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2,5-Dichloroaniline, a monoclinic structure with a pseudo-tetragonal unit cell

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.026
wR factor = 0.074
Data-to-parameter ratio = 10.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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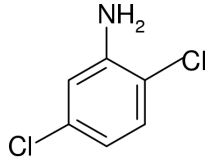
The pseudo-tetragonal cell of the title compound, $C_6H_5Cl_2N$, is correctly described as monoclinic with β = 90.033 (2)°. Amine groups are linked by intermolecular hydrogen bonding involving only one H atom of each group.

Comment

The crystal structure of 2,5-dichloroaniline, (I), was previously determined (Sakurai *et al.*, 1963) from Weissenberg film data. The space group reported was $P2_1/c$ and refinement converged at R = 0.126. The original cell dimensions were a = 13.237 (7), b = 3.892 (6), c = 18.80 (2) Å and β = 135.2 (2)°. The large β angle led to the examination of the cell dimensions with *LEPAGE* (Spek, 1988) and the possibility of a tetragonal or orthorhombic cell was suggested. A new data set collected at 120 K refined to R = 0.026 in the space group $P2_1/n$ with cell dimensions a = 13.1141 (7), b = 3.8137 (6), c = 13.1699 (7) Å and β = 90.033 (2)°. Final analysis with *PLATON* (Spek, 2001) showed that the lattice featured metrical symmetry (pseudo-tetragonal or pseudo-orthorhombic) not supported by the cell contents which confirmed the crystal system as monoclinic. The $P2_1/n$ designation is related to the size of the β angle, which is much closer to 90° in this setting, compared to the transformed cell. Taking the temperature of the determination into consideration, the cell dimensions originally reported and the cell dimensions transformed into $P2_1/c$ from this study are equivalent; hence polymorphism is not shown.



(I)

Details of the 2,5-dichloroaniline structure (Fig. 1) not previously reported include hydrogen-bond formation between amine groups that involves only one of the H atoms (H1*B*) (Fig. 2). This results in continuous chains of molecules running in the direction of the *b* axis that each contain two of the four symmetry-related molecules per unit cell required by the space group (Fig. 3). The aromatic rings pack face-to-face to each other in these chains by translational symmetry along the *b* axis. The close separation of these rings (3.490 Å) indicates π–π-stacking interactions. There is also a short intramolecular H1*B*···Cl1 separation of 2.63 (2) Å but the N1—H1*B*···Cl1 angle is only 107 (2)°. The N atom deviates by 0.24 (1) Å from the plane defined by atoms C1, H1*A* and H1*B*.

