

Graham Atwell,<sup>a</sup> Peter D.W. Boyd,<sup>b\*</sup> William A. Denny<sup>a</sup> and Shangjin Yang<sup>a</sup><sup>a</sup>Cancer Research Laboratory, University of Auckland, Private Bag 92019, Auckland, New Zealand, and <sup>b</sup>Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New ZealandCorrespondence e-mail:  
pdw.boyd@auckland.ac.nz

## Key indicators

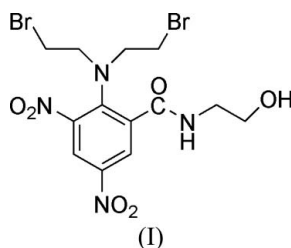
Single-crystal X-ray study  
 $T = 86\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.016  
 $wR$  factor = 0.038  
Data-to-parameter ratio = 16.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.2-[Bis(2-bromoethyl)amino]-*N*-(2-hydroxyethyl)-3,5-dinitrobenzamide

The title compound,  $\text{C}_{13}\text{H}_{16}\text{Br}_2\text{N}_4\text{O}_6$ , is a dinitrobenzamide dibromo mustard. The tetrasubstituted benzene ring is significantly distorted from both planarity and ideal hexagonal symmetry. The molecules assemble in the crystal structure *via* hydrogen-bonding interactions between the amide groups on adjacent molecules, and by  $\text{O}-\text{H}\cdots\text{O}(\text{nitro})$  and  $\text{O}-\text{H}\cdots\text{Br}$  contacts. There are short  $\text{Br}\cdots\text{Br}$  contacts ( $3.388\text{ \AA}$ ) that are significantly less than the sum of the van der Waals radii of two Br atoms.

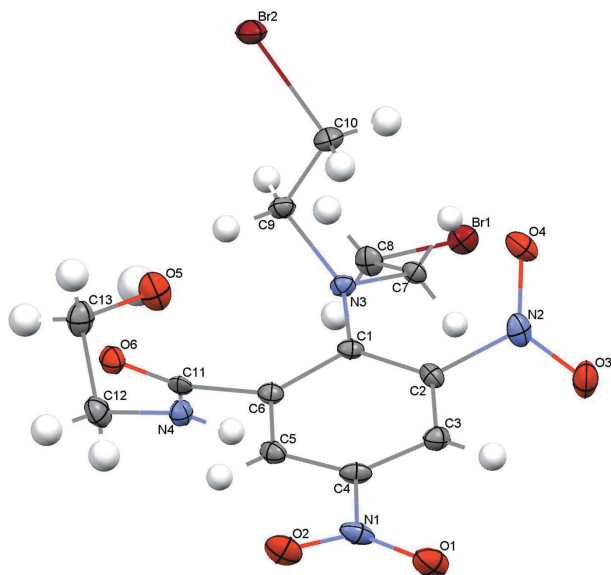
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## Comment

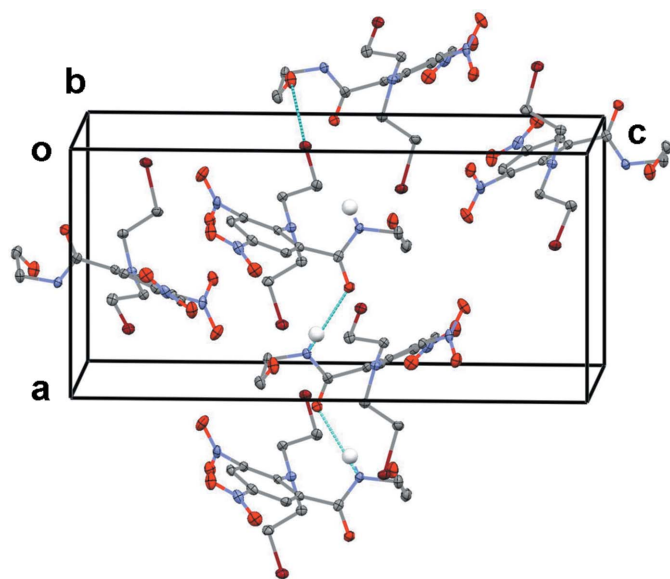
The title compound, (I), is a dinitrobenzamide mustard, closely related to the compound PR-104 which is currently in clinical trial as a potential hypoxia-activated prodrug for cancer therapy (Patterson *et al.*, 2006).



