Table 1. *Selected bond angles (°)*

C2—C1—C6	117.2 (2)	C42—C37—C38	117.3 (2)
C12—C7—C8	117.4 (2)	C48—C43—C44	117.0 (2)
C18—C13—C14	115.9 (2)	C54—C49—C50	117.3 (2)
C24—C19—C20	116.8 (2)	C56—C55—C60	117.5 (2)
C26—C25—C30	117.7 (2)	C62—C61—C66	117.6 (2)
C36—C31—C32	117.3 (2)	C72—C67—C68	117.6 (2)

Atoms C15 and C23 reveal very anisotropic atomic displacement parameters. However, introducing split sites for these atoms did not improve the refinement results. All criteria of quality such as R values, goodness-of-fit and final difference electron-density residues became worse.

Data collection: *IPDS* (Stoe & Cie, 1997a). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XSTEP* (Stoe & Cie, (1997b). Software used to prepare material for publication: *SHELXL*93.

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2,6-Dibromo-4-nitroaniline

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Abstract

In the crystal structure of 2,6-dibromo-4-nitroaniline, $C_6H_4Br_2N_2O_2$, weak hydrogen bonds exist between the pair of amino protons on one molecule and the

pair of *p*-nitro O atoms on an adjacent molecule, with further interactions, perpendicular to these weak hydrogen bonds, between O and Br atoms on neighbouring molecules, forming π-stacked two-dimensional layers in the crystallographic **a** direction.

Comment

The molecular structures of substituted benzene derivatives have aroused much interest because of potential non-linear optical properties. In particular, nitroaniline derivatives comprise both electron-donating amine and electron-withdrawing nitro groups and exhibit intriguing three-dimensional arrays with extensive hydrogen bonding. Molecules of this type are often observed to form infinite polar chains linked by intermolecular hydrogen bonding between amine H and nitro O atoms on neighbouring molecules. Extensive studies have been undertaken on hydrogen bonding in nitroaniline derivatives (Etter *et al.*, 1987) and it has been found that the most common bonding mode, often referred to as the primary interaction, involves a three-centre interaction with one proton of the amino group located between the two 'inside' lone pairs of electrons of a single nitro group. In primary amines, this leaves a second amine proton to hydrogen bond either intramolecularly to *ortho* substituents or intermolecularly to other molecules. Such interactions are observed in nitroaniline (Tonogaki *et al.*, 1993), 2-methyl-4-nitroaniline (Garito *et al.*, 1981), 2,6-dichloro-4-nitroaniline (Hughes & Trotter, 1971), as well as in secondary amines such as *N*-methyl-4-nitroaniline (Butcher *et al.*, 1992). Much less common is the hydrogen-bonding mode in which both amine protons are involved in hydrogen bonding to one nitro group on a neighbouring molecule. This rare type of interaction is observed in 3-trifluoromethyl-2,4,6-trinitroaniline (Butcher *et al.*, 1992). Substituents on the nitroaniline allow further intermolecular interactions. Hydroxy and halide groups, in particular, may contribute to intermolecular bonding in the crystal structure.

The crystal structure of 2,6-dibromo-4-nitroaniline, (I), provides another example of the less common paired-hydrogen-bonding mode in which both amine

