

(Z)-1,2-Bis(3-bromophenyl)diazene 1-oxide

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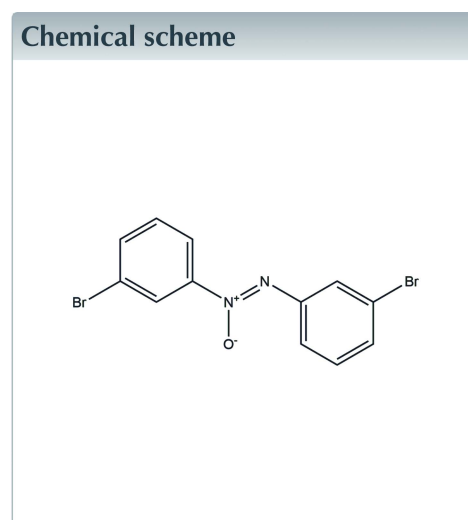
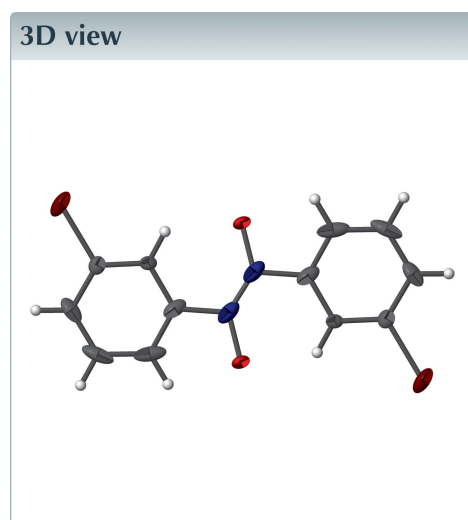
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Keywords: crystal structure; diazene; a doubtful polymorph; hydrogen bonds; π - π stacking.

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Structural data: full structural data are available from iucrdata.iucr.org

The title compound $C_{12}H_8Br_2N_2O$, lies on an inversion centre in the space group $P2_1/n$. Doubts are cast on the report of a polymorph of this structure in the non-centrosymmetric space group $P2_1$ [Zhu, R.-T., Liu, J.-C., Jin, S., Liu, B. & Guo J.-P. (2006). *Hecheng Huaxue (Chin. J. Synth. Chem.)* **14**, 591] as ADDSYM alerts point strongly to a centrosymmetric structure. In the crystal, C—H \cdots O and C—H \cdots Br hydrogen bonds together with offset π - π interactions stack the molecules along the *a*-axis direction.



Structure description

The title azoxybenzene was prepared by the reduction of 1-bromo-3-nitrobenzene. It readily undergoes a benzidine rearrangement to provide a useful precursor for substituted biphenyl diamines (Chen *et al.*, 2011; Li *et al.*, 2012).

The Cambridge Structural Database (CSD, version 5.39, November 2017, with four updates; Groom *et al.*, 2016) reveals what appears to be a polymorph of the title compound, SIYHAK, with data collected at 293 (2) K in the non-centrosymmetric spacegroup $P2_1$ (Zhu *et al.*, 2006). However, the CIF from this deposition generates significant ADDSYM alerts, suggesting that the correct spacegroup is $P2_1/n$ as was found in the refinement reported here. It appears, therefore, that the earlier report is not a polymorph of the structure reported here but that they are in fact the same structures.

The title (*Z*)-diazene derivative, $C_{12}H_8Br_2N_2O$ (I), lies about an inversion centre located at the mid-point of the N1=N1 diazene bond with the oxide O1 atom disordered in equal occupancy about this centre. Each diazene nitrogen atom also carries a 3-bromobenzene ring (Fig. 1). The BrC_6NO half of the molecule is almost planar with an r.m.s. deviation of only 0.0009 Å. Furthermore, the coplanar benzene rings are inclined to the O1/N1/C1 plane by 9.7 (7)°. An intramolecular C2—H2 \cdots O1 hydrogen bond (Table 1) supports this planarity. The N1=N1¹ distance observed here [1.274 (9) Å,

