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N,*N*′-(1,4-Phenylene)bis(4-chlorobutanamide)

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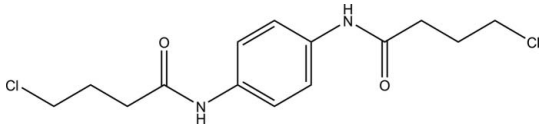
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.092; data-to-parameter ratio = 15.9.

The title molecule, $C_{14}H_{18}Cl_2N_2O_2$, lies on a crystallographic inversion center and the each 4-chlorobutanamide group adopts an *anti*-staggered conformation. In the crystal, adjacent molecules are linked through N—H···O contacts, forming infinite ribbons extending parallel to the *a* axis.

Related literature

For details and syntheses of chloroamides as precursors for new azamacrocycles see: Benaglia *et al.* (2005); Harte & Gunnlaugsson (2006); Humphrey & Chamberlin (1997); Mangalagiu *et al.* (2007); Zbancioc *et al.* (2012).



Experimental

Crystal data

$C_{14}H_{18}Cl_2N_2O_2$
M_r = 317.20
Triclinic, $P\overline{1}$
a = 5.105 (5) Å
b = 6.876 (5) Å
c = 10.549 (5) Å
α = 97.735 (5)°
β = 93.214 (5)°
γ = 90.512 (5)°
V = 366.3 (5) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 200 K
0.25 × 0.2 × 0.2 mm

Data collection

Agilent Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.914, T_{max} = 1.000
2575 measured reflections
1446 independent reflections
1189 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 1.03
1446 reflections
91 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.88	2.10	2.941 (3)	161

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

Data collection: *CrysAlis PRO* (Agilent, 2011); 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); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2130).

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N,*N*′-(1,4-Phenylene)bis(4-chlorobutanamide)

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S1. Comment

With the aim of synthesizing new chloroamides as precursors for new azamacrocycles (Zbancioc *et al.*, 2012), we report the synthesis and crystal structure of the title compound $C_{14}H_{18}Cl_2N_2O_2$, which represents a diamide with aliphatic arms, consisting of two moieties of butyryl chloride and a phenylenediamine unit. Amides are important building blocks in preparative macrocycle chemistry (Harte & Gunnlaugsson, 2006), due to their spectroscopic proprieties as well as to their arms ability to coordinate to metal centers. The X-ray structure of the title compound with the atom numbering scheme is shown in Fig. 1. The molecule is assembled from two centro-symmetrically related units through the C_i at the center of the aromatic ring. The amide group is rotated by 32.4 (2)° in respect with the phenyl ring. The butyryl chloride fragment adopts an anti-staggered conformation. The main crystal structure motif arises from the parallel packing of the ribbon (Fig. 2) along the crystallographic *a* axis. The infinite ribbons are stabilized *via* intermolecular N1—H1···O1^{ii} H-bond with N1—H1 = 0.88 Å, N1···O1^{ii} = 2.941 (3) Å, [symmetry code ii: *x*–1, *y*, *z*], H1···O1^{ii} = 2.10 Å and N1HO1 angle of 161°.

S2. Experimental

p-Phenylenediamine (5 mmol, 0.54 g) was dissolved in sodium hydroxide solution (0.4 N, 50 ml) and 4-chlorobutyryl chloride (30 mmol, 3.4 ml) was added dropwise under stirring at 0° C for 1 h. Afterwards the mixture was stirred at room temperature overnight resulting in a white precipitate, which was separated by filtration, washed several times with water and dried in vacuum; yield 60%. The purity of *N*,*N*′-(1,4-phenylene)bis(4-chlorobutanamide) was confirmed by ^{1}H and ^{13}C NMR spectra.

^{1}H NMR (DMSO-d$_6$) δ (p.p.m.): 9.876 (s, 2NH), 7.492 (s, 4H, Ar), 3.675–3.708 (t, J = 6.8 Hz, 4H, CH_2, adjacent to chlor), 2.433–2.469 (t, J = 7.2 Hz, 4H, CH_2, adjacent to amido), 1.988–2.057 (c, J = 6.8 Hz J = 7.2 Hz, 4H, CH_2).

^{13}C NMR (DMSO-d$_6$) δ (p.p.m.): 169.72 (2 C, C═O), 134.46 (2 C, Ar), 119.37 (4 C, Ar), 44.97 (2 C, CH_2, adjacent to chlor), 33.19 (2 C, CH_2, adjacent to amido), 27.90 (2 C, CH_2).

S3. Refinement

The H atoms were positioned geometrically and refined using a riding model with C—H = 0.95–0.99 Å and with U_{iso}(H) = 1.2 times U_{eq}(C).