(I)
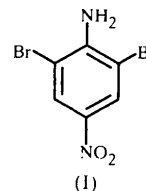
protons on one molecule interact with a nitro group of a neighbouring molecule. These interactions link the molecules in a linear polar chain, as shown in Fig. 1, which lies astride a crystallographic mirror plane. The hydrogen-bond contacts are of typical lengths for primary amines [N⋯O 2.941 (9) and N—H⋯O 2.334 (9) Å].
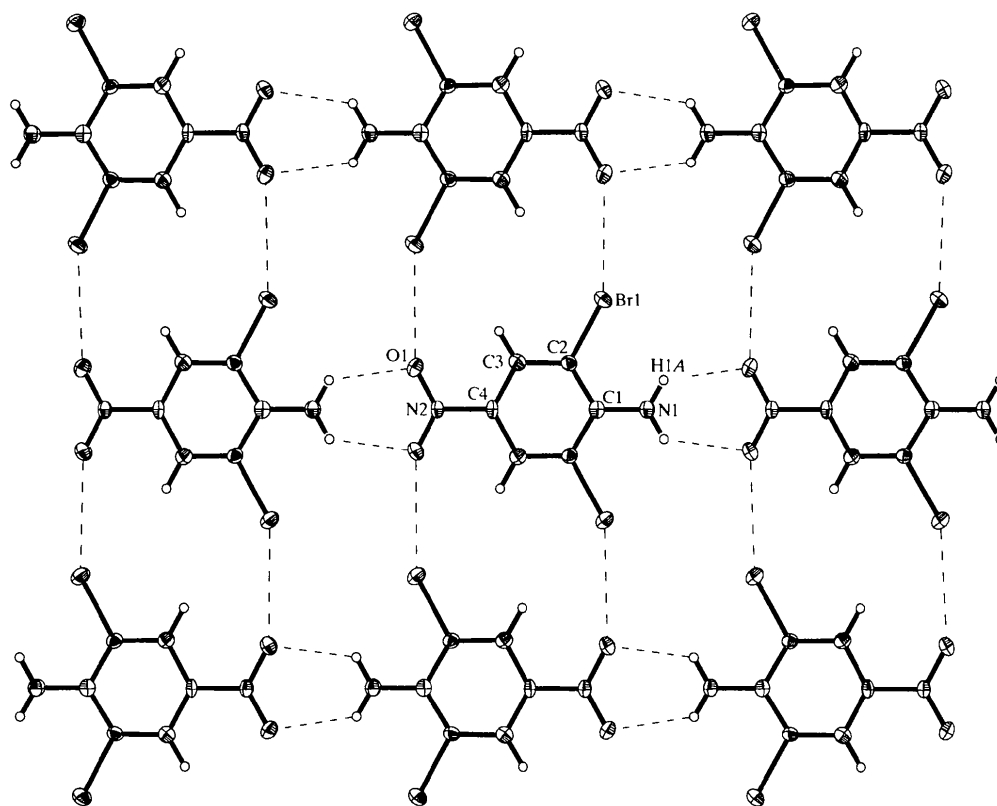
Fig. 1. Interlayer interactions between molecules of 2,6-dibromo-4-nitroaniline, showing hydrogen bonding between amine and nitro groups, and contacts between Br and O atoms. Displacement ellipsoids are drawn at the 50% probability level.

Perpendicular interactions [of length 3.218 (5) Å] are formed between Br and O atoms on adjacent molecules, in a plane coplanar with the molecular plane. The resulting two-dimensional sheets π stack above one another, with an interplanar distance of 3.335 (12) Å. This mode of intermolecular bonding can be described, using standard nomenclature (Bernstein *et al.*, 1995), as the basic unitary graph set $C(6)R_2^2(12)C_2^2(8)[R_2^2(6)]$ and basic binary graph set $R_4^2(12)$. Here we have taken the Br$\cdots$O contacts to behave as pseudo-hydrogen bonds, with the O atom playing the part of the hydrogen-bond acceptor and the Br atom as the hydrogen-bond donor.

Experimental

Dark-orange block-like crystals of 2,6-dibromo-4-nitroaniline were grown from a minimum amount of tetrahydrofuran (2 ml), layered with hexane (10 ml). Crystals were mounted in silicone grease, under an atmosphere of argon, in oil.

Crystal data

$C_6H_4Br_2N_2O_2$	Mo $K\alpha$ radiation
$M_r = 295.92$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 65
$P2_1/m$	reflections
$a = 4.2308$ (3) Å	$\theta = 5-50°$
$b = 14.2071$ (9) Å	$\mu = 9.760$ mm^{-1}
$c = 7.0308$ (5) Å	$T = 173$ (2) K
$\beta = 101.9610$ (10)°	Block
$V = 413.43$ (5) Å^3	$0.5 \times 0.4 \times 0.2$ mm
$Z = 2$	Dark red
$D_x = 2.377$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens CCD area-detector diffractometer	989 independent reflections
ω rotation scans with narrow frame	739 reflections with $I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.050$
SADABS (Sheldrick, 1996)	$\theta_{max} = 27.48°$
$T_{min} = 0.247$, $T_{max} = 0.746$	$h = -5 \rightarrow 5$
2673 measured reflections	$k = -9 \rightarrow 18$
	$l = -8 \rightarrow 9$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R(F) = 0.059$	$\Delta\rho_{max} = 2.097$ e Å^{-3}
$wR(F^2) = 0.146$	(0.9 Å from Br1)
$S = 1.145$	$\Delta\rho_{min} = -1.474$ e Å^{-3}
989 reflections	(1.34 Å from Br1)
61 parameters	Extinction correction: none

