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1-Bromo-2,6-bis(*N*-morpholinylmethyl)-benzene

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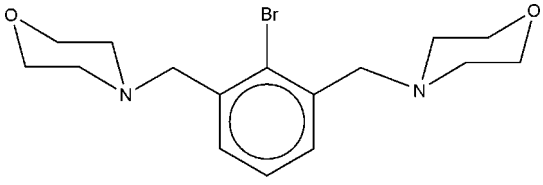
Key indicators: single-crystal X-ray study; T = 297 K; mean σ(C–C) = 0.005 Å; R factor = 0.051; wR factor = 0.100; data-to-parameter ratio = 15.3.

The crystal structure of the title compound, $C_{16}H_{23}BrN_2O_2$, contains two crystallographically independent molecules in the asymmetric unit. In both molecules, the morpholinyl rings adopt a chair conformation. One of the molecules is associated into centrosymmetric dimers through C—H···Br interactions (3.01 Å), but there are no other hydrogen bonds in the crystal structure.

Related literature

For general background, see: Dega-Szafran *et al.* (2004); Airaksinen *et al.* (2006); D'Hooghe *et al.* (2006); Avent *et al.* (2003); Iravani & Neumüller (2006); Kulcsar *et al.* (2007). For related compounds, see: Raj, Ponnuswamy *et al.* (1994); Raj, Velmurugan *et al.* (1994). For hydrogen-bonding nomenclature, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{16}H_{23}BrN_2O_2$
M_r = 355.27
Monoclinic, $P2_1/n$
a = 9.7086 (6) Å
b = 18.1384 (12) Å
c = 18.7167 (12) Å
β = 92.6850 (10)°
V = 3292.4 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.50 mm^{-1}
T = 297 (2) K
0.33 × 0.22 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2001)
T_{min} = 0.477, T_{max} = 0.669
23653 measured reflections
5817 independent reflections
4588 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.100
S = 1.07
5817 reflections
379 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14A···Br1^{i}	0.97	3.01	3.860 (5)	146

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND3* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2140).

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supplementary materials

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1-Bromo-2,6-bis(*N*-morpholinylmethyl)benzene

L. Copolovici, V. Bojan, C. Silvestru and R. A. Varga

Comment

Morpholine derivatives and their salts have gained much interest in recent years due to the considerable biological activities ascribed to many representatives (Dega-Szafran *et al.*, 2004; Airaksinen *et al.*, 2006) and their use as chiral reagents in asymmetric synthesis (D'Hooghe *et al.*, 2006). Mopholine derivatives can be used as bidentate or monodentate ligands towards metals due to the capacity of the N and O heteroatoms to coordinate a metal center (Avent *et al.*, 2003; Iravani & Neumüller, 2006; Kulcsar *et al.*, 2007).

For the title compound two crystallographically independent molecules are present in the unit cell. (Fig. 1). Each morpholinyl ring is in a chair conformation with the torsion angles in the range ±57.4 (4) – ±58.2 (4)° for molecule A and ±56.7 (4) – ±58.2 (4)° for molecule B. The average C—O [1.4111 (3) Å] and C—N [1.453 (5) Å] bond distances in the morpholinyl rings are similar to the corresponding values found in related systems (Raj, Ponnuswamy *et al.*, 1994; Raj, Velmurugan *et al.*, 1994).

Molecule A shows dimer associations built through intermolecular interactions H14A···Br1^{i} and Br1···H14A^{i} [3.01 Å; symmetry code: (i) = $-x + 1, -y + 2, -z$] with graph-set motif $R^2_2(16)$ (Bernstein *et al.*, 1995). For molecule B no associations were observed. There are no further hydrogen-bonding interactions between morpholinyl groups belonging to other neighbouring molecules.

Experimental

To a solution of 1-bromo-2,6-bis(bromomethyl)benzene (5.0 g, 14,5 mmol) in benzene (150 ml) was added dropwise a solution of *N*-morpholine (5.073 g, 58 mmol) in benzene (150 ml). The mixture was stirred at reflux for 8 h. After cooling to room temperature the precipitate was filtered off and the solvent was evaporated at reduced pressure to give a pale yellow solid. The reaction product was purified by recrystallization from a saturated hexane solution, giving the title compound as a white crystalline solid (4.157 g, Yield: 80%). Needle crystals suitable for single-crystal X-ray diffraction were obtained from hot hexane solution. ^{1}H NMR ($CDCl_3$, 300 MHz): δ(p.p.m.) 2.52 (t, 8H, N—CH_2—CH_2—O, $^3J_{HH}$ = 4.5 Hz); 3.61 (s, 4H, C_6H_3—CH_2—N); 3.72 (t, 8H, N—CH_2—CH_2—O, $^3J_{HH}$ = 4.5 Hz); 7.24 (d, 1H, C_6H_3, H-4), 7.37 (br s, 2H, C_6H_3, H-3,5). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ(p.p.m.) 53.62 (s, N—CH_2—CH_2—O), 62.76 (s, C_6H_3—CH_2—N), 67.03 (s, N—CH_2—CH_2—O), 126.53 (s, C-4), 126,79 (s, C-1), 129.13 (s, C-3,5), 137.74 (s, C-2,6).

Refinement

All hydrogen atoms were placed in calculated positions using a riding model, with C—H = 0.93–0.97 Å and $U_{iso} = 1.2U_{eq}$ (C) for aryl H.