The molecular structure of (I) is shown in Fig. 1. There are significant deviations in the benzene ring from ideal hexagonal symmetry (Table 1). The C—C bond lengths nearest to the amino substituent are lengthened, with a corresponding decrease in the *ipso* C2—C1—C6 angle to  $115.3(2)^\circ$ . This has been observed in a range of 1-amino-2,4-dinitrobenzene derivatives (Punte *et al.*, 1989, 1991; Low *et al.*, 1996; Villalgorido *et al.*, 1990; Mackay *et al.*, 2000; Ferretti *et al.*, 1993). The benzene ring C1—C6 deviates from planarity [r.m.s. deviation  $0.025(1)\text{ \AA}$ ] in the form of a boat, with atoms C3 and C6  $0.033(1)$  and  $0.037(1)\text{ \AA}$ , respectively, above the mean plane and the remaining ring atoms below the plane [average deviation  $-0.017(1)\text{ \AA}$ ]. Atoms C11 and N2 are displaced in opposite directions with respect to the benzene ring, by  $0.257(3)$  and  $-0.179(3)\text{ \AA}$ , respectively. The dihedral angle between the 2-nitro group/C2 plane [r.m.s. deviation  $0.001(1)\text{ \AA}$ ] and the phenyl ring plane is  $53.32(8)^\circ$ , while the 4-nitro group/C4 plane [r.m.s. deviation  $0.004(1)\text{ \AA}$ ] is twisted by  $13.04(11)^\circ$ . The amide group C11/O6/N4/C6 plane [r.m.s. deviation  $0.011(1)\text{ \AA}$ ] is also rotated  $59.48(7)^\circ$  with respect to the benzene mean plane. The C7/N3/C9 plane of the *N,N'*-dibromoethyl group makes an angle of  $49.92(9)^\circ$  with respect to the benzene mean plane, which is significantly greater than is commonly observed in 1-dialkylamino-2,4-dinitrobenzenes (Mackay *et al.* 2000).

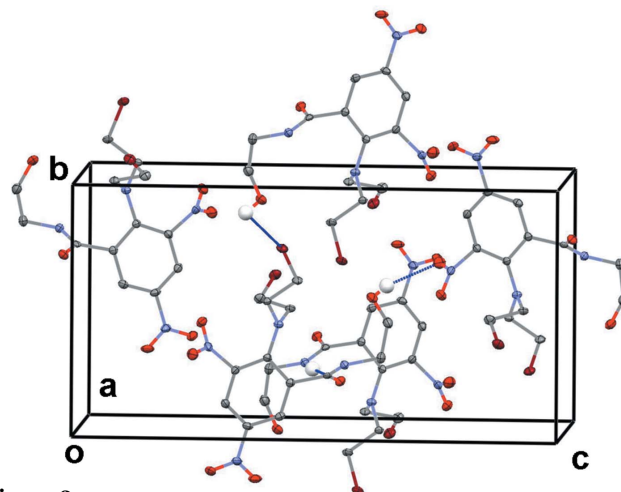


**Figure 1**  
The molecular structure of (I), showing 50% probability displacement ellipsoids for non-H atoms and H atoms as arbitrary spheres.



**Figure 2**  
The packing of (I) in the crystal structure, viewed along the *b* axis, showing the amide  $N-H \cdots O$  hydrogen-bonding (dashed lines) arrangement.

