0.0057 (6)	0.0031 (6)
O4	0.0698 (8)	0.0597 (8)	0.0385 (6)	-0.0307 (7)	-0.0139 (6)	0.0111 (6)
O5	0.0967 (12)	0.0929 (12)	0.0499 (8)	-0.0596 (10)	-0.0235 (8)	0.0280 (8)
O6	0.0715 (9)	0.0722 (9)	0.0433 (7)	-0.0173 (7)	-0.0040 (6)	0.0210 (6)
C14	0.0632 (3)	0.0586 (3)	0.0450 (2)	-0.0288 (2)	-0.0107 (2)	0.0078 (2)
C15	0.0709 (3)	0.0774 (3)	0.0373 (2)	-0.0156 (3)	-0.0160 (2)	0.0162 (2)
C16	0.0557 (3)	0.0606 (3)	0.0443 (2)	-0.0203 (2)	-0.0140 (2)	0.0024 (2)

Geometric parameters (Å, °)

C1—O1	1.2304 (18)	C11—O4	1.2309 (19)
C1—N1	1.349 (2)	C11—N2	1.346 (2)
C1—C2	1.485 (2)	C11—C12	1.476 (2)
C2—C3	1.329 (2)	C12—C13	1.328 (2)
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.489 (2)	C13—C14	1.484 (2)
C3—H3	0.9300	C13—H13	0.9300
C4—O3	1.2121 (18)	C14—O6	1.211 (2)
C4—O2	1.3111 (18)	C14—O5	1.301 (2)
C5—C10	1.391 (2)	C15—C20	1.390 (2)
C5—C6	1.398 (2)	C15—C16	1.399 (2)
C5—N1	1.406 (2)	C15—N2	1.404 (2)
C6—C7	1.380 (2)	C16—C17	1.379 (2)

supplementary materials

C6—C11	1.7274 (16)	C16—C14	1.7315 (16)
C7—C8	1.380 (3)	C17—C18	1.381 (2)
C7—H7	0.9300	C17—H17	0.9300
C8—C9	1.383 (2)	C18—C19	1.385 (2)
C8—C12	1.7292 (16)	C18—C15	1.7301 (16)
C9—C10	1.387 (2)	C19—C20	1.382 (2)
C9—C13	1.7240 (16)	C19—C16	1.7292 (16)
C10—H10	0.9300	C20—H20	0.9300
N1—H1N	0.77 (2)	N2—H2N	0.81 (2)
O2—H2A	0.8200	O5—H5A	0.8200
O1—C1—N1	122.38 (14)	O4—C11—N2	122.58 (14)
O1—C1—C2	123.03 (14)	O4—C11—C12	123.73 (14)
N1—C1—C2	114.58 (13)	N2—C11—C12	113.65 (14)
C3—C2—C1	128.39 (15)	C13—C12—C11	128.82 (15)
C3—C2—H2	115.8	C13—C12—H12	115.6
C1—C2—H2	115.8	C11—C12—H12	115.6
C2—C3—C4	133.25 (15)	C12—C13—C14	132.80 (15)
C2—C3—H3	113.4	C12—C13—H13	113.6
C4—C3—H3	113.4	C14—C13—H13	113.6
O3—C4—O2	120.49 (14)	O6—C14—O5	120.67 (16)
O3—C4—C3	119.25 (14)	O6—C14—C13	118.86 (16)
O2—C4—C3	120.25 (13)	O5—C14—C13	120.47 (15)
C10—C5—C6	117.71 (14)	C20—C15—C16	117.90 (14)
C10—C5—N1	123.25 (14)	C20—C15—N2	123.35 (14)
C6—C5—N1	119.04 (14)	C16—C15—N2	118.74 (14)
C7—C6—C5	121.26 (15)	C17—C16—C15	121.51 (15)
C7—C6—C11	118.52 (13)	C17—C16—C14	118.70 (13)
C5—C6—C11	120.22 (12)	C15—C16—C14	119.79 (12)
C6—C7—C8	120.35 (15)	C16—C17—C18	119.95 (15)
C6—C7—H7	119.8	C16—C17—H17	120.0
C8—C7—H7	119.8	C18—C17—H17	120.0
C7—C8—C9	119.22 (15)	C17—C18—C19	119.22 (14)
C7—C8—C12	119.33 (13)	C17—C18—C15	119.50 (13)
C9—C8—C12	121.46 (13)	C19—C18—C15	121.28 (13)
C8—C9—C10	120.56 (15)	C20—C19—C18	120.96 (15)
C8—C9—C13	121.27 (13)	C20—C19—C16	118.32 (12)
C10—C9—C13	118.16 (13)	C18—C19—C16	120.72 (12)
C9—C10—C5	120.85 (14)	C19—C20—C15	120.44 (15)
C9—C10—H10	119.6	C19—C20—H20	119.8
C5—C10—H10	119.6	C15—C20—H20	119.8
C1—N1—C5	127.17 (14)	C11—N2—C15	128.30 (14)
C1—N1—H1N	115.5 (15)	C11—N2—H2N	114.0 (13)
C5—N1—H1N	117.3 (15)	C15—N2—H2N	117.0 (13)
C4—O2—H2A	109.5	C14—O5—H5A	109.5
O1—C1—C2—C3	0.1 (3)	O4—C11—C12—C13	-7.6 (3)
N1—C1—C2—C3	-178.97 (18)	N2—C11—C12—C13	174.36 (18)
C1—C2—C3—C4	1.6 (3)	C11—C12—C13—C14	-2.5 (3)
C2—C3—C4—O3	179.39 (19)	C12—C13—C14—O6	-173.1 (2)