H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0924P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
International Tables for
Crystallography (Vol. C)

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Table 1. *Selected geometric parameters (Å, °)*

Br1—C2	1.890 (7)	C4—N2	1.455 (12)
C1—N1	1.349 (12)	N1···O1"	2.941 (9)
C1—C2'	1.404 (8)	N1···O1""	2.941 (9)
C1—C2	1.404 (8)	N2—O1'	1.234 (6)
C2—C3	1.384 (10)	N2—O1	1.234 (6)
C3—C4	1.388 (8)	O1···H1A'"	2.334 (9)
C4—C3'	1.388 (8)	O1···Br1'	3.218 (5)
N1—C1—C2'	121.6 (4)	C1—N1—O1"	157.9 (2)
N1—C1—C2	121.6 (4)	C1—N1—O1""	157.9 (2)
C2'—C1—C2	116.9 (8)	O1"—N1—O1""	43.1 (2)
C3—C2—C1	122.3 (6)	O1'—N2—O1	122.7 (8)
C3—C2—Br1	118.4 (5)	O1'—N2—C4	118.6 (4)
C1—C2—Br1	119.3 (5)	O1—N2—C4	118.6 (4)
C2—C3—C4	118.1 (6)	N2—O1···H1A'"	110.6 (5)
C3'—C4—C3	122.2 (9)	N2—O1···Br1'	149.3 (5)
C3'—C4—N2	118.9 (5)	H1A'"···O1···Br1'	97.5 (2)
C3—C4—N2	118.9 (5)		

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

Unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω), each at 20 s exposure. A full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 90 and 180°, with the area detector held at 2θ = −29°. The crystal-to-detector distance was 4.974 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed. H atoms were constrained to idealized geometries; each was assigned an isotropic displacement parameter of 1.2 times the U_{eq} value of the attached aromatic C or amide N atom.

Data collection: *SMART* (Siemens, 1995a). Cell refinement: *SAINT* (Siemens, 1995a). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995b). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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17β-Hydroxymethyl-3-methoxy-19,21-dinorestra-1,3,5(10)-trieno-18,20-lactone

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Abstract

An intramolecular oxygenation sequence leads to the hitherto unknown C-17,C-18-bridged title estrane derivative, $C_{20}H_{24}O_3$. The requisite assignment of its configuration was carried out by X-ray analysis.

Comment

For the synthesis of norestradiol (Kuhl *et al.*, 1997), we investigated one route *via* functionalization of the angular C-18 methyl group of alcohol (1) (Kuhl & Kreiser, 1998; Precigoux *et al.*, 1980) by an intramolecular radical-mediated oxygenation known as the hypoiodite reaction (Kalvoda & Heusler, 1971). The structure of the previously unknown title lactone (2) displays some outstanding features of estrane derivatives with an aromatic *A* ring. In contrast to the usual case, where the *B* ring adopts a significantly distorted half-chair or deformed sofa conformation (Geise *et al.*, 1967), compound (2)

(1)   (2)
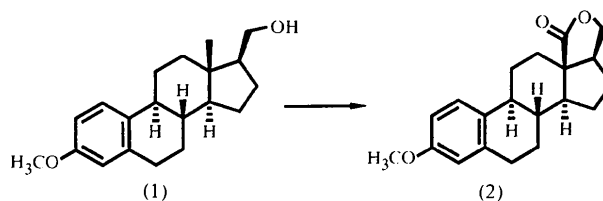
approximates an ideal half-chair, indicated by the torsion angle C7—C8—C9—C10 of 50.6 (3)°. As a result of this, the *C* ring possesses an undistorted chair conformation, verified by the mean of the absolute values of the corresponding torsion angles of 55 (1)° (Kutschabsky *et al.*, 1985). In contrast, the *D* ring displays a dramatically deformed C14α-envelope conformation (Δ = −17.9 and φ_m = 34.4°) in terms of puckering (Altona