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The crystal structure of 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro-3,5-dinitrophenyl) diazene 1-oxide, $C_{12}H_4Cl_2N_6O_9$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.23 × 0.21 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.47 mm ⁻¹
Diffractometer, scan mode:	PHOTON 100 CMOS, ω -scans
$\theta_{\max}$, completeness:	25.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16784, 5924, 0.054
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 44283
$N(\text{param})_{\text{refined}}$:	523
Programs:	Bruker programs [1], SHELX [2, 3]

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Abstract

$C_{12}H_4Cl_2N_6O_9$, monoclinic, $C2/c$ (no. 15), $a = 50.136(3)$ Å, $b = 8.1074(5)$ Å, $c = 15.9816(11)$ Å, $\beta = 91.927(2)^\circ$, $V = 6492.4(7)$ Å³, $Z = 16$, $R_{\text{gt}}(F) = 0.0427$, $wR_{\text{ref}}(F^2) = 0.0969$, $T = 173(2)$ K.

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One of the two crystallographically independent title molecules is shown in the figure. Tables 1 and 2 contain details on measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a stirred suspension of 4-chloroaniline (8.50 g) in toluene (233.33 mL) was added manganese(IV) dioxide (28.97 g).

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1A	0.22933(4)	0.7533(2)	0.13873(13)	0.0261(5)
O2A	0.10185(5)	0.4890(4)	0.17507(16)	0.0545(8)
O3A	0.13100(5)	0.3029(3)	0.20785(14)	0.0417(6)
O4A	0.16121(6)	0.6386(3)	−0.13086(14)	0.0540(7)
O5A	0.14760(6)	0.8704(4)	−0.08457(16)	0.0598(8)
O6A	0.29196(5)	0.6329(4)	0.11404(14)	0.0610(9)
O7A	0.25941(4)	0.4593(3)	0.11086(12)	0.0308(5)
O8A	0.20051(4)	0.6792(3)	0.35871(14)	0.0392(6)
O9A	0.21735(4)	0.5486(3)	0.46613(14)	0.0425(6)
O1B	0.95327(4)	0.3045(3)	0.24551(12)	0.0329(5)
O2B	0.87693(4)	−0.1948(3)	−0.01900(13)	0.0300(5)
O3B	0.91943(4)	−0.1897(3)	−0.03548(13)	0.0329(5)
O4B	0.89251(4)	−0.0934(3)	0.37174(13)	0.0344(5)
O5B	0.85526(4)	−0.0897(3)	0.29932(14)	0.0365(6)
O6B	0.95376(4)	0.7545(3)	0.19408(13)	0.0323(5)
O7B	0.93411(4)	0.5627(3)	0.12148(15)	0.0406(6)
O8B	1.00398(5)	0.0643(3)	0.13355(16)	0.0459(6)
O9B	1.02383(4)	0.1210(3)	0.01829(15)	0.0365(6)
N1A	0.21515(4)	0.6396(3)	0.16596(14)	0.0174(5)
N2A	0.22098(4)	0.5420(3)	0.22598(14)	0.0195(5)
N3A	0.12375(5)	0.4306(3)	0.17325(15)	0.0297(6)
N4A	0.15532(5)	0.7326(3)	−0.07549(16)	0.0266(6)
N5A	0.27425(5)	0.5568(3)	0.14686(15)	0.0272(6)
N6A	0.21858(5)	0.6068(3)	0.39649(15)	0.0258(6)
N1B	0.94919(4)	0.2392(3)	0.17577(14)	0.0178(5)
N2B	0.96142(5)	0.2703(3)	0.10942(14)	0.0219(6)
N3B	0.89958(5)	−0.1634(3)	0.00462(14)	0.0196(5)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
N4B	0.87943(5)	−0.0786(3)	0.30656(15)	0.0228(6)
N5B	0.95392(5)	0.6286(3)	0.15257(15)	0.0222(6)
N6B	1.01215(5)	0.1600(3)	0.08119(17)	0.0274(6)
Cl1A	0.10813(2)	0.57844(9)	−0.00203(5)	0.02560(18)
Cl2A	0.32000(2)	0.64070(10)	0.43496(5)	0.0298(2)
Cl1B	0.86541(2)	−0.28033(10)	0.15009(5)	0.0308(2)
Cl2B	1.05268(2)	0.73773(9)	0.10846(5)	0.02625(18)
C1A	0.13861(5)	0.5902(3)	0.04922(16)	0.0163(6)
C2A	0.14421(5)	0.5197(3)	0.12720(17)	0.0178(6)
C3A	0.16927(5)	0.5303(3)	0.16593(17)	0.0173(6)
H3A	0.1730	0.4790	0.2185	0.021*
C4A	0.18864(5)	0.6174(3)	0.12609(16)	0.0157(6)
C5A	0.18441(5)	0.6884(3)	0.04844(17)	0.0190(6)
H5A	0.1981	0.7480	0.0219	0.023*
C6A	0.15942(5)	0.6688(3)	0.01112(16)	0.0175(6)
C7A	0.29165(5)	0.6196(3)	0.37139(17)	0.0182(6)
C8A	0.29389(5)	0.6067(4)	0.28557(18)	0.0215(7)
H8A	0.3108	0.6139	0.2607	0.026*
C9A	0.27092(6)	0.5830(4)	0.23693(17)	0.0197(6)
C10A	0.24547(5)	0.5781(3)	0.26960(16)	0.0158(6)
C11A	0.24464(5)	0.5970(3)	0.35597(17)	0.0176(6)
C12A	0.26713(5)	0.6145(3)	0.40753(17)	0.0192(6)
H12A	0.2657	0.6229	0.4665	0.023*
C1B	0.88857(5)	−0.1256(3)	0.15552(17)	0.0173(6)
C2B	0.90384(5)	−0.0832(3)	0.08700(16)	0.0166(6)
C3B	0.92360(5)	0.0350(3)	0.09233(16)	0.0161(6)
H3B	0.9337	0.0617	0.0450	0.019*
C4B	0.92837(5)	0.1132(3)	0.16758(17)	0.0157(6)
C5B	0.91428(5)	0.0751(3)	0.23775(17)	0.0170(6)
H5B	0.9181	0.1287	0.2897	0.020*
C6B	0.89455(5)	−0.0430(3)	0.23029(17)	0.0181(6)
C7B	1.02603(5)	0.6043(3)	0.11146(16)	0.0168(6)
C8B	1.00133(5)	0.6625(3)	0.13406(16)	0.0169(6)
H8B	0.9990	0.7752	0.1483	0.020*
C9B	0.98009(5)	0.5546(3)	0.13563(16)	0.0165(6)
C10B	0.98240(5)	0.3874(3)	0.11764(16)	0.0170(6)
C11B	1.00778(6)	0.3365(3)	0.09622(17)	0.0193(6)
C12B	1.02947(5)	0.4402(3)	0.09115(16)	0.0186(6)
H12B	1.0463	0.4000	0.0742	0.022*