Figures

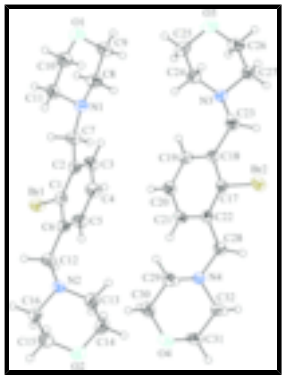


Fig. 1. The title molecule (I) showing the atom-numbering scheme at the 30% probability thermal ellipsoids for molecules A (containing Br1 atom) and B (containing Br2 atom). H atoms are drawn as spheres of arbitrary radii.

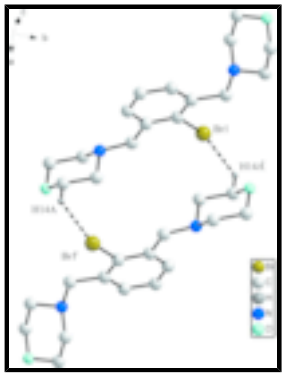


Fig. 2. The dimer association for molecule A. H atoms not involved in hydrogen-bonding contacts have been omitted for clarity (hydrogen bonds showed as dashed lines).

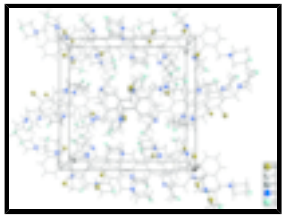


Fig. 3. Crystal packing along the *c* axis for the title compound.

1-Bromo-2,6-bis(*N*-morpholinylmethyl)benzene

Crystal data

$C_{16}H_{23}BrN_2O_2$	F_{000} = 1472
M_r = 355.27	D_x = 1.433 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 3430 reflections
a = 9.7086 (6) Å	θ = 2.3–20.0º
b = 18.1384 (12) Å	μ = 2.50 mm^{-1}
c = 18.7167 (12) Å	*T* = 297 (2) K
β = 92.6850 (10)º	Block, colourless
V = 3292.4 (4) Å^3	0.33 × 0.22 × 0.16 mm
Z = 8	

Data collection

Bruker SMART CCD area-detector diffractometer	5817 independent reflections
Radiation source: fine-focus sealed tube	4588 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.053$
$T = 297(2)$ K	$\theta_{max} = 25.0^{o}$
φ and ω scans	$\theta_{min} = 2.2^{o}$
Absorption correction: multi-scan (SHELXTL; Bruker, 2001)	$h = -11 \rightarrow 11$
$T_{min} = 0.477$, $T_{max} = 0.669$	$k = -21 \rightarrow 21$
23653 measured reflections	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 1.9306P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
5817 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
379 parameters	$\Delta\rho_{min} = -0.53$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.16374 (4)	1.11940 (2)	0.02444 (2)	0.04951 (14)
Br2	0.44157 (5)	−0.08378 (2)	0.70448 (2)	0.05994 (16)
C1	0.2087 (4)	1.03883 (19)	0.08779 (19)	0.0379 (9)
C2	0.2169 (4)	1.0512 (2)	0.16072 (19)	0.0386 (9)
C3	0.2476 (4)	0.9909 (2)	0.2043 (2)	0.0469 (10)

H3	0.2545	0.9972	0.2536	0.056*
C4	0.2681 (4)	0.9220 (2)	0.1761 (2)	0.0508 (11)
H4	0.2870	0.8821	0.2062	0.061*
C5	0.2603 (4)	0.9125 (2)	0.1026 (2)	0.0508 (11)
H5	0.2747	0.8658	0.0838	0.061*
C6	0.2320 (4)	0.9702 (2)	0.0566 (2)	0.0400 (9)
C7	0.2000 (4)	1.1272 (2)	0.19304 (19)	0.0477 (10)
H7A	0.2821	1.1561	0.1854	0.057*
H7B	0.1226	1.1518	0.1687	0.057*
C8	0.2190 (4)	1.1916 (2)	0.3066 (2)	0.0519 (11)
H8A	0.1618	1.2323	0.2895	0.062*
H8B	0.3141	1.2030	0.2974	0.062*
C9	0.2038 (5)	1.1812 (2)	0.3857 (2)	0.0575 (12)
H9A	0.2646	1.1419	0.4028	0.069*
H9B	0.2316	1.2261	0.4106	0.069*
C10	0.0255 (5)	1.0994 (3)	0.3643 (2)	0.0650 (13)
H10A	−0.0693	1.0883	0.3746	0.078*
H10B	0.0823	1.0584	0.3812	0.078*
C11	0.0364 (4)	1.1067 (3)	0.2846 (2)	0.0558 (11)
H11A	0.0093	1.0609	0.2613	0.067*
H11B	−0.0248	1.1454	0.2665	0.067*
C12	0.2232 (4)	0.9589 (2)	−0.02350 (19)	0.0485 (10)
H12A	0.1281	0.9644	−0.0408	0.058*
H12B	0.2770	0.9968	−0.0459	0.058*
C13	0.4226 (4)	0.8842 (2)	−0.0478 (3)	0.0615 (12)
H13A	0.4649	0.8991	−0.0021	0.074*
H13B	0.4523	0.9181	−0.0840	0.074*
C14	0.4677 (5)	0.8074 (3)	−0.0654 (3)	0.0702 (14)
H14A	0.5674	0.8062	−0.0673	0.084*
H14B	0.4415	0.7740	−0.0279	0.084*
C15	0.2629 (5)	0.7873 (3)	−0.1303 (3)	0.0650 (13)
H15A	0.2316	0.7531	−0.0946	0.078*
H15B	0.2228	0.7721	−0.1765	0.078*
C16	0.2135 (4)	0.8631 (2)	−0.1135 (2)	0.0528 (11)
H16A	0.2398	0.8971	−0.1505	0.063*
H16B	0.1137	0.8631	−0.1124	0.063*
C17	0.3327 (3)	−0.01732 (19)	0.64600 (18)	0.0345 (8)
C18	0.2771 (4)	0.04389 (19)	0.67931 (18)	0.0350 (8)
C19	0.1967 (4)	0.0910 (2)	0.6366 (2)	0.0410 (9)
H19	0.1560	0.1319	0.6568	0.049*
C20	0.1766 (4)	0.0777 (2)	0.5639 (2)	0.0429 (9)
H20	0.1214	0.1092	0.5358	0.051*
C21	0.2379 (4)	0.0179 (2)	0.53320 (19)	0.0404 (9)
H21	0.2251	0.0103	0.4842	0.049*
C22	0.3179 (4)	−0.03099 (19)	0.57329 (18)	0.0348 (8)
C23	0.3087 (4)	0.0591 (2)	0.75801 (19)	0.0442 (10)
H23A	0.2722	0.0191	0.7859	0.053*
H23B	0.4079	0.0600	0.7669	0.053*
C24	0.1105 (4)	0.1201 (2)	0.8057 (2)	0.0501 (10)

