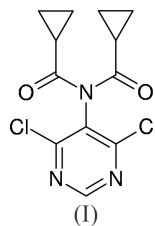


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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.043
 wR factor = 0.104
Data-to-parameter ratio = 17.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.5-[Bis(cyclopropanecarbonyl)amino]-4,6-dichloro-
pyrimidine containing a short cyclopropyl C—H...O
interactionThe title compound, $\text{C}_{12}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_2$, possesses normal intramolecular geometrical parameters. The crystal packing is influenced by C—H...O and possible weak π - π stacking interactions.Received 20 May 2004
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Comment

A great deal of research has been carried out on pyrimidine systems, fuelled by their important biological applications and properties (Brown, 1994). Various dihaloaminopyridines and dihaloaminopyrimidines have proven to be useful in terms of their antiviral activity, particularly for their action towards the Herpes virus (Giovanninetti *et al.*, 1980). As part of our general investigations in this area, the title compound, (I), $\text{C}_{12}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_2$, has been synthesized, albeit in moderate yield. Similarly low yields have also been observed by Giovanninetti *et al.* (1980) in acylation reactions of dichloroaminopyrimidines.Compound (I) possesses normal intramolecular geometrical parameters (Table 1). The 4,6-dichloropyrimidine moiety (C1—C4/N1/N2/Cl1/Cl2) is close to being planar; for the non-H atoms, the r.m.s. deviation from the least-squares plane is 0.031 Å. Atom N3 is significantly displaced from the mean plane by 0.204 (3) Å. The dihedral angle between the aromatic ring and the C5/N3/C9 group is 74.81 (10)°. The major conformational difference in the cyclopropanecarbonyl 'arms' of (I) concerns the amide carbonyl (C5=O1 and C9=O2) groups. The first of these is close to being eclipsed with respect to the N3—C3 bond, whereas the second is almost *anti* with respect to the same pair of atoms (Table 1). The cyclopropyl rings [mean C—C = 1.504 (3) Å; mean C—C—C = 60.0 (2)°] are unexceptional.As well as van der Waals forces, the crystal packing in (I) appears to be influenced by C—H...O interactions (Table 2). The first of these bonds involves the atoms C1—H1...O1ⁱⁱ (see Table 2 for symmetry code), *i.e.* the aromatic H atom and an amide carbonyl O-atom acceptor. These bonds help stabilize the [001] stacks of (I) and are generated by *c*-glide symmetry. The second, with a near-linear C7—H4...O2ⁱ bond angle of 173° and a very short H...O separation of 2.35 Å,

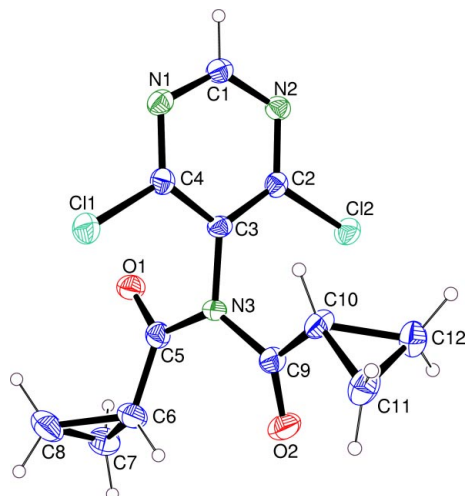


Figure 1
View of (I) (50% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radii.

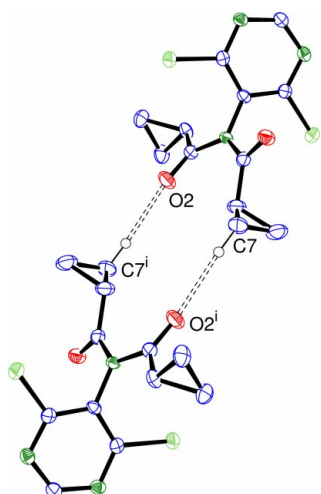


Figure 2
Dimerization of molecules of (I) *via* the C7—H4...O2ⁱ bond (symmetry code as in Table 2), with 50% probability displacement ellipsoids; all H atoms, except H4, have been omitted for clarity.

involves a cyclopropyl H atom and the other amide carbonyl O atom as the acceptor species, the acceptor generated by inversion symmetry (Fig. 2), which results in dimers of (I). Allen *et al.* (1996) have shown that C—H...O hydrogen bonds from cyclopropyl methylene groups are enhanced because strain inherent in the C3 ring tends to increase the acidity of the CH moieties involved, although the example here appears to be a particularly strong bond.

There may be π – π stacking effects involving the pyrimidine rings (C1–C4/N1/N2, with centroid Cg) in (I). The Cg...Cgⁱⁱⁱ [symmetry code: (iii) $x, \frac{3}{2} - y, -\frac{1}{2} + z$; *i.e.* the *c*-glide] separation is 3.7160 (12) Å, but the centroids are laterally displaced by the large value of 1.87 Å, suggesting that this is a very weak interaction.

