

1,2-Bis(chloromethyl)-4,5-dimethyl-3-nitrobenzene

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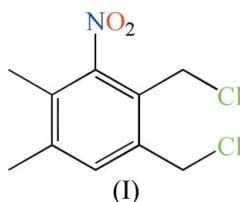
Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.060
 wR factor = 0.150
Data-to-parameter ratio = 17.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{10}\text{H}_{11}\text{Cl}_2\text{NO}_2$, consists of a benzene core functionalized by one nitro group, two methyl groups, and two chloromethyl groups. The crystal structure is stabilized by intermolecular $\text{C}-\text{H}\cdots\text{O}$ non-classical hydrogen bonds and weak $\text{C}-\text{H}\cdots\text{Cl}$ interactions.

Comment

1,2-Bis(chloromethyl)benzene and its derivatives (Shahak & Bergmann, 1966) are used to synthesize conformationally constrained cyclic α -amino acid derivatives (Kotha & Brahmachary, 2000), and are also important building blocks for supramolecular chemistry. For example, they serve as important alkylating agents in the synthesis of molecular clips (Wu *et al.*, 2002; Chakraborty *et al.*, 2002; Yin *et al.*, 2006; Li *et al.*, 2006). As the side-wall of molecular clips, they can affect the arrangement of molecular clips for studies in crystal engineering (Wang *et al.*, 2006). In this paper, we report the synthesis and structure of the title compound, (I) (Fig. 1).



The crystal packing is stabilized by $\text{C}-\text{H}\cdots\text{O}$ non-classical hydrogen bonds involving an aromatic CH group as donor (Table 1), forming a chain structure (Fig. 2). In addition, weak intermolecular $\text{C}-\text{H}\cdots\text{Cl}$ interactions further stabilize the crystal packing, the $\text{H}\cdots\text{Cl}$ separation being 2.85 Å. A combination of both interactions allows the formation of a quasi-network (Fig. 2).

Experimental

To a solution of 1,2-bis(chloromethyl)-4,5-dimethylbenzene (0.5 g, 2.5 mmol) in trifluoroacetic acid (5 ml), concentrated HNO_3 was added dropwise, with stirring, the mixture being cooled in an ice-water bath. The mixture was then stirred for another 4 h at room temperature. After evaporation of the solvent under reduced pressure, the residue was dissolved in EtOAc (50 ml), washed with saturated aqueous Na_2CO_3 and the organic layer was dried over anhydrous Na_2SO_4 . Flash chromatography of the residue on silica gel (petroleum ether as eluent) gave 0.54 g of the title compound (yield 88%). Crystals suitable for X-ray diffraction were grown by slow evaporation of an ethyl acetate–petroleum ether (1:4) solution at 298 K.

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Crystal data

$C_{10}H_{11}Cl_2NO_2$
 $M_r = 248.10$
 Monoclinic, Pn
 $a = 8.350(4) \text{ \AA}$
 $b = 4.5282(19) \text{ \AA}$
 $c = 15.370(7) \text{ \AA}$
 $\beta = 103.118(6)^\circ$
 $V = 566.0(4) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.456 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.55 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Plate, colourless
 $0.10 \times 0.06 \times 0.02 \text{ mm}$

Data collection

Bruker SMART 4K CCD area-
 detector diffractometer
 φ and ω scans
 Absorption correction: none
 4357 measured reflections

2456 independent reflections
 1709 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.151$
 $S = 1.00$
 2456 reflections
 138 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1259 Friedel pairs
 Flack parameter: 0.11 (11)