H24A	0.1098	0.0855	0.8453	0.060*
H24B	0.0519	0.1007	0.7668	0.060*
C25	0.0563 (4)	0.1936 (2)	0.8289 (3)	0.0609 (12)
H25A	0.0531	0.2272	0.7885	0.073*
H25B	−0.0370	0.1876	0.8444	0.073*
C26	0.2758 (5)	0.2326 (2)	0.8633 (2)	0.0588 (12)
H26A	0.3327	0.2528	0.9025	0.071*
H26B	0.2764	0.2672	0.8238	0.071*
C27	0.3363 (4)	0.1608 (2)	0.8404 (2)	0.0496 (10)
H27A	0.4288	0.1689	0.8246	0.060*
H27B	0.3420	0.1270	0.8806	0.060*
C28	0.3908 (4)	−0.0950 (2)	0.53941 (19)	0.0421 (9)
H28A	0.4895	−0.0870	0.5444	0.051*
H28B	0.3701	−0.1398	0.5651	0.051*
C29	0.2203 (4)	−0.1441 (2)	0.4531 (2)	0.0469 (10)
H29A	0.1486	−0.1178	0.4769	0.056*
H29B	0.2280	−0.1932	0.4734	0.056*
C30	0.1838 (4)	−0.1491 (2)	0.3741 (2)	0.0547 (11)
H30A	0.0969	−0.1750	0.3669	0.066*
H30B	0.1720	−0.0998	0.3547	0.066*
C31	0.4156 (4)	−0.1513 (3)	0.3489 (2)	0.0602 (12)
H31A	0.4113	−0.1020	0.3289	0.072*
H31B	0.4855	−0.1786	0.3247	0.072*
C32	0.4562 (4)	−0.1466 (2)	0.4276 (2)	0.0491 (10)
H32A	0.4644	−0.1957	0.4478	0.059*
H32B	0.5448	−0.1222	0.4342	0.059*
N1	0.1774 (3)	1.12437 (16)	0.26938 (15)	0.0406 (7)
N2	0.2732 (3)	0.88674 (17)	−0.04468 (16)	0.0439 (8)
N3	0.2509 (3)	0.12886 (16)	0.78245 (16)	0.0407 (8)
N4	0.3515 (3)	−0.10516 (16)	0.46372 (15)	0.0379 (7)
O1	0.0672 (3)	1.16374 (18)	0.40182 (15)	0.0653 (8)
O2	0.4074 (3)	0.78350 (17)	−0.13187 (16)	0.0674 (9)
O3	0.1395 (3)	0.22436 (15)	0.88525 (15)	0.0599 (8)
O4	0.2865 (3)	−0.18625 (16)	0.33683 (14)	0.0597 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0671 (3)	0.0412 (2)	0.0405 (2)	0.0070 (2)	0.00581 (19)	0.00573 (18)
Br2	0.0811 (3)	0.0517 (3)	0.0452 (3)	0.0274 (2)	−0.0169 (2)	−0.0063 (2)
C1	0.038 (2)	0.033 (2)	0.043 (2)	−0.0020 (17)	0.0027 (17)	0.0026 (17)
C2	0.040 (2)	0.038 (2)	0.038 (2)	−0.0010 (17)	0.0029 (17)	0.0003 (18)
C3	0.061 (3)	0.047 (3)	0.032 (2)	0.000 (2)	−0.0055 (19)	0.0017 (19)
C4	0.071 (3)	0.032 (2)	0.048 (3)	0.006 (2)	−0.001 (2)	0.0071 (19)
C5	0.069 (3)	0.035 (2)	0.049 (3)	0.003 (2)	0.002 (2)	−0.0039 (19)
C6	0.042 (2)	0.036 (2)	0.042 (2)	−0.0006 (17)	0.0009 (18)	−0.0031 (18)
C7	0.066 (3)	0.038 (2)	0.039 (2)	0.001 (2)	0.008 (2)	−0.0001 (18)
C8	0.065 (3)	0.044 (2)	0.047 (2)	−0.008 (2)	0.010 (2)	−0.007 (2)

