

trans-1,2-Bis(3-chlorophenyl)diazene oxide

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Key indicators

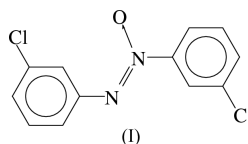
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in main residue
R factor = 0.048
wR factor = 0.140
Data-to-parameter ratio = 12.5

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title molecule, $\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_2\text{O}$, lacks a centre of symmetry. However, as a result of the positional disorder of the O atom, molecules of the title compound lie across a crystallographic inversion centre in the centrosymmetric space group $P2_1/n$. The *trans* orientation of the aromatic rings around the $\text{N}=\text{N}$ bond is confirmed.

Comment

Diazene oxide derivatives, commonly known as azoxybenzenes, are useful in the preparation of liquid crystals (Tsuji *et al.*, 2000). They are also used as ligands in coordination chemistry (Bassi & Scordamaglia, 1975). They are photochemically active (Rhee & Jaffe, 1973), like the related azo (Tamai & Miyasika, 2000) and nitron derivatives (Hamer & Macaluso, 1964). Preparation of non-centrosymmetric azoxybenzene derivatives will be of interest for the study of their non-linear optical properties (Long, 1995) because of electron delocalization within the molecule. The structures of *para*-substituted azoxybenzenes are known, and most of them assume *trans* configurations of the benzene ring around the $\text{N}=\text{N}$ bond in the solid state (Ej-smont *et al.*, 2000). During our investigations of the use of tin(II) chloride for the reductive coupling of nitro compounds with aldehydes and ketones, the title compound, (I), was isolated. The structure determination was undertaken to assign its configuration and the space-group symmetry.



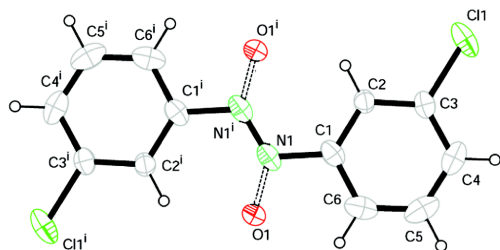
Although the molecule lacks a centre of symmetry, it lies across the inversion centre in the centrosymmetric space group $P2_1/n$, due to the positional disorder of the O atom. The asymmetric unit therefore consists of one half of the title molecule. Furthermore, the molecule adopts a thermodynamically stable configuration in which the two chlorophenyl groups are oriented *trans* with respect to the $\text{N}=\text{N}$ bond.

The C–C bond lengths in the chlorophenyl groups vary from 1.368 (6) to 1.384 (5) Å. The $\text{N}=\text{N}$ [1.267 (5) Å] bond distance is comparable to the corresponding bond distance of 1.27 Å observed in *trans* azoxybenzene through electron diffraction studies. The computed values for the above bond in the same molecule is 1.232 Å at the RHF/6–31G** level of calculations (Tsuji *et al.*, 2000). The $\text{N}=\text{N}$ bond distance in

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Figure 1

The molecular structure of the title compound, showing 30% probability displacement ellipsoids for non-H atoms. The O atom is disordered over two inversion-related positions, O1 and O1ⁱ [symmetry code: (i) 1 - x, 1 - y, 1 - z].

5,5'-dichloro-2-hydroxy-2'-(phenylsulfonyl)azoxybenzene is 1.31 (1) Å (Cameron *et al.*, 1976), which is different from that in the title compound. As a consequence of disorder in the title molecule, the N—O and C—N distances are elongated compared to the corresponding distances of 1.27 (1) Å and 1.43 (1) Å in *p*-azoxyanisole (Krigbaum *et al.*, 1970).

In the crystal structure, the inversion-related molecules are linked by C6—H6···O1(2 - x, 2 - y, 1 - z) hydrogen bonds (Table 2) involving the disordered O atom, to form molecular chains along [110].