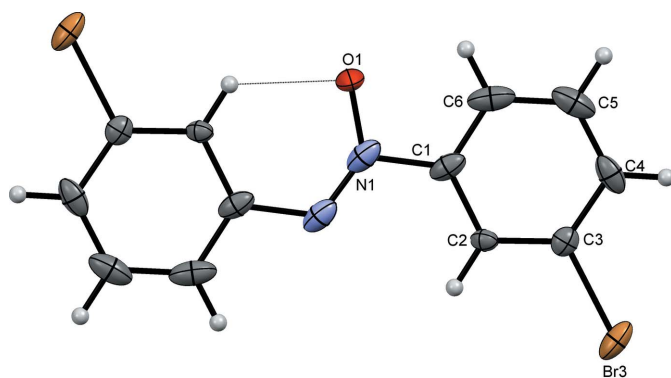


Figure 1
The molecular structure of (I) showing the atom numbering with ellipsoids drawn at the 50% probability level. Labelled atoms are related to unlabelled atoms by the symmetry operation $-x + 1, -y + 1, -z + 1$. An intramolecular hydrogen bond is drawn as a dotted black line. In this and subsequent figures, the equivalent disorder component of the O1 atom is not shown.

symmetry code: (i) $1 - x, 1 - y, 1 - z$] is not strikingly different from those observed in the two unique molecules of the supposed monoclinic polymorph [1.263 (5) and 1.264 (5) Å; Zhu *et al.*, 2006], especially taking into account the significant variation in the temperatures at which the data were collected. Furthermore, this distance is also similar to the mean value, 1.27 (5) Å, observed for the 42 other similar diazene structures found in the CSD. These include the structure of the chloro analogue of (I), (*Z*)-1,2-bis(3-chlorophenyl)diazene 1-oxide (Jose Kavitha *et al.*, 2003).

In the crystal structure, C6–H6···O1 contacts link the molecules into *C*(6) chains along the *b*-axis direction and combine with weaker C4–H4···Br3 hydrogen bonds that form *C*(12) chains, generating sheets of molecules along the *ac* diagonal (Table 1, Fig. 2). Offset π – π stacking interactions with centroid-to-centroid distances of 3.894 (3) Å occur between adjacent bromobenzene rings, generating a three-dimensional network of molecules stacked along the *a*-axis direction (Fig. 3).

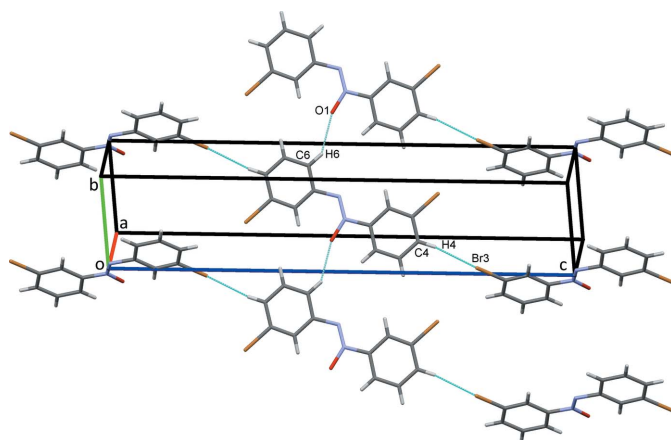


Figure 2
Sheets of molecules of (I) with hydrogen bonds shown as blue dashed lines.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C2–H2···O1 ⁱ	0.95	2.07	2.722 (7)	124
C6–H6···O1 ⁱⁱ	0.95	2.39	3.199 (8)	143
C4–H4···Br3 ⁱⁱⁱ	0.95	3.11	3.974 (5)	151

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₈ Br ₂ N ₂ O
<i>M_r</i>	356.02
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Temperature (K)	90
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.8938 (2), 5.8223 (3), 25.8645 (16)
β (°)	92.044 (5)
<i>V</i> (Å ³)	586.00 (6)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	8.65
Crystal size (mm)	0.38 × 0.19 × 0.08
Data collection	
Diffractometer	Agilent SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2014)
<i>T_{min}</i> , <i>T_{max}</i>	0.334, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3440, 1171, 1128
<i>R_{int}</i>	0.036
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.626
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.137, 1.00
No. of reflections	1171
No. of parameters	82
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.85, -0.99

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *TITAN* (Hunter & Simpson, 1999), *Mercury* (Macrae *et al.*, 2008), *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009), *pubCIF* (Westrip 2010) and *WinGX* (Farrugia, 2012).

