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## Synthesis and Crystal Structure of 2,2',5,5'-Tetrachloro-1,1'-azo-1,3,4-triazole

LI Sheng-hua<sup>1,2</sup>, SHI Hong-gang<sup>1</sup>, SUN Cheng-hui<sup>2</sup>, LI Xiao-tong<sup>1,2</sup>,  
PANG Si-ping<sup>1</sup>, YU Yong-zhong<sup>2</sup>, ZHAO Xin-qi<sup>2</sup>

(1. School of Life Science & Technology, Beijing Institute of Technology, Beijing 100081, China;

2. School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China)

**Abstract:** 2,2',5,5'-tetrachloro-1,1'-azo-1,3,4-triazole (**1**) was synthesized by reaction of 4-amino-1,2,4-triazole and sodium dichloroisocyanurate (SDCI). Its structure was determined by X-ray single crystal diffraction. It crystallizes in the triclinic space group *P