C9	0.071 (3)	0.054 (3)	0.046 (3)	−0.004 (2)	−0.005 (2)	−0.008 (2)
C10	0.058 (3)	0.084 (4)	0.054 (3)	−0.016 (3)	0.013 (2)	−0.004 (3)
C11	0.048 (3)	0.072 (3)	0.047 (3)	−0.011 (2)	−0.003 (2)	−0.004 (2)
C12	0.060 (3)	0.046 (2)	0.040 (2)	0.003 (2)	0.004 (2)	−0.0051 (19)
C13	0.053 (3)	0.060 (3)	0.071 (3)	−0.001 (2)	−0.003 (2)	−0.015 (2)
C14	0.049 (3)	0.073 (3)	0.088 (4)	0.015 (2)	−0.002 (3)	−0.019 (3)
C15	0.062 (3)	0.062 (3)	0.070 (3)	−0.001 (2)	−0.002 (2)	−0.022 (2)
C16	0.052 (3)	0.057 (3)	0.049 (3)	0.005 (2)	0.000 (2)	−0.015 (2)
C17	0.035 (2)	0.034 (2)	0.034 (2)	−0.0005 (16)	−0.0009 (16)	0.0040 (16)
C18	0.039 (2)	0.032 (2)	0.034 (2)	−0.0007 (17)	0.0013 (16)	0.0000 (16)
C19	0.043 (2)	0.039 (2)	0.042 (2)	0.0030 (18)	0.0087 (18)	−0.0012 (18)
C20	0.048 (2)	0.040 (2)	0.041 (2)	0.0060 (18)	−0.0040 (18)	0.0068 (18)
C21	0.048 (2)	0.047 (2)	0.0265 (19)	−0.0008 (19)	−0.0007 (17)	0.0008 (17)
C22	0.035 (2)	0.033 (2)	0.037 (2)	−0.0065 (16)	0.0033 (16)	−0.0022 (16)
C23	0.055 (3)	0.039 (2)	0.039 (2)	0.0075 (19)	0.0015 (19)	−0.0040 (18)
C24	0.049 (3)	0.047 (2)	0.054 (3)	−0.001 (2)	0.002 (2)	−0.005 (2)
C25	0.054 (3)	0.055 (3)	0.074 (3)	0.006 (2)	0.016 (2)	−0.002 (2)
C26	0.076 (3)	0.050 (3)	0.051 (3)	−0.009 (2)	0.009 (2)	−0.017 (2)
C27	0.049 (3)	0.055 (3)	0.045 (2)	−0.006 (2)	0.005 (2)	−0.014 (2)
C28	0.049 (2)	0.037 (2)	0.040 (2)	−0.0001 (18)	−0.0027 (18)	−0.0067 (17)
C29	0.045 (2)	0.054 (3)	0.042 (2)	−0.012 (2)	0.0052 (19)	−0.0030 (19)
C30	0.053 (3)	0.059 (3)	0.052 (3)	−0.013 (2)	−0.004 (2)	−0.002 (2)
C31	0.060 (3)	0.079 (3)	0.042 (3)	0.000 (3)	0.014 (2)	−0.013 (2)
C32	0.048 (3)	0.054 (3)	0.045 (2)	0.003 (2)	0.0039 (19)	−0.007 (2)
N1	0.0456 (19)	0.0392 (18)	0.0374 (18)	−0.0045 (15)	0.0071 (14)	−0.0026 (14)
N2	0.049 (2)	0.0433 (19)	0.0386 (18)	0.0034 (16)	−0.0019 (15)	−0.0108 (15)
N3	0.0437 (19)	0.0380 (18)	0.0408 (18)	0.0033 (15)	0.0046 (15)	−0.0048 (15)
N4	0.0378 (18)	0.0413 (19)	0.0349 (17)	−0.0058 (14)	0.0052 (14)	−0.0071 (14)
O1	0.066 (2)	0.084 (2)	0.0469 (18)	0.0065 (18)	0.0123 (15)	−0.0065 (17)
O2	0.064 (2)	0.068 (2)	0.071 (2)	0.0128 (16)	0.0091 (17)	−0.0233 (17)
O3	0.074 (2)	0.0481 (18)	0.0592 (19)	0.0059 (15)	0.0206 (17)	−0.0124 (15)
O4	0.076 (2)	0.0581 (19)	0.0440 (17)	−0.0065 (17)	−0.0017 (15)	−0.0161 (14)

Geometric parameters (Å, °)