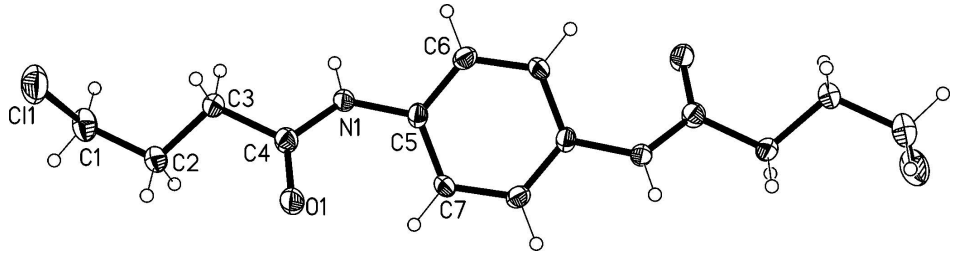

Figure 1

The molecular structure of $C_{14}H_{18}Cl_2N_2O_2$. Displacement ellipsoids are drawn at 50% probability level. H atoms are presented as small spheres of arbitrary radius. Symmetry code: (i) –x, –y+1, –z+1.

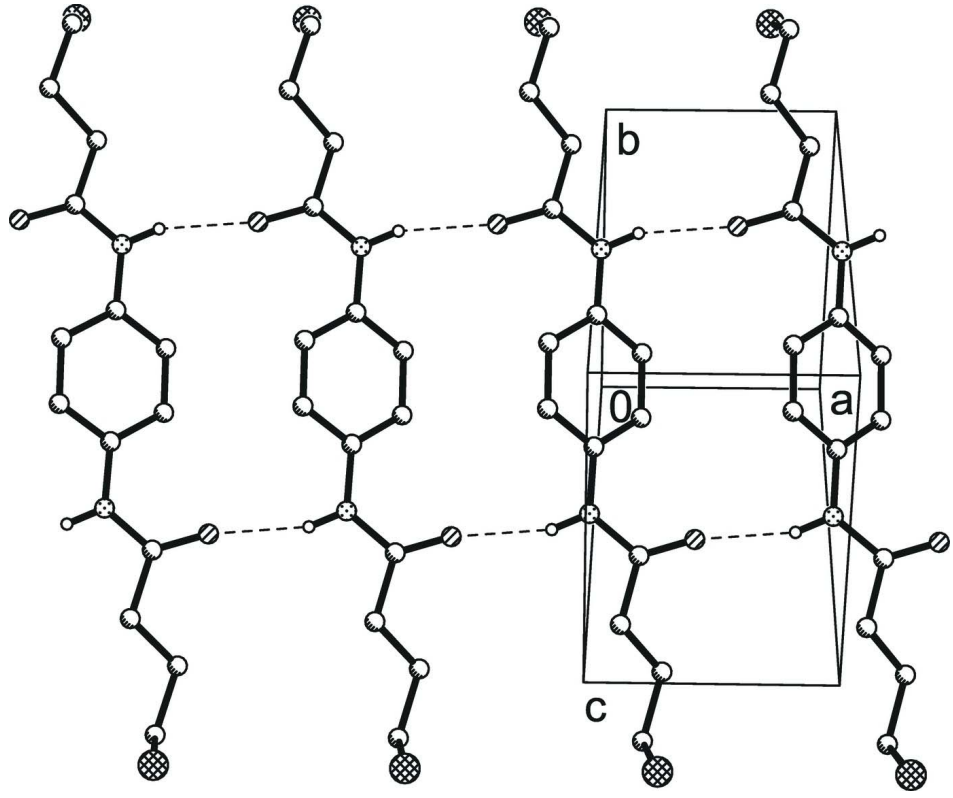

Figure 2

Part of the crystal structure of $C_{14}H_{18}Cl_2N_2O_2$. Molecular chains generated by N—H···O hydrogen bonds are shown by dashed lines. H atoms not involved in intermolecular bonding have been omitted.

N,N′-(1,4-Phenylene)bis(4-chlorobutanamide)

Crystal data

$C_{14}H_{18}Cl_2N_2O_2$
$M_r = 317.20$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.105$ (5) Å
$b = 6.876$ (5) Å
$c = 10.549$ (5) Å
$\alpha = 97.735$ (5)°
$\beta = 93.214$ (5)°
$\gamma = 90.512$ (5)°
$V = 366.3$ (5) Å^3
$Z = 1$
$F(000) = 166$
$D_x = 1.438$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1244 reflections

θ = 3.0–29.4°
μ = 0.45 mm^{-1}
T = 200 K

Prism, clear light yellow
0.25 × 0.2 × 0.2 mm

Data collection

Agilent Xcalibur Eos diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.1593 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.914, T_{max} = 1.000

2575 measured reflections
1446 independent reflections
1189 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 26.0°, θ_{min} = 3.0°
h = −5→6
k = −8→7
l = −12→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 1.03
1446 reflections
91 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.0691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.29972 (11)	−0.27268 (9)	1.02884 (5)	0.0434 (2)
O1	0.4276 (2)	0.1286 (2)	0.67205 (14)	0.0337 (4)
C5	0.0022 (3)	0.3420 (3)	0.57107 (17)	0.0189 (4)
C6	−0.1885 (3)	0.4863 (3)	0.58668 (18)	0.0201 (4)
H6	−0.3186	0.4768	0.6466	0.024*
N1	−0.0077 (3)	0.1862 (2)	0.64528 (14)	0.0207 (4)
H1	−0.1645	0.1441	0.6607	0.025*
C2	0.3081 (3)	−0.2263 (3)	0.77558 (18)	0.0241 (4)
H2A	0.2956	−0.2923	0.6860	0.029*
H2B	0.4926	−0.1826	0.7966	0.029*
C1	0.2360 (4)	−0.3719 (3)	0.86319 (19)	0.0309 (5)
H1A	0.3385	−0.4927	0.8437	0.037*
H1B	0.0476	−0.4077	0.8477	0.037*