The mixture was refluxed for 8 h and then filtered through Celite. The filter cake was washed with toluene, and the filtrate was evaporated to give 1,2-bis(4-chlorophenyl)diazene (3.20 g).

The acid nitration mixture was made up and cooled to 283 K; it consists of 465 mL of 96% sulfuric acid, 672 mL of 90% fuming nitric acid. Over a fifteen minutes period, 3 g of 1,2-bis(4-chlorophenyl)diazene was added to the stirred acid mixture, keeping the reaction temperature below 283 K. The reaction was slowly heated to 393 K and held there for 4 h with constant stirring. The mixture was poured into deionized

water and filtered. The product was dried under vacuum and a yellow solid was obtained. The colourless transparent crystals were obtained by slow evaporation from acetone at room temperature.

Experimental details

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

Discussion

Polynitroaryl compounds play an important role in energetic material area [4]. Nitroazobenzene systems have been investigated extensively owing to their detonation performance [5–7]. Recently, these so called “high energy density materials” have attracted renewed attention in conjunction with their favorable detonation performance [8–11]. As a promising mid product, 2-(4-chloro-2,6-dinitrophenyl)-1-(4-chloro-3,5-dinitrophenyl)diazene 1-oxide was synthesized by the nitration of 1,2-bis(4-chlorophenyl)diazene. Here we report the crystal structure of the title compound (*cf.* the figure).

As shown in the figure two substituted phenyl moieties exist in the molecule. The dihedral angle between these rings is 59.5° due a rotation about the C–N bonds. Owing to space steric effect, the dihedral angle of the four nitro groups and benzene rings are 28.1 (N5B/O6B,O7B), 37.6 (N3B/O2B,O3B), 44.6 (N4B/O4B,O5B) and 49.2 (N6B/O8B,O9B)°, respectively.

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