Br1—C1	1.919 (4)	C16—H16B	0.9700
Br2—C17	1.913 (3)	C17—C22	1.384 (5)
C1—C2	1.382 (5)	C17—C18	1.395 (5)
C1—C6	1.398 (5)	C18—C19	1.386 (5)
C2—C3	1.388 (5)	C18—C23	1.516 (5)
C2—C7	1.517 (5)	C19—C20	1.386 (5)
C3—C4	1.374 (5)	C19—H19	0.9300
C3—H3	0.9300	C20—C21	1.375 (5)
C4—C5	1.386 (5)	C20—H20	0.9300
C4—H4	0.9300	C21—C22	1.378 (5)
C5—C6	1.375 (5)	C21—H21	0.9300
C5—H5	0.9300	C22—C28	1.514 (5)
C6—C12	1.512 (5)	C23—N3	1.466 (4)
C7—N1	1.457 (4)	C23—H23A	0.9700

C7—H7A	0.9700	C23—H23B	0.9700
C7—H7B	0.9700	C24—N3	1.459 (5)
C8—N1	1.452 (4)	C24—C25	1.505 (5)
C8—C9	1.507 (5)	C24—H24A	0.9700
C8—H8A	0.9700	C24—H24B	0.9700
C8—H8B	0.9700	C25—O3	1.413 (5)
C9—O1	1.410 (5)	C25—H25A	0.9700
C9—H9A	0.9700	C25—H25B	0.9700
C9—H9B	0.9700	C26—O3	1.412 (5)
C10—O1	1.412 (5)	C26—C27	1.499 (5)
C10—C11	1.506 (5)	C26—H26A	0.9700
C10—H10A	0.9700	C26—H26B	0.9700
C10—H10B	0.9700	C27—N3	1.454 (4)
C11—N1	1.447 (5)	C27—H27A	0.9700
C11—H11A	0.9700	C27—H27B	0.9700
C11—H11B	0.9700	C28—N4	1.461 (4)
C12—N2	1.457 (4)	C28—H28A	0.9700
C12—H12A	0.9700	C28—H28B	0.9700
C12—H12B	0.9700	C29—N4	1.462 (4)
C13—N2	1.456 (5)	C29—C30	1.507 (5)
C13—C14	1.500 (6)	C29—H29A	0.9700
C13—H13A	0.9700	C29—H29B	0.9700
C13—H13B	0.9700	C30—O4	1.414 (5)
C14—O2	1.418 (5)	C30—H30A	0.9700
C14—H14A	0.9700	C30—H30B	0.9700
C14—H14B	0.9700	C31—O4	1.413 (5)
C15—O2	1.406 (5)	C31—C32	1.509 (5)
C15—C16	1.494 (5)	C31—H31A	0.9700
C15—H15A	0.9700	C31—H31B	0.9700
C15—H15B	0.9700	C32—N4	1.455 (4)
C16—N2	1.453 (5)	C32—H32A	0.9700
C16—H16A	0.9700	C32—H32B	0.9700
C2—C1—C6	123.6 (3)	C20—C19—H19	119.7
C2—C1—Br1	119.2 (3)	C21—C20—C19	120.2 (3)
C6—C1—Br1	117.2 (3)	C21—C20—H20	119.9
C1—C2—C3	117.0 (3)	C19—C20—H20	119.9
C1—C2—C7	122.6 (3)	C20—C21—C22	121.6 (3)
C3—C2—C7	120.4 (3)	C20—C21—H21	119.2
C4—C3—C2	121.5 (4)	C22—C21—H21	119.2
C4—C3—H3	119.3	C21—C22—C17	116.8 (3)
C2—C3—H3	119.3	C21—C22—C28	121.9 (3)
C3—C4—C5	119.5 (4)	C17—C22—C28	121.3 (3)
C3—C4—H4	120.3	N3—C23—C18	113.4 (3)
C5—C4—H4	120.3	N3—C23—H23A	108.9
C6—C5—C4	121.8 (4)	C18—C23—H23A	108.9
C6—C5—H5	119.1	N3—C23—H23B	108.9
C4—C5—H5	119.1	C18—C23—H23B	108.9
C5—C6—C1	116.7 (3)	H23A—C23—H23B	107.7
C5—C6—C12	121.2 (3)	N3—C24—C25	109.5 (3)

