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The crystal structure of 2-(4-chloro-6-nitrophenyl)-1-(4-chloro-3-nitrophenyl)diazene 1-oxide, $C_{12}H_6Cl_2N_4O_5$

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Abstract

$C_{12}H_6Cl_2N_4O_5$, monoclinic, $P2_1/c$ (no. 14), $a = 11.4268(16)$ Å, $b = 5.1250(8)$ Å, $c = 23.569(4)$ Å, $\beta = 91.738(6)^\circ$, $V = 1379.62(40)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0555$, $wR_{ref}(F^2) = 0.1632$, $T = 100$ K.

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The title molecular structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

An amount of 17.5 g of manganese(IV) dioxide was added to 140 mL of toluene at room temperature. Addition of 5 g of 4-chloroaniline was done with stirring for 10 min. The reaction takes place at 110° for 6 h. After the reaction, the reaction solution (25°) was washed with several volumes of toluene, and the filtrate was evaporated to give 1,2-bis(4-chlorophenyl) diazene (1) (3 g).

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Table 1: Data collection and handling.

Crystal:	Needle, colorless
Size:	0.08 × 0.04 × 0.02 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.50 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{max} , completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	13102, 3160, 0.083
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2159
$N(param)_{refined}$:	208
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Cl1	0.75384(8)	1.37305(18)	0.60943(4)	0.0272(2)
Cl2	−0.07410(8)	−0.18693(19)	0.65590(4)	0.0295(3)
O1	0.4785(2)	1.4111(5)	0.71470(11)	0.0320(6)
O2	0.6646(2)	1.3235(6)	0.72567(12)	0.0413(8)
O3	0.3692(2)	0.4381(5)	0.55879(10)	0.0246(6)
O4	0.1593(2)	0.7025(5)	0.52866(10)	0.0252(6)
O5	0.1094(2)	0.3319(5)	0.48992(10)	0.0262(6)
N1	0.5692(3)	1.3053(6)	0.70027(12)	0.0258(7)
N2	0.3636(2)	0.6114(6)	0.59636(12)	0.0197(6)
N3	0.2841(2)	0.6385(6)	0.63281(12)	0.0218(6)
N4	0.1341(2)	0.4705(6)	0.53126(11)	0.0207(6)
C1	0.5604(3)	1.1362(7)	0.65026(14)	0.0209(7)
C2	0.6427(3)	1.1484(7)	0.60794(15)	0.0218(7)
C3	0.6304(3)	0.9843(7)	0.56169(15)	0.0238(8)
H3	0.685123	0.992964	0.532181	0.029*
C4	0.5390(3)	0.8071(7)	0.55801(15)	0.0213(7)
H4	0.531694	0.690815	0.526708	0.026*
C5	0.4583(3)	0.8021(7)	0.60070(14)	0.0187(7)
C6	0.4666(3)	0.9659(7)	0.64676(14)	0.0203(7)
H6	0.409781	0.962321	0.675330	0.024*
C7	0.1974(3)	0.4385(7)	0.63311(14)	0.0206(7)
C8	0.1782(3)	0.3328(8)	0.68652(15)	0.0269(8)
H8	0.221852	0.396386	0.718569	0.032*
C9	0.0972(3)	0.1378(8)	0.69359(15)	0.0272(8)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H9	0.087130	0.061977	0.729896	0.033*
C10	0.0301(3)	0.0531(7)	0.64692(15)	0.0226(8)
C11	0.0443(3)	0.1577(7)	0.59385(14)	0.0211(7)
H11	−0.002026	0.098765	0.562250	0.025*
C12	0.1278(3)	0.3508(7)	0.58743(14)	0.0187(7)

The title compound was prepared in a second step by nitrifying the aforementioned diazene. 3 g of powdered 1,2-bis(4-chlorophenyl)diazene is added to 8 mL of nitric acid (98%) below 10° and stirred for 15 min. The reaction was completed at 85° for 4 h. The reaction solution (25°) was poured into ice water. A pale yellow solid was collected, washed and dried.

The title compound was obtained by column chromatography. At room temperature in ethanol solvent crystallization was performed to obtain crystals.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Nitroazobenzene compounds are very important intermediates of heat-resistant explosives and have a lot of derivatives [4]. Therefore the exploration of new nitrobenzene compounds with heat-resistant properties are of interest [3, 5, 6]. The title compound, as a promising mid product, is synthesized by the nitration of 1,2-bis(4-chlorophenyl)diazene, soluble in ethanol or acetone but insoluble in water.

As shown in the figure the crystal structure of the title compound revealed that there is a nitro group at the benzene ring where H8 is. Compared with 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro)diazene oxide [7], the angle of the title compound between the two aryl moieties is 40.2°. However, in the literature structure [7] they are approximately parallel to each other. The two nitro groups are attached to C(1) and C(12), respectively. And the dihedral angles with the aryl ring are 31.6°, 43.3°, 49.4°, 72.8°, respectively.

The bond lengths of the two chlorines with the benzene ring were 1.71 and 1.73, respectively. These were different than 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro-3-nitrophenyl)diazene 1-oxide [8]. This is because the two molecules contain different amounts of nitro groups. The bond length of C1–N1 and C12–N4 is 1.46 and 1.46, respectively. Because the halogen atom has a smaller steric hindrance than the nitro group [9]. A very closely related structure was reported recently [10].

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