C4	0.2010 (3)	0.0948 (3)	0.69526 (18)	0.0206 (4)
C3	0.1331 (3)	−0.0471 (3)	0.78585 (18)	0.0229 (4)
H3A	−0.0520	−0.0909	0.7674	0.027*
H3B	0.1498	0.0214	0.8748	0.027*
C7	0.1922 (3)	0.3575 (3)	0.48302 (17)	0.0199 (4)
H7	0.3238	0.2610	0.4710	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0626 (4)	0.0419 (3)	0.0274 (3)	0.0172 (3)	0.0011 (3)	0.0104 (2)
O1	0.0155 (7)	0.0434 (9)	0.0481 (9)	0.0006 (6)	0.0023 (6)	0.0278 (7)
C5	0.0161 (8)	0.0198 (9)	0.0210 (10)	−0.0022 (7)	−0.0029 (7)	0.0060 (8)
C6	0.0154 (8)	0.0251 (10)	0.0203 (9)	−0.0005 (7)	0.0031 (7)	0.0045 (8)
N1	0.0148 (7)	0.0222 (8)	0.0269 (9)	−0.0006 (6)	0.0014 (6)	0.0102 (7)
C2	0.0237 (9)	0.0244 (10)	0.0254 (10)	0.0034 (8)	0.0017 (8)	0.0073 (8)
C1	0.0379 (11)	0.0248 (11)	0.0307 (12)	0.0049 (8)	−0.0020 (9)	0.0075 (9)
C4	0.0173 (9)	0.0206 (10)	0.0243 (10)	0.0012 (7)	−0.0004 (7)	0.0046 (8)
C3	0.0184 (8)	0.0252 (10)	0.0272 (10)	0.0042 (7)	0.0042 (8)	0.0104 (8)
C7	0.0158 (8)	0.0212 (9)	0.0230 (10)	0.0023 (7)	0.0000 (7)	0.0047 (8)

Geometric parameters (Å, º)

Cl1—C1	1.799 (2)	C2—C3	1.524 (3)
O1—C4	1.222 (2)	C2—H2A	0.9900
C5—C7	1.393 (2)	C2—H2B	0.9900
C5—C6	1.397 (3)	C1—H1A	0.9900
C5—N1	1.412 (2)	C1—H1B	0.9900
C6—C7^{i}	1.381 (3)	C4—C3	1.505 (3)
C6—H6	0.9500	C3—H3A	0.9900
N1—C4	1.359 (2)	C3—H3B	0.9900
N1—H1	0.8800	C7—C6^{i}	1.381 (3)
C2—C1	1.508 (3)	C7—H7	0.9500
C7—C5—C6	118.79 (17)	Cl1—C1—H1A	109.4
C7—C5—N1	123.01 (16)	C2—C1—H1B	109.4
C6—C5—N1	118.20 (16)	Cl1—C1—H1B	109.4
C7^{i}—C6—C5	121.48 (17)	H1A—C1—H1B	108.0
C7^{i}—C6—H6	119.3	O1—C4—N1	122.99 (17)
C5—C6—H6	119.3	O1—C4—C3	122.17 (16)
C4—N1—C5	126.45 (15)	N1—C4—C3	114.81 (15)
C4—N1—H1	116.8	C4—C3—C2	112.75 (15)
C5—N1—H1	116.8	C4—C3—H3A	109.0
C1—C2—C3	113.03 (16)	C2—C3—H3A	109.0
C1—C2—H2A	109.0	C4—C3—H3B	109.0
C3—C2—H2A	109.0	C2—C3—H3B	109.0
C1—C2—H2B	109.0	H3A—C3—H3B	107.8
C3—C2—H2B	109.0	C6^{i}—C7—C5	119.73 (17)

H2A—C2—H2B	107.8	C6^{i}—C7—H7	120.1
C2—C1—Cl1	111.34 (14)	C5—C7—H7	120.1
C2—C1—H1A	109.4		
C7—C5—C6—C7^{i}	0.1 (3)	C5—N1—C4—C3	171.72 (16)
N1—C5—C6—C7^{i}	−179.67 (15)	O1—C4—C3—C2	−37.8 (2)
C7—C5—N1—C4	35.9 (3)	N1—C4—C3—C2	144.32 (17)
C6—C5—N1—C4	−144.38 (18)	C1—C2—C3—C4	−178.27 (15)
C3—C2—C1—Cl1	−67.01 (19)	C6—C5—C7—C6^{i}	−0.1 (3)
C5—N1—C4—O1	−6.1 (3)	N1—C5—C7—C6^{i}	179.66 (16)

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{ii}	0.88	2.10	2.941 (3)	161

Symmetry code: (ii) *x*−1, *y*, *z*.