The molecules of (I) assemble in the crystal structure along the *a* axis via  $N-H \cdots O$  hydrogen-bonding interactions between the amide groups of adjacent molecules. These are connected to adjacent chains by  $O-H \cdots O$  (nitro) hydrogen bonds (Table 2) and  $O5-H16 \cdots Br1$  contacts (3.180 Å). There is a short  $Br1 \cdots Br2(1+x, y, z)$  contact [3.3876 (3) Å], significantly less than the sum of the van der Waals radii of two Br atoms. An examination of structures within the Cambridge Structural Database (Version 5.27; Allen, 2002) shows several structures with short  $Br \cdots Br$  contacts although most distances are closer to that expected for van der Waals contacts.



**Figure 3**  
The packing of (I) in the crystal structure, viewed along the *a* axis, showing the  $O-H \cdots O$  (nitro) and  $O-H \cdots Br$  hydrogen-bonding contacts as dashed lines.

## Experimental

The title compound was prepared from 2-chloro-3,5-dinitrobenzoyl chloride (2.00 g, 7.6 mmol) by reaction with 2-aminoethanol (1.15 g, 18.8 mmol), followed by treatment of the resulting amide (1.53 g, 5.3 mmol) with bis(2-chloroethyl)amine hydrochloride (1.89 g, 10.6 mmol) and triethylamine (1.60 g, 15.8 mmol) in dioxane (50 ml) at room temperature for 16 h. The resulting dichloro-mustard (1.78 g, 4.5 mmol) was heated under reflux in 3-methyl-2-butanone (20 ml) with lithium bromide (7.65 g, 90 mmol) for 6 h and the product was purified by chromatography on silica gel and crystallization from EtOAc/petroleum ether (1:1) (yield 2.07 g, 56%; m.p. 378–381 K). HRMS (G+FAB) calculated for  $C_{13}H_{17}^{79}Br_2N_4O_6$  ( $MH^+$ ):  $m/z$  482.9515; found: 482.9492. Crystals of (I) were grown from a benzene solution.

### Crystal data

$C_{13}H_{16}Br_2N_4O_6$	$Z = 4$
$M_r = 484.10$	$D_x = 1.812 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 9.2950$ (1) Å	$\mu = 4.61 \text{ mm}^{-1}$
$b = 9.9641$ (2) Å	$T = 86$ (2) K
$c = 19.1575$ (2) Å	Block, yellow
$V = 1774.30$ (4) Å <sup>3</sup>	$0.4 \times 0.18 \times 0.18 \text{ mm}$

### Data collection

Siemens SMART CCD diffractometer	10742 measured reflections
$\omega$ scans	3643 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3541 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.391$ , $T_{\max} = 0.551$	$R_{\text{int}} = 0.018$
(expected range = 0.310–0.436)	$\theta_{\text{max}} = 26.4^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0164P)^2 + 0.6655P]$
$R[F^2 > 2\sigma(F^2)] = 0.016$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.038$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
3643 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
227 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	with 1548 Friedel pairs
	Flack parameter: $-0.007$ (5)

**Table 1**

Selected geometric parameters (Å, °).

C4—C5	1.382 (3)	C2—C1	1.405 (3)
C4—C3	1.382 (3)	C5—C6	1.391 (3)
C2—C3	1.384 (3)	C6—C1	1.422 (3)
C5—C4—C3	121.74 (17)	C5—C6—C1	121.43 (17)
C3—C2—C1	124.19 (17)	C4—C3—C2	117.52 (17)
C4—C5—C6	119.45 (17)	C2—C1—C6	115.28 (16)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N4-H15\cdots O6^i$	0.86	2.21	3.057 (2)	171
$O5-H16\cdots O3^{ii}$	0.82	2.26	3.009 (2)	152

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

H atoms were placed in calculated positions and refined using a riding model [ $C-H = 0.93-0.97$  Å and  $U_{iso}(H) = 1.2$  or  $1.5$  times  $U_{eq}(C)$ ].

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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