C1—C6—C12	122.1 (3)	N3—C24—H24A	109.8
N1—C7—C2	112.5 (3)	C25—C24—H24A	109.8
N1—C7—H7A	109.1	N3—C24—H24B	109.8
C2—C7—H7A	109.1	C25—C24—H24B	109.8
N1—C7—H7B	109.1	H24A—C24—H24B	108.2
C2—C7—H7B	109.1	O3—C25—C24	111.7 (3)
H7A—C7—H7B	107.8	O3—C25—H25A	109.3
N1—C8—C9	109.2 (3)	C24—C25—H25A	109.3
N1—C8—H8A	109.8	O3—C25—H25B	109.3
C9—C8—H8A	109.8	C24—C25—H25B	109.3
N1—C8—H8B	109.8	H25A—C25—H25B	107.9
C9—C8—H8B	109.8	O3—C26—C27	112.1 (3)
H8A—C8—H8B	108.3	O3—C26—H26A	109.2
O1—C9—C8	112.0 (3)	C27—C26—H26A	109.2
O1—C9—H9A	109.2	O3—C26—H26B	109.2
C8—C9—H9A	109.2	C27—C26—H26B	109.2
O1—C9—H9B	109.2	H26A—C26—H26B	107.9
C8—C9—H9B	109.2	N3—C27—C26	110.0 (3)
H9A—C9—H9B	107.9	N3—C27—H27A	109.7
O1—C10—C11	112.8 (4)	C26—C27—H27A	109.7
O1—C10—H10A	109.0	N3—C27—H27B	109.7
C11—C10—H10A	109.0	C26—C27—H27B	109.7
O1—C10—H10B	109.0	H27A—C27—H27B	108.2
C11—C10—H10B	109.0	N4—C28—C22	113.4 (3)
H10A—C10—H10B	107.8	N4—C28—H28A	108.9
N1—C11—C10	109.0 (3)	C22—C28—H28A	108.9
N1—C11—H11A	109.9	N4—C28—H28B	108.9
C10—C11—H11A	109.9	C22—C28—H28B	108.9
N1—C11—H11B	109.9	H28A—C28—H28B	107.7
C10—C11—H11B	109.9	N4—C29—C30	109.0 (3)
H11A—C11—H11B	108.3	N4—C29—H29A	109.9
N2—C12—C6	112.8 (3)	C30—C29—H29A	109.9
N2—C12—H12A	109.0	N4—C29—H29B	109.9
C6—C12—H12A	109.0	C30—C29—H29B	109.9
N2—C12—H12B	109.0	H29A—C29—H29B	108.3
C6—C12—H12B	109.0	O4—C30—C29	112.0 (3)
H12A—C12—H12B	107.8	O4—C30—H30A	109.2
N2—C13—C14	109.9 (3)	C29—C30—H30A	109.2
N2—C13—H13A	109.7	O4—C30—H30B	109.2
C14—C13—H13A	109.7	C29—C30—H30B	109.2
N2—C13—H13B	109.7	H30A—C30—H30B	107.9
C14—C13—H13B	109.7	O4—C31—C32	111.8 (3)
H13A—C13—H13B	108.2	O4—C31—H31A	109.3
O2—C14—C13	111.3 (4)	C32—C31—H31A	109.3
O2—C14—H14A	109.4	O4—C31—H31B	109.3
C13—C14—H14A	109.4	C32—C31—H31B	109.3
O2—C14—H14B	109.4	H31A—C31—H31B	107.9
C13—C14—H14B	109.4	N4—C32—C31	109.0 (3)
H14A—C14—H14B	108.0	N4—C32—H32A	109.9

O2—C15—C16	112.3 (4)	C31—C32—H32A	109.9
O2—C15—H15A	109.1	N4—C32—H32B	109.9
C16—C15—H15A	109.1	C31—C32—H32B	109.9
O2—C15—H15B	109.1	H32A—C32—H32B	108.3
C16—C15—H15B	109.1	C11—N1—C8	109.6 (3)
H15A—C15—H15B	107.9	C11—N1—C7	112.9 (3)
N2—C16—C15	109.9 (3)	C8—N1—C7	112.9 (3)
N2—C16—H16A	109.7	C16—N2—C13	108.2 (3)
C15—C16—H16A	109.7	C16—N2—C12	112.5 (3)
N2—C16—H16B	109.7	C13—N2—C12	112.7 (3)
C15—C16—H16B	109.7	C27—N3—C24	109.1 (3)
H16A—C16—H16B	108.2	C27—N3—C23	111.3 (3)
C22—C17—C18	123.9 (3)	C24—N3—C23	112.1 (3)
C22—C17—Br2	118.6 (3)	C32—N4—C28	111.1 (3)
C18—C17—Br2	117.4 (3)	C32—N4—C29	108.1 (3)
C19—C18—C17	116.9 (3)	C28—N4—C29	112.2 (3)
C19—C18—C23	122.1 (3)	C9—O1—C10	109.3 (3)
C17—C18—C23	121.0 (3)	C15—O2—C14	109.8 (3)
C18—C19—C20	120.5 (3)	C26—O3—C25	109.6 (3)
C18—C19—H19	119.7	C31—O4—C30	110.3 (3)
C6—C1—C2—C3	−1.2 (6)	N3—C24—C25—O3	−58.9 (5)
Br1—C1—C2—C3	179.0 (3)	O3—C26—C27—N3	57.9 (5)
C6—C1—C2—C7	176.1 (4)	C21—C22—C28—N4	−8.4 (5)
Br1—C1—C2—C7	−3.8 (5)	C17—C22—C28—N4	174.0 (3)
C1—C2—C3—C4	−0.4 (6)	N4—C29—C30—O4	58.8 (4)
C7—C2—C3—C4	−177.7 (4)	O4—C31—C32—N4	−59.3 (5)
C2—C3—C4—C5	1.1 (6)	C10—C11—N1—C8	−57.5 (5)
C3—C4—C5—C6	−0.3 (7)	C10—C11—N1—C7	175.7 (3)
C4—C5—C6—C1	−1.1 (6)	C9—C8—N1—C11	58.2 (4)
C4—C5—C6—C12	−179.7 (4)	C9—C8—N1—C7	−175.0 (3)
C2—C1—C6—C5	1.9 (6)	C2—C7—N1—C11	−79.8 (4)
Br1—C1—C6—C5	−178.2 (3)	C2—C7—N1—C8	155.2 (3)
C2—C1—C6—C12	−179.5 (4)	C15—C16—N2—C13	57.9 (4)
Br1—C1—C6—C12	0.3 (5)	C15—C16—N2—C12	−177.0 (3)
C1—C2—C7—N1	165.2 (3)	C14—C13—N2—C16	−58.5 (5)
C3—C2—C7—N1	−17.6 (5)	C14—C13—N2—C12	176.5 (4)
N1—C8—C9—O1	−58.9 (5)	C6—C12—N2—C16	155.2 (3)
O1—C10—C11—N1	57.9 (5)	C6—C12—N2—C13	−82.2 (4)
C5—C6—C12—N2	−11.1 (5)	C26—C27—N3—C24	−56.7 (4)
C1—C6—C12—N2	170.4 (3)	C26—C27—N3—C23	179.0 (3)
N2—C13—C14—O2	59.1 (5)	C25—C24—N3—C27	57.2 (4)
O2—C15—C16—N2	−58.6 (5)	C25—C24—N3—C23	−179.0 (3)
C22—C17—C18—C19	3.4 (5)	C18—C23—N3—C27	−149.3 (3)
Br2—C17—C18—C19	−179.0 (3)	C18—C23—N3—C24	88.1 (4)
C22—C17—C18—C23	−174.2 (3)	C31—C32—N4—C28	−176.4 (3)
Br2—C17—C18—C23	3.3 (5)	C31—C32—N4—C29	60.1 (4)
C17—C18—C19—C20	−1.4 (5)	C22—C28—N4—C32	158.6 (3)
C23—C18—C19—C20	176.2 (3)	C22—C28—N4—C29	−80.2 (4)
C18—C19—C20—C21	−0.9 (6)	C30—C29—N4—C32	−59.9 (4)

