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The crystal structure of 3,5-dichloro-6-diazo-2,4-dinitrocyclohexa-2,4-dien-1-one, $C_6Cl_2N_4O_5$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.10 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.69 mm ⁻¹
Diffractometer, scan mode:	D8 VENTURE, φ and ω
θ_{max} , completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	4699, 1986, 0.058
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1388
$N(param)_{refined}$:	154
Programs:	Bruker [1], Olex2 [2], SHELX [3]

Source of material

The title compound was prepared by 4-chloro-3,5-nitroaniline. 4-Chloro-3,5-dinitroaniline was added to concentrated sulfuric acid (Tech 98%) and nitric acid (Tech 98%). After the reaction, and the filtrate was evaporated to give 1-nitro-amino-4-chloro-2,3,5,6-nitrobenzene. Add 10 mL of acetonitrile to a 50 mL four-neck glass bottle, dissolve 1 g of compound 1-nitro-amino-4-chloro-2,3,5,6-nitrobenzene in acetonitrile, prepare a sodium dichloroisocyanurate (SDCI) solution (3 g SDCI, 10 mL distilled water, 0.5 mL glacial acetic acid) in advance, add the above SDCI solution in a four-neck flask. Then the mixture was stirred at -10°C for 2 h, and slowly evaporated at room temperature to obtain the title compound as needle crystals. It was recrystallized from water-acetonitrile-acetic acid solution at room temperature to give colorless crystals. The raw material 4-chloro-3,5-dinitroaniline was self-made in the laboratory [4, 5]. As the compound is an energetic material the material must be handled carefully by trained persons.

Comment

In recent years, a series of new compounds with high nitrogen content have attracted interest, such as 3-nitro-4-diazo-5-imoxypyrazole [6], 1,2,5-thiadiazole [7], 6-diazo-2,4-dinitrocyclohexa-2,4-dien-1-one etc. These compounds can have different pharmacological and explosive properties due to the introduction of different groups. Energy groups such as nitro, amino and diazo groups can increase the energy of the compounds [8–11].

<https://doi.org/10.1515/ncrs-2020-0491>

Received September 25, 2020; accepted October 21, 2020;
published online November 13, 2020

Abstract

$C_6Cl_2N_4O_5$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 6.0044(6)$ Å, $b = 8.9660(11)$ Å, $c = 18.0544(18)$ Å, $V = 971.97(18)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0501$, $wR_{ref}(F^2) = 0.0987$, $T = 170.0$ K.

CCDC no.: 2039780.

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
C1	0.3439 (10)	0.3564 (7)	0.3284 (3)	0.0285 (14)
C2	0.4659 (10)	0.4824 (7)	0.3529 (3)	0.0291 (16)
C3	0.6425 (11)	0.4610 (7)	0.3995 (3)	0.0303 (15)
C4	0.7271 (11)	0.3193 (7)	0.4229 (3)	0.0304 (15)
C5	0.5877 (11)	0.1989 (7)	0.3960 (3)	0.0275 (15)
C6	0.3959 (10)	0.2151 (7)	0.3518 (3)	0.0274 (15)
Cl1	0.3803 (3)	0.65826 (19)	0.33005 (10)	0.0447 (5)
Cl2	0.2513 (3)	0.05980 (18)	0.32585 (9)	0.0406 (4)
N1	0.7644 (11)	0.5919 (6)	0.4285 (3)	0.0425 (15)
N2	0.1685 (9)	0.3776 (6)	0.2727 (3)	0.0336 (14)
N3	0.6458 (9)	0.0613 (7)	0.4232 (3)	0.0340 (13)
N4	0.7099 (11)	−0.0395 (7)	0.4495 (3)	0.0502 (18)
O1	0.8833 (10)	0.6617 (7)	0.3865 (3)	0.0676 (17)
O2	0.7394 (11)	0.6173 (5)	0.4946 (3)	0.0596 (16)
O3	0.8919 (9)	0.3009 (5)	0.4613 (2)	0.0431 (13)
O4	−0.0193 (7)	0.3269 (6)	0.2849 (2)	0.0425 (13)
O5	0.2199 (7)	0.4436 (5)	0.2162 (2)	0.0462 (13)

4-Chloro-3,5-dinitroaniline is the raw material of the precursor 4,4-dichloro-2,2',3,3',5,5',6,6'-octanitroazobenzene of heat resistant explosive. In this paper, 4-chloro-3,5-dinitroaniline was used as raw material. Therefore, it can be inferred that this compound has good energy and is worthy of further research and development.

There is one title molecule in the asymmetric unit. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation. It can be seen that diazo group N3–N4 is attached to C(5) with bond length of 1.373(8) Å (see the figure), the O(3) is attached to C(4) with bond length of 1.219(7) Å, two nitro groups are attached to C(1) and C(3) with bond length of 1.468(7) and 1.480(8) Å, respectively, and Cl(1) and Cl(2) are attached to C(2) and C(6) with bond length of 1.706(6) and 1.709(6) Å, respectively. Since each six-membered ring molecule of the title compound contains two nitro groups, and the steric hindrance of the nitro group is greater than that of halogen atoms, the C–Cl of the title compound is less stable and easier to be substituted, and more derivatives are synthesized. It can also be found from the structure of the

substance that the presence of the diazo group gives the compound high energy.

Acknowledgment: We thank the Center of Testing and Analysis, Shanghai Institute, for support.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

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