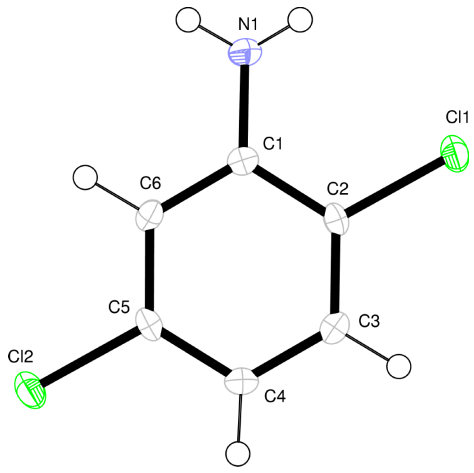


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

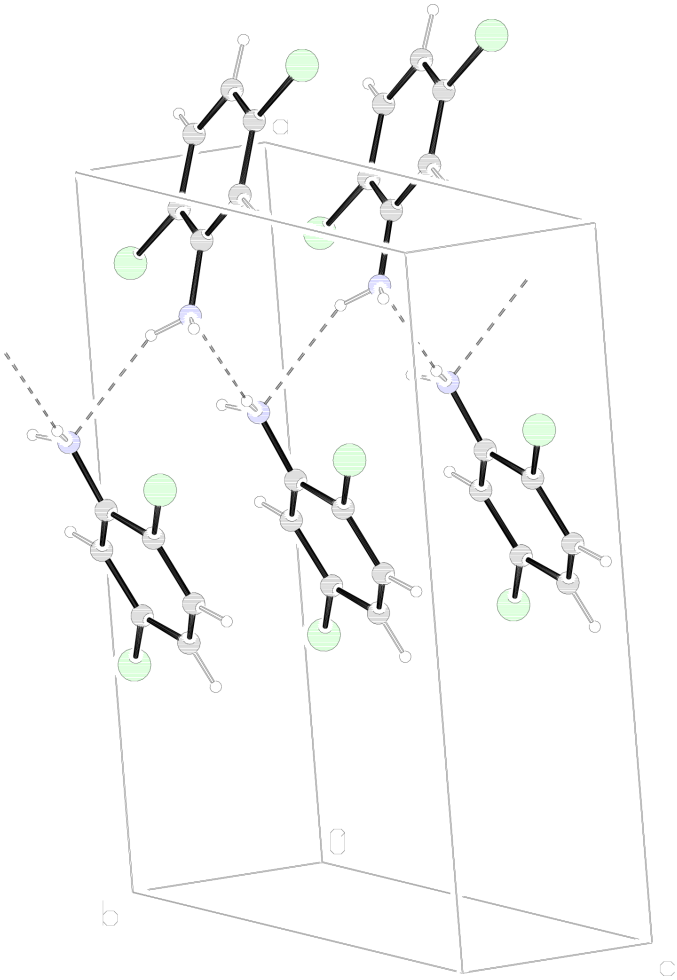


Figure 2
Crystal packing diagram showing (x, *y*, *z*) molecules linked to $(-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2})$ molecules by translation along the *b* axis.

The shortest Cl···Cl separation is Cl1···Cl2$(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ = 3.3219 (8) Å, compared to the previously reported value of 3.37 Å.

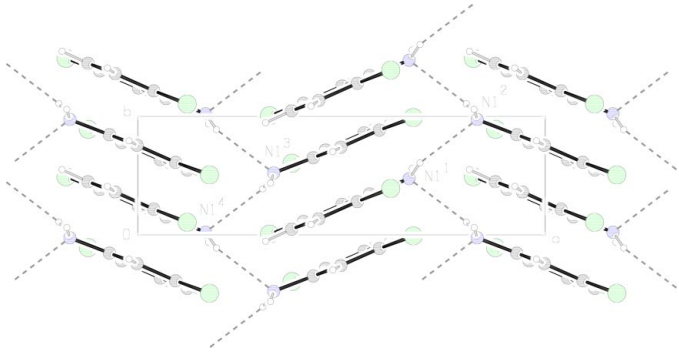


Figure 3
Crystal packing diagram showing the two chains of hydrogen-bonded molecules within the unit cell. [Symmetry-code suffixes: (1) *x*, *y*, *z*; (2) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (3) $1-x, 1-y, 1-z$; (4) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.]

The crystal structures of 2,3-, 2,4-, 2,6-, 3,4- and 3,5-dichloroaniline (Dou *et al.*, 1993) also show N—H···N hydrogen bonds and short Cl···Cl interactions.

Experimental

2,5–Dichloroaniline was purchased from Aldrich and colourless crystals were obtained by sublimation.

Crystal data

$C_6H_5Cl_2N$
M_r = 162.01
Monoclinic, $P2_1/n$
a = 13.1141 (6) Å
b = 3.8137 (1) Å
c = 13.1699 (7) Å
β = 90.033 (2)°
V = 658.67 (11) Å^3
Z = 4
D_x = 1.634 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1724 reflections
θ = 2.9–26.0°
μ = 0.88 mm^{-1}
T = 120 (2) K
Lozenge, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.844, T_{max} = 0.917
2663 measured reflections
1088 independent reflections
1026 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.0°
$h = -16 \rightarrow 16$
$k = -4 \rightarrow 4$
$l = -16 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.074
S = 1.03
1088 reflections
102 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.1577P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.7356 (17)	Cl2—C5	1.7432 (18)
C6—C1—C2	117.46 (13)	C3—C4—C5	118.24 (14)
C3—C2—C1	121.36 (15)	C4—C5—C6	121.61 (16)
N1—C1—C2—Cl1	4.6 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···N1^{i}	0.87 (2)	2.45 (2)	3.241 (2)	151 (2)

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

Refined N—H and C—H distances are in the ranges 0.85 (2)–0.87 (2) and 0.93 (2)–0.97 (2) Å, respectively.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PLATON*.

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