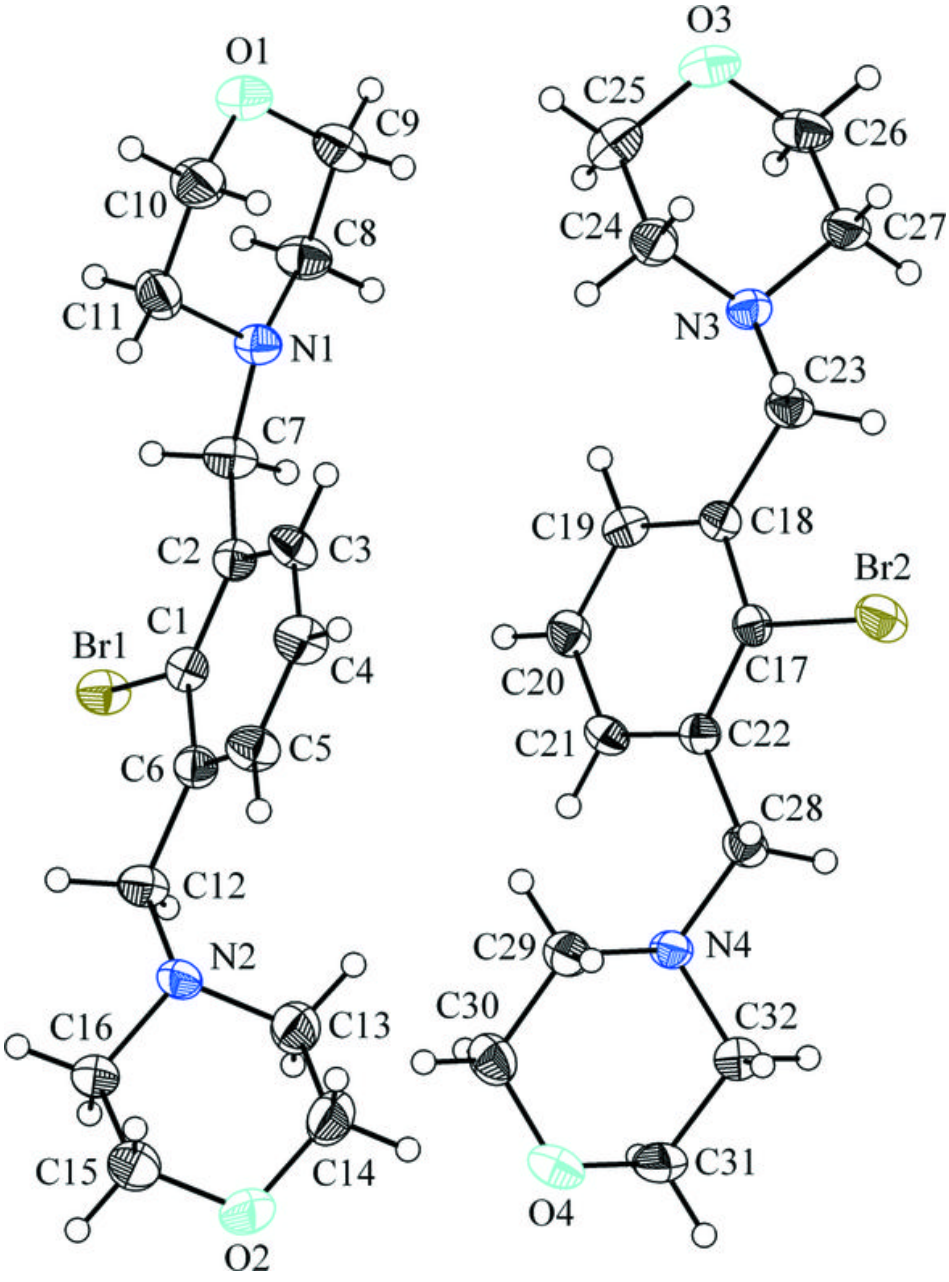
C19—C20—C21—C22	1.4 (6)	C30—C29—N4—C28	177.3 (3)
C20—C21—C22—C17	0.4 (5)	C8—C9—O1—C10	57.5 (5)
C20—C21—C22—C28	−177.3 (3)	C11—C10—O1—C9	−57.3 (5)
C18—C17—C22—C21	−2.9 (5)	C16—C15—O2—C14	57.2 (5)
Br2—C17—C22—C21	179.6 (3)	C13—C14—O2—C15	−57.2 (5)
C18—C17—C22—C28	174.8 (3)	C27—C26—O3—C25	−57.8 (4)
Br2—C17—C22—C28	−2.7 (5)	C24—C25—O3—C26	58.3 (4)
C19—C18—C23—N3	−2.3 (5)	C32—C31—O4—C30	56.6 (5)
C17—C18—C23—N3	175.2 (3)	C29—C30—O4—C31	−56.5 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14A···Br1^{i}	0.97	3.01	3.860 (5)	146