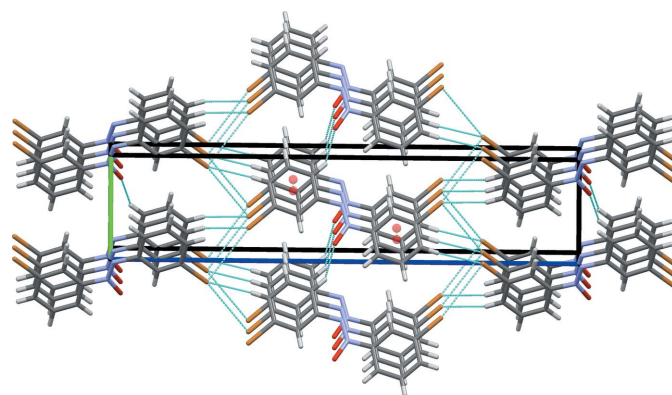


Figure 3
Overall packing of (I) viewed along the *a*-axis direction. Representative π – π contacts are shown as dotted green lines with ring centroids drawn as red spheres.

Synthesis and crystallization

The title compound was synthesized from 1-bromo-3-nitrobenzene following a literature procedure (Chen *et al.*, 2011). Crystals suitable for the X-ray analysis were grown by evaporation from diethyl ether solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The molecule of (I) lies about an inversion centre located at the midpoint of the N1=N1 bond with the oxide O1 atom disordered in equal occupancy about this centre.

Funding information

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References

- Agilent (2014). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Chen, J.-C., Liu, Y.-C., Ju, J.-J., Chiang, C.-J. & Chern, Y.-T. (2011). *Polymer*, **52**, 954–964.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hunter, K. A. & Simpson, J. (1999). *TITAN2000*. University of Otago, New Zealand.
- Jose Kavitha, S., Chandrasekar, S. & Panchanatheswaran, K. (2003). *Acta Cryst.* **E59**, o947–o949.
- Li, Y., Chu, Y., Fang, R., Ding, S., Wang, Y., Shen, Y. & Zheng, A. (2012). *Polymer*, **53**, 229–240.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zhu, R.-T., Liu, J.-C., Jin, S., Liu, B. & Guo, J.-P. (2006). *Hecheng Huaxue*, **14**, 591–593.

full crystallographic data

IUCrData (2018). 3, x181486 [https://doi.org/10.1107/S2414314618014864]

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(Z)-1,2-Bis(3-bromophenyl)diazene 1-oxide*Crystal data*

$C_{12}H_8Br_2N_2O$

$M_r = 356.02$

Monoclinic, $P2_1/n$

$a = 3.8938$ (2) Å

$b = 5.8223$ (3) Å

$c = 25.8645$ (16) Å

$\beta = 92.044$ (5)°

$V = 586.00$ (6) Å³

$Z = 2$

$F(000) = 344$

$D_x = 2.018$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 2305 reflections

$\theta = 7.6$ – 74.4 °

$\mu = 8.65$ mm⁻¹

$T = 90$ K

Plate, yellow

$0.38 \times 0.19 \times 0.08$ mm

Data collection

Agilent SuperNova, Dual, Cu at zero, Atlas diffractometer

Radiation source: SuperNova (Cu) X-ray Source

Detector resolution: 5.1725 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)

$T_{\min} = 0.334$, $T_{\max} = 1.000$

3440 measured reflections

1171 independent reflections

1128 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 74.9$ °, $\theta_{\min} = 6.9$ °

$h = -4 \rightarrow 4$

$k = -7 \rightarrow 5$

$l = -31 \rightarrow 30$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.137$

$S = 1.00$

1171 reflections

82 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0939P)^2 + 2.3574P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.85$ e Å⁻³

$\Delta\rho_{\min} = -0.99$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.224 (2)	0.2546 (11)	0.4785 (2)	0.0334 (16)	0.5
N1	0.4136 (12)	0.4117 (7)	0.50608 (16)	0.0311 (9)	
C1	0.3955 (13)	0.3550 (8)	0.56013 (19)	0.0275 (10)	
C2	0.5144 (10)	0.4990 (6)	0.60040 (15)	0.0184 (8)	
H2	0.618227	0.642861	0.593489	0.022*	