In combination, these effects result (Fig. 3) in stacks of molecules of (I) propagating along [001]. The stacks are crosslinked along [010] by the proposed C7—H4...O2ⁱ (Table 2) bonds, whereas along [100] only van der Waals

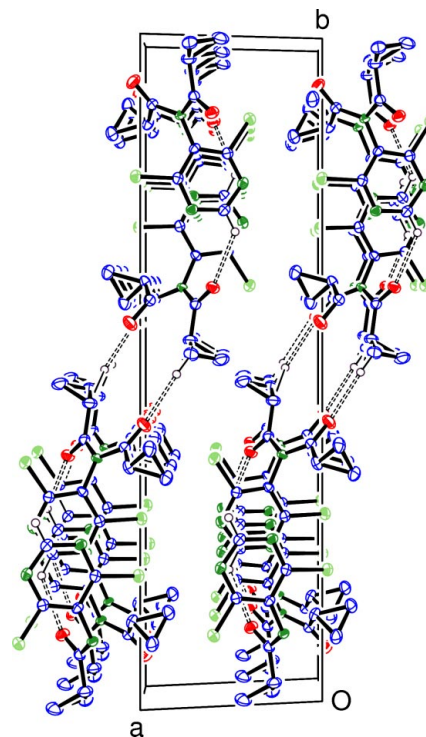


Figure 3
The packing in (I), viewed down [001], with C—H...O interactions indicated by dashed lines (50% probability displacement ellipsoids); all H atoms, except H1 and H4, have been omitted for clarity.

interactions hold the adjacent stacks together. In this direction, the N1...Cl2^{iv} [symmetry code (iv) $x - 1, y, z$] contact of 3.252 (2) Å is slightly less than the van der Waals radius sum of 3.30 Å for these species (Spek, 2003).

Experimental

To prepare (I), 4,6-dichloro-5-aminopyrimidine (0.412 g, 2.512 mmol) was placed in a twin-necked flask and was stirred in dry dichloromethane (35 ml) under a nitrogen atmosphere. The reaction mixture was cooled to 273 K, whereupon Hünig's base (7.54 mmol, 1.30 ml) was added, and the reaction was stirred for approximately 10 min. Cyclopropane carbonyl chloride (7.54 mmol, 0.68 ml) was then added, and the reaction was warmed to room temperature and stirred for 24 h. The progress of the reaction was monitored using thin-layer chromatography (TLC, solvent dichloromethane), showing the product with an R_F of 0.19. The reaction mixture was then washed with saturated brine (3×20 ml) and dried with magnesium sulfate, and the solvent was removed at reduced pressure. The resultant organic liquor was purified using flash chromatography (solvent 3:0.1 chloroform/methanol). Overlap of the starting material with the product required the use of a different solvent system (2:2:0.1 dichloromethane/hexane/methanol) to further purify the product ($R_F = 0.17$). Vapour diffusion crystallization was used to obtain white crystals of (I); dichloromethane was used as the solvent and hexane was used as the precipitant. The yield obtained was 0.063 g (8.4%). M.p. 406–409 K. FT-IR (KBr, cm^{-1}): ν_{max} 3062 (*w*, CH, cyclopropane), 1697, 1713 (C=O, carbonyl), 1517, 1413 (*s*, C=N, conjugated, cyclic, pyrimidine), 1541 (*m*, C—N, tertiary amine), 1174 (*s*, pyrimidine-NR₂), 813 (*s*, pyrimidine-Cl); ¹H (400 MHz; CDCl₃): δ 0.96 (4H, *ddd*), 1.20 (4H, *ddd*), 2.01 (2H, *tt*), 8.76 (1H, *s*); ¹³C

(100 MHz, CDCl₃): δ 11.2, 15.7, 131.4, 157.3, 161.9, 174.1. Elemental analysis data were consistent with the crystallographic results: found: C 47.93, H 3.58, N 13.75, Cl 22.78%; calculated for C₁₂H₁₁Cl₂N₃O₂: C 48.02, H 3.69, N 14.00, Cl 23.62%.

Crystal data

C₁₂H₁₁Cl₂N₃O₂ $D_x = 1.548 \text{ Mg m}^{-3}$
 $M_r = 300.14$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/c$ Cell parameters from 14 708 reflections
 $a = 7.6677(3) \text{ \AA}$ $\theta = 2.9\text{--}27.5^\circ$
 $b = 26.7366(12) \text{ \AA}$ $\mu = 0.51 \text{ mm}^{-1}$
 $c = 6.6477(3) \text{ \AA}$ $T = 120(2) \text{ K}$
 $\beta = 109.065(2)^\circ$ Rod, colourless
 $V = 1288.08(10) \text{ \AA}^3$ $0.50 \times 0.10 \times 0.10 \text{ mm}$
 $Z = 4$

Data collection

Nonius KappaCCD diffractometer 1960 reflections with $I > 2\sigma(I)$
 ω and φ scans $R_{\text{int}} = 0.077$
 Absorption correction: multi-scan (SORTAV; Blessing, 1995) $\theta_{\text{max}} = 27.5^\circ$
 $T_{\text{min}} = 0.787, T_{\text{max}} = 0.951$ $h = -9 \rightarrow 9$
 13 247 measured reflections $k = -34 \rightarrow 34$
 2937 independent reflections $l = -8 \rightarrow 8$

Refinement

Refinement on F^2 H-atom parameters constrained
 $R[F^2 > 2\sigma(F^2)] = 0.043$ $w = 1/[\sigma^2(F_o^2) + (0.0514P)^2]$
 $wR(F^2) = 0.104$ where $P = (F_o^2 + 2F_c^2)/3$
 $S = 0.98$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 2937 reflections $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
 172 parameters $\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

C1—N2	1.331 (3)	C3—C4	1.386 (3)
C1—N1	1.336 (3)	C3—N3	1.425 (3)
C2—N2	1.330 (3)	C4—N1	1.322 (3)
C2—C3	1.381 (3)	C4—Cl1	1.725 (2)
C2—Cl2	1.725 (2)		
O2—C9—N3—C3	−156.7 (2)	O1—C5—N3—C3	10.6 (3)

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C7—H4 \cdots O2 ⁱ	0.99	2.35	3.339 (3)	173
Cl1—H1 \cdots O1 ⁱⁱ	0.95	2.51	3.203 (3)	130

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

All H atoms were placed in calculated positions ($C\text{—}H = 0.95\text{--}1.00 \text{ \AA}$) and refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK, and SORTAV (Blessing, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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