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*.

Fig. 1


O1
C9
C10
C8
C11
N1
C7
C2
C3
C1
Br1
C4
C6
C5
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N2
C16
C13
C15
C14
O2
O3
C25
C26
C24
C27
N3
C23
C19
C18
Br2
C20
C17
C21
C22
C28
C29
N4
C30
C32
C31
O4

Fig. 2

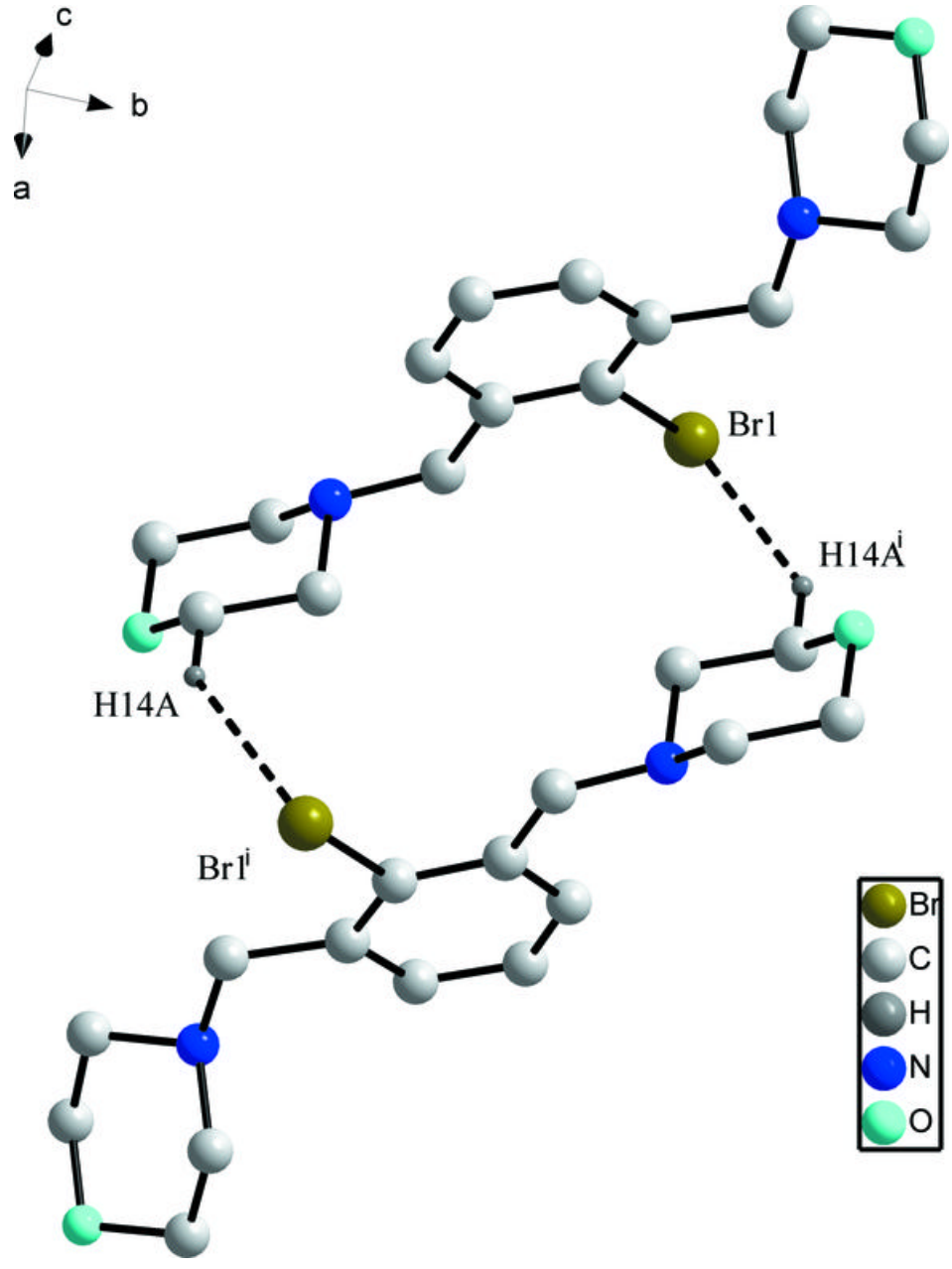

Fig. 3