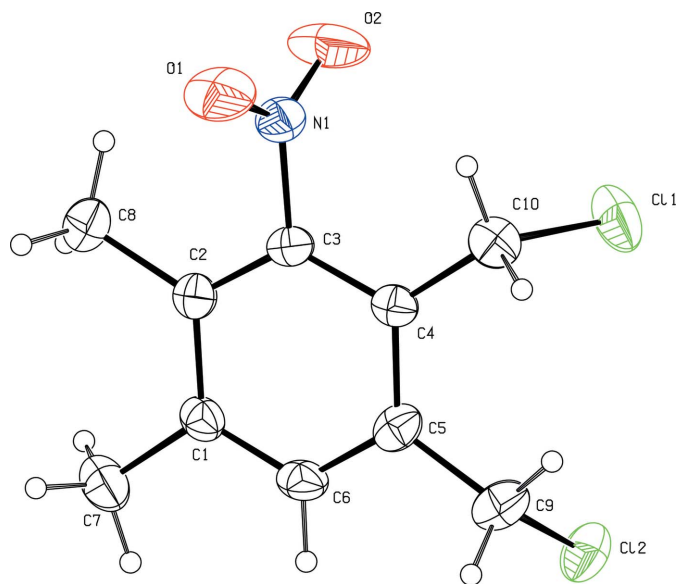


Figure 1

The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary size.

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C6-H6\cdots O1^i$	0.93	2.51	3.401 (5)	161

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

All H atoms were initially located in a difference map, but were constrained to an idealized geometry. Constrained bond lengths and isotropic displacement parameters: $C-H = 0.96 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for methyl, $C-H = 0.97 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ for methylene, and $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ for aromatic H atoms.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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References

- Bruker (2001). SMART (Version 5.628) and SAINT (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
 Chakraborty, A., Wu, A., Witt, D., Lagona, J., Fetting, J. C. & Isaacs, L. (2002). *J. Am. Chem. Soc.* **124**, 8297–8306.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Kotha, S. & Brahmachary, E. (2000). *J. Org. Chem.* **65**, 1359–1365.
 Li, Y., Yin, G., Guo, H., Zhou, B. & Wu, A. (2006). *Synthesis*, pp. 2897–2902.
 Shahak, I. & Bergmann, E. D. (1966). *J. Chem. Soc. C*, pp. 1005–1009.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.

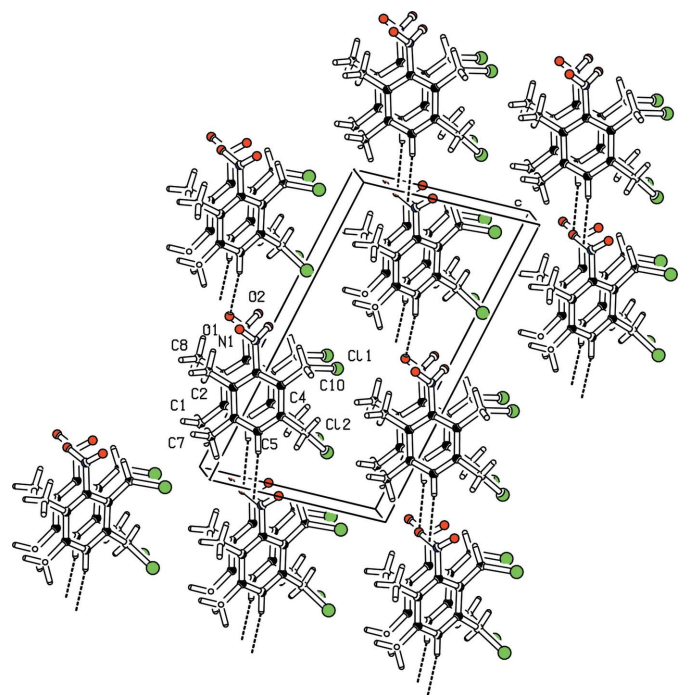


Figure 2

The packing of (I), with intermolecular $C-H\cdots O$ hydrogen bonds shown as dashed lines.

- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Wang, Z.-G., Zhou, B.-H., Chen, Y.-F., Yin, G.-D., Li, Y.-T., Wu, A.-X. & Isaacs, L. (2006). *J. Org. Chem.* **71**, 4502–4508.
 Wu, A., Chakraborty, A., Witt, D., Lagona, J., Damkaci, F., Ofori, M. A., Chiles, J. K., Fetting, J. C. & Isaacs, L. (2002). *J. Org. Chem.* **67**, 5817–5830.
 Yin, G., Wang, Z., Chen, Y., Wu, A. & Pan, Y. (2006). *Synlett*, pp. 49–52.