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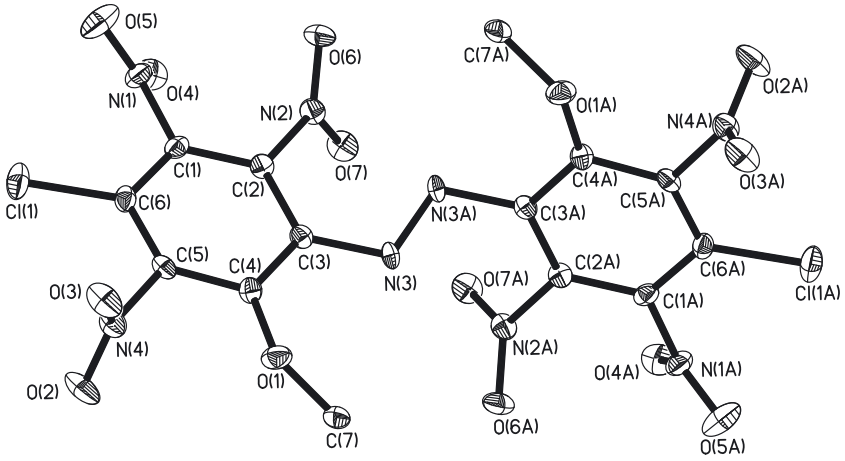
The crystal structure of 4,4′-dichloro-6,6′-dimethoxy-2,2′,3,3′,5,5′-hexanitroazobenzene, $C_{14}H_6N_8O_{14}Cl_2$



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Abstract

$C_{14}H_6N_8O_{14}Cl_2$, orthorhombic, *Fdd*2 (no. 43), a = 21.2891(12) Å, b = 39.532(3) Å, c = 5.1686(3) Å, V = 4349.9(4) Å^3, Z = 8, $R_{gt}(F)$ = 0.0469, w$R_{ref}(F^2)$ = 0.1051, T = 140 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red needle
Size:	0.12 × 0.05 × 0.02 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.39 mm^{-1}
Diffractometer, scan mode:	D8 VENTURE, φ and ω
θ_{max}, completeness:	26.4°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5374, 1917, 0.052
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1515
$N(param)_{refined}$:	173
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

At 298 K, 0.5 g of 4-chloro-3,5-dinitroaniline was added to 11.25 mL concentrated sulfuric acid and 0.8 mL fuming nitric acid. The temperature increased slowly to 363 K and reacted for 2 h. After the reaction, the temperature droped to room temperature. The reaction solution was added to ice water and filtered to get a crude yellow product. The product was separated by column chromatography with methanol as eluent. Finally, needle yellow crystals were obtained by evaporation at room temperature.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3916 (3)	0.57762 (16)	0.3614 (12)	0.0234 (15)
C2	0.4344 (3)	0.55179 (16)	0.3430 (12)	0.0225 (14)
C3	0.4270 (3)	0.52106 (16)	0.4752 (12)	0.0232 (14)
C4	0.3729 (3)	0.51667 (17)	0.6273 (12)	0.0251 (15)
C5	0.3313 (3)	0.54411 (16)	0.6450 (11)	0.0232 (15)
C6	0.3380 (3)	0.57402 (15)	0.5164 (13)	0.0249 (14)
C7	0.3697 (3)	0.45655 (16)	0.6925 (14)	0.0323 (17)
H7A	0.365212	0.455393	0.504028	0.048*
H7B	0.339083	0.441412	0.773939	0.048*
H7C	0.412279	0.449587	0.741330	0.048*
Cl1	0.28138 (8)	0.60451 (5)	0.5360 (4)	0.0414 (5)
N1	0.4002 (3)	0.60834 (14)	0.2049 (12)	0.0317 (14)
N2	0.4889 (2)	0.55651 (14)	0.1726 (11)	0.0270 (13)
N3	0.47206 (19)	0.49457 (13)	0.4770 (9)	0.0220 (12)
N4	0.2757 (2)	0.53902 (14)	0.8103 (11)	0.0304 (13)
O1	0.3590 (2)	0.49022 (11)	0.7769 (10)	0.0332 (11)
O2	0.2305 (2)	0.52457 (13)	0.7183 (10)	0.0456 (14)
O3	0.2790 (2)	0.55000 (13)	1.0314 (10)	0.0427 (13)
O4	0.4095 (2)	0.60412 (13)	−0.0289 (9)	0.0399 (13)
O5	0.3996 (3)	0.63533 (13)	0.3137 (13)	0.0587 (17)
O6	0.5251 (2)	0.57954 (12)	0.2258 (9)	0.0368 (13)
O7	0.4932 (2)	0.53716 (12)	−0.0129 (9)	0.0348 (11)

Experimental details

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

Comment

Nitroazobenzene compounds have conjugated systems, which can improve the thermal stability of the compounds [5, 6]. Therefore, the development of new nitroazo compounds has become a research focus of high energy materials [7–10]. The title product is a nitroazobenzene compound with thermal stability, with research value.

Because the title product has intramolecular symmetry, the asymmetric unit of the title product is a half molecule.

As shown in the figure, N(3) and N(3A) form a double bond, connecting the 3-chloro-1-methoxy-2,4,5-trinitrobenzene moieties. The dihedral angle between the two benzene rings is 77° due to rotation between the C–N(C(3)–N(3)/C(3A)–N(3A)) bonds [9]. The dihedral angles of the nitro group and its connected benzene ring are 53.3°((N1)/O(4),O(5)), 61.6°(N(2)/O(6),O(7)), 84.0°(N(4)/O(2),O(3)), 53.3°(N(1A)/O(4A),O(5A)), 61.6°(N(2A)/O(6A),O(7A)), 84.0°(N(4A)/O(2A),O(3A)) [8]. Similarly, N(4) and N(4A) have larger dihedral angles than other nitro groups. This may be due to the spatial effects of chlorine atoms and methoxy group.

In the title product, both C(4) and C(4A) are linked to a methoxy group. The initial therory was that the nitro group replaces all the hydrogen atoms in the benzene ring, resulting in an octaedro-nitro product [7]. However, there is a large steric hindrance between the substituents, making the nitro group unstable. So the methoxy group replaces the nitro group to form the title product.

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