C2—C3—C4—O2	0.8 (3)	C12—C13—C14—O5	6.7 (3)
C10—C5—C6—C7	2.3 (2)	C20—C15—C16—C17	1.2 (2)
N1—C5—C6—C7	-177.16 (15)	N2—C15—C16—C17	-177.78 (16)
C10—C5—C6—C11	-178.08 (12)	C20—C15—C16—C14	-179.11 (13)
N1—C5—C6—C11	2.4 (2)	N2—C15—C16—C14	1.9 (2)
C5—C6—C7—C8	-1.3 (3)	C15—C16—C17—C18	-1.2 (3)
C11—C6—C7—C8	179.06 (13)	C14—C16—C17—C18	179.12 (14)
C6—C7—C8—C9	-0.9 (3)	C16—C17—C18—C19	0.1 (3)
C6—C7—C8—C12	179.30 (13)	C16—C17—C18—C15	-179.56 (14)
C7—C8—C9—C10	2.0 (2)	C17—C18—C19—C20	0.8 (3)
C12—C8—C9—C10	-178.14 (13)	C15—C18—C19—C20	-179.46 (13)
C7—C8—C9—C13	-178.97 (13)	C17—C18—C19—C16	180.00 (14)
C12—C8—C9—C13	0.9 (2)	C15—C18—C19—C16	-0.3 (2)
C8—C9—C10—C5	-1.0 (2)	C18—C19—C20—C15	-0.8 (3)
C13—C9—C10—C5	179.95 (12)	C16—C19—C20—C15	-179.99 (12)
C6—C5—C10—C9	-1.1 (2)	C16—C15—C20—C19	-0.2 (2)
N1—C5—C10—C9	178.32 (15)	N2—C15—C20—C19	178.71 (15)
O1—C1—N1—C5	1.4 (3)	O4—C11—N2—C15	5.9 (3)
C2—C1—N1—C5	-179.53 (15)	C12—C11—N2—C15	-176.01 (16)
C10—C5—N1—C1	5.1 (3)	C20—C15—N2—C11	-1.6 (3)
C6—C5—N1—C1	-175.47 (15)	C16—C15—N2—C11	177.28 (16)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2A...O1	0.82	1.69	2.5080 (15)	175
O5—H5A...O4	0.82	1.72	2.5332 (17)	175
N1—H1N...O3 ⁱ	0.77 (2)	2.30 (2)	3.0356 (18)	161.2 (19)
N2—H2N...O6 ⁱⁱ	0.81 (2)	2.481 (19)	3.0775 (19)	131.3 (16)
N1—H1N...C11	0.77 (2)	2.56 (2)	2.9628 (14)	114.2 (17)
N2—H2N...C14	0.81 (2)	2.519 (18)	2.9476 (14)	114.3 (15)
C2—H2...O3 ⁱ	0.93	2.29	3.123 (2)	149
C12—H12...O2	0.93	2.47	3.330 (2)	154

Symmetry codes: (i) $-x+1, y+1/2, -z+3/2$; (ii) $-x, y+1/2, -z+3/2$.

Table 2

Table 2. Halogen-bond geometry (Å, °).

C—Cl...O	Cl...O	C—Cl...O
C9—C13...O6 ⁱⁱⁱ	3.1267 (15)	158.99 (6)
C16—C14...O1	3.0523 (12)	159.62 (7)

Symmetry code: (iii) $x, -y+1/2, z-1/2$.

Fig. 1

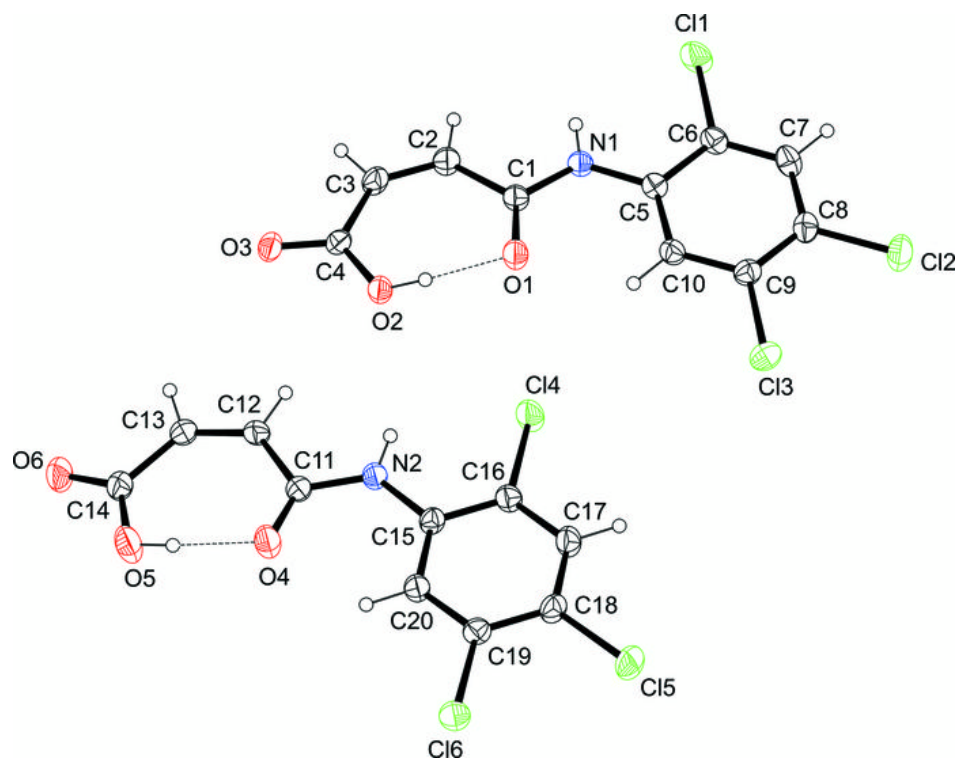


Fig. 2

