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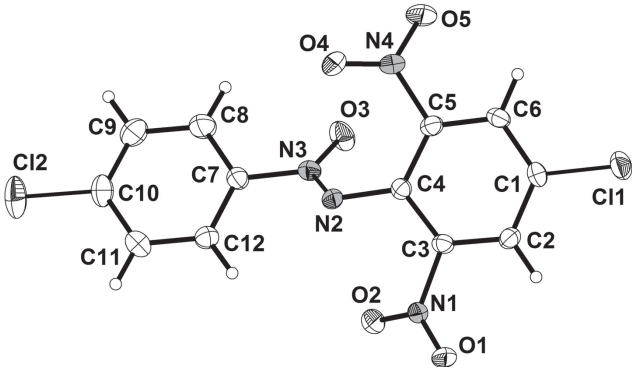
The crystal structure of 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro)diazene oxide, $C_{12}H_6Cl_2N_4O_5$



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Abstract

$C_{12}H_6Cl_2N_4O_5$, triclinic, $P\bar{1}$ (no. 2), $a = 8.1022(14)$ Å, $b = 9.6916(17)$ Å, $c = 10.2476(17)$ Å, $\alpha = 78.346(4)°$, $\beta = 68.657(4)°$, $\gamma = 71.167(4)°$, $V = 706.1(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0356$, $wR_{ref}(F^2) = 0.1109$, $T = 120$ K.

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The asymmetric unit of the title crystal 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

To a mechanically stirred suspension of 4-chloroaniline (8.50 g) in toluene (233.3 mL) was added manganese(IV) dioxide (28.97 g). The mixture was refluxed for 8 h and then filtered through Celite. The filter cake was washed

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.29 × 0.15 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.49 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.4°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6603, 2820, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2440
$N(param)_{refined}$:	208
Programs:	Bruker [1], SHELX [2, 3]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cl1	0.93895(6)	−0.00835(5)	0.73292(4)	0.02365(15)
Cl2	0.28449(8)	0.93466(6)	−0.10383(5)	0.04127(19)
O1	0.35073(16)	0.11942(15)	0.58530(14)	0.0250(3)
O2	0.42850(18)	0.22119(15)	0.37129(14)	0.0266(3)
O3	0.84837(16)	0.39266(16)	0.16344(14)	0.0276(3)
O4	0.81352(18)	0.57460(15)	0.37067(15)	0.0278(3)
O5	1.08170(19)	0.42651(18)	0.35842(19)	0.0415(4)
N1	0.44980(19)	0.18154(16)	0.48640(16)	0.0190(3)
N2	0.58402(19)	0.42812(17)	0.34785(15)	0.0177(3)
N3	0.68088(19)	0.45349(17)	0.22023(15)	0.0184(3)
N4	0.9145(2)	0.45351(18)	0.38889(17)	0.0232(4)
C1	0.8376(2)	0.1187(2)	0.62031(18)	0.0182(4)
C2	0.6817(2)	0.1057(2)	0.60318(18)	0.0181(4)
H2	0.6270	0.0296	0.6551	0.022*
C3	0.6072(2)	0.20631(19)	0.50844(18)	0.0167(4)
C4	0.6786(2)	0.32253(19)	0.43103(17)	0.0160(4)
C5	0.8335(2)	0.3314(2)	0.45684(18)	0.0178(4)
C6	0.9154(2)	0.2312(2)	0.54697(18)	0.0188(4)
H6	1.0230	0.2392	0.5585	0.023*
C7	0.5846(2)	0.5679(2)	0.13686(18)	0.0190(4)
C8	0.6813(3)	0.6552(2)	0.0350(2)	0.0293(5)
H8	0.8098	0.6378	0.0163	0.035*
C9	0.5881(3)	0.7687(3)	−0.0395(2)	0.0339(5)
H9	0.6512	0.8319	−0.1087	0.041*
C10	0.4017(3)	0.7895(2)	−0.0126(2)	0.0269(4)
C11	0.3068(2)	0.6979(2)	0.0858(2)	0.0244(4)
H11	0.1800	0.7116	0.1004	0.029*
C12	0.3987(2)	0.5861(2)	0.16272(18)	0.0202(4)
H12	0.3358	0.5228	0.2320	0.024*

with several volumes of toluene, and the filtrate was evaporated to give 1,2-bis(4-chlorophenyl)diazene (3.20 g).

The title compound was prepared in a second step by nitrifying the aforementioned 1,2-bis(4-chlorophenyl) diazene,2-bis(4-chlorophenyl)diazene. 3 g of powdered 1, 2-bis(4-chlorophenyl)diazene is added to 98% nitric acid (8.0 mL). The reaction was slowly heated to 293.15 K, and held there for 4 h with constant stirring. The mixture was poured into deionized water and filtered at room temperature. The product was dried under vacuum drying oven and a yellow solid 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro)diazene oxide was obtained. Colorless transparent crystals were obtained by slow evaporation from an ethyl acetate solution in a quiet environment at room temperature.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. All the non-hydrogen atoms were refined anisotropically.

Comment

Nitroazobenzene systems have been investigated extensively owing to their detonation performance [4–6]. Recently, these so called “high energy density materials” have attracted renewed attention in conjunction with their favorable detonation performance [7–10]. As a promising mid product, 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro)diazene oxide was synthesized by the nitration of 1,2-bis(4-chlorophenyl)diazene. Here we report the crystal structure of the title compound (the figure), as part of our continuing interest in nitro compounds [11].

In the title crystal structure 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro)diazene oxide molecules are present in pairs. The two molecules are approximately parallel to each other. Owing to space steric effect, the dihedral angle of the two nitro groups and the aryl ring are 27.3° and 36.5°, respectively.

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