Experimental

The compound was formed by the reduction of 1-chloro-3-nitrobenzene (2.0 g) by tin(II) chloride (2.5 g) in tetrahydrofuran. The product was isolated by the addition of dilute hydrochloric acid followed by extraction with diethyl ether. Yield was 45.5%. Diffraction quality crystals were obtained by recrystallization of the crude product in hexane.

Crystal data

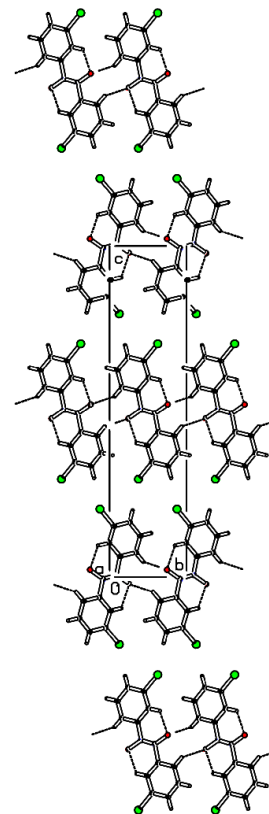
C ₁₂ H ₈ Cl ₂ N ₂ O	$D_x = 1.521 \text{ Mg m}^{-3}$
$M_r = 267.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 1179 reflections
$a = 3.911 (5) \text{ \AA}$	$\theta = 3.2\text{--}24.6^\circ$
$b = 5.893 (5) \text{ \AA}$	$\mu = 0.54 \text{ mm}^{-1}$
$c = 25.367 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 94.155 (5)^\circ$	Block, pale yellow
$V = 583.1 (9) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.015$
ω -2 θ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 4$
$T_{\text{min}} = 0.813$, $T_{\text{max}} = 0.898$	$k = 0 \rightarrow 7$
1179 measured reflections	$l = -30 \rightarrow 30$
1021 independent reflections	3 standard reflections every 100 reflections
807 reflections with $I > 2\sigma(I)$	intensity decay: negligible

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 0.337P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.140$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
1021 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
82 parameters	
H-atom parameters constrained	


Figure 2

Packing of the molecules, viewed down the *a* axis, showing the chain formation.

Table 1

Selected geometric parameters (Å, °).

C11—C3	1.735 (3)	C1—C6	1.384 (5)
O1—N1	1.367 (5)	C2—C3	1.373 (4)
N1—N1 ⁱ	1.267 (5)	C3—C4	1.381 (5)
N1—C1	1.449 (4)	C4—C5	1.368 (6)
C1—C2	1.383 (4)	C5—C6	1.372 (6)
N1 ⁱ —N1—O1	134.6 (3)	C2—C3—C4	121.6 (3)
N1 ⁱ —N1—C1	117.7 (3)	C2—C3—C11	118.8 (2)
O1—N1—C1	107.7 (3)	C4—C3—C11	119.6 (2)
C2—C1—C6	120.7 (3)	C5—C4—C3	118.9 (3)
C2—C1—N1	124.5 (3)	C4—C5—C6	121.0 (3)
C6—C1—N1	114.8 (3)	C5—C6—C1	119.3 (3)
C3—C2—C1	118.4 (3)		
N1 ⁱ —N1—C1—C2	-6.4 (5)	N1 ⁱ —N1—C1—C6	174.1 (3)
O1—N1—C1—C2	172.5 (3)	O1—N1—C1—C6	-7.0 (4)

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

Table 2

Hydrogen-bonding 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	0.93	2.08	2.735 (6)	126
C6—H6···O1	0.93	2.05	2.450 (7)	104
C6—H6···O1 ⁱⁱ	0.93	2.48	3.271 (7)	144

Symmetry codes: (i) 1 - x, 1 - y, 1 - z; (ii) 2 - x, 2 - y, 1 - z.

The O atom is disordered over two centrosymmetrically-related positions, O1 and O1ⁱ [symmetry code: (i) 1 - x, 1 - y, 1 - z]. H atoms were placed in geometrical positions and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MoLEN* (Fair, 1990); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1983).

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