C3	0.4750 (11)	0.4241 (7)	0.65016 (17)	0.0211 (8)
Br3	0.63666 (13)	0.61575 (9)	0.70533 (2)	0.0335 (3)
C4	0.3228 (12)	0.2162 (8)	0.6618 (2)	0.0321 (11)
H4	0.298842	0.170406	0.696715	0.038*
C5	0.2071 (14)	0.0774 (8)	0.6218 (3)	0.0407 (14)
H5	0.102440	-0.065852	0.629059	0.049*
C6	0.2435 (14)	0.1471 (8)	0.5705 (3)	0.0391 (14)
H6	0.163488	0.051244	0.542931	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.049 (4)	0.030 (3)	0.020 (3)	-0.021 (3)	-0.008 (3)	-0.003 (2)
N1	0.036 (2)	0.0327 (19)	0.024 (2)	0.0138 (16)	-0.0080 (17)	-0.0113 (15)
C1	0.025 (2)	0.028 (2)	0.029 (2)	0.0114 (18)	-0.0094 (18)	-0.0117 (17)
C2	0.020 (2)	0.0133 (17)	0.0217 (19)	0.0007 (14)	-0.0023 (15)	-0.0010 (14)
C3	0.018 (2)	0.0245 (19)	0.021 (2)	0.0052 (16)	0.0023 (15)	-0.0020 (15)
Br3	0.0287 (4)	0.0520 (4)	0.0192 (4)	0.0121 (2)	-0.0056 (2)	-0.01095 (18)
C4	0.026 (2)	0.024 (2)	0.047 (3)	0.0106 (18)	0.0119 (19)	0.019 (2)
C5	0.021 (3)	0.0147 (19)	0.087 (5)	-0.0004 (17)	0.008 (3)	0.006 (2)
C6	0.022 (2)	0.025 (2)	0.069 (4)	0.0057 (18)	-0.013 (2)	-0.022 (2)

Geometric parameters (Å, °)

O1—N1	1.360 (7)	C3—C4	1.385 (6)
N1—N1 ⁱ	1.274 (9)	C3—Br3	1.901 (4)
N1—C1	1.440 (7)	C4—C5	1.375 (9)
C1—C6	1.378 (8)	C4—H4	0.9500
C1—C2	1.403 (6)	C5—C6	1.399 (10)
C2—C3	1.373 (6)	C5—H5	0.9500
C2—H2	0.9500	C6—H6	0.9500
N1 ⁱ —N1—O1	134.0 (6)	C4—C3—Br3	118.9 (4)
N1 ⁱ —N1—C1	118.0 (5)	C5—C4—C3	118.8 (5)
O1—N1—C1	108.0 (5)	C5—C4—H4	120.6
C6—C1—C2	120.8 (5)	C3—C4—H4	120.6
C6—C1—N1	115.3 (4)	C4—C5—C6	120.0 (4)
C2—C1—N1	123.9 (4)	C4—C5—H5	120.0
C3—C2—C1	117.5 (4)	C6—C5—H5	120.0
C3—C2—H2	121.3	C1—C6—C5	119.9 (5)
C1—C2—H2	121.3	C1—C6—H6	120.0
C2—C3—C4	122.9 (4)	C5—C6—H6	120.0
C2—C3—Br3	118.2 (3)		
N1 ⁱ —N1—C1—C6	-172.0 (5)	C1—C2—C3—Br3	179.7 (3)
O1—N1—C1—C6	9.0 (6)	C2—C3—C4—C5	0.3 (7)
N1 ⁱ —N1—C1—C2	9.4 (8)	Br3—C3—C4—C5	-179.8 (4)
O1—N1—C1—C2	-169.6 (5)	C3—C4—C5—C6	-0.1 (7)

C6—C1—C2—C3	0.4 (6)	C2—C1—C6—C5	-0.1 (7)
N1—C1—C2—C3	178.9 (4)	N1—C1—C6—C5	-178.8 (4)
C1—C2—C3—C4	-0.5 (6)	C4—C5—C6—C1	0.0 (7)

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
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Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1/2, y-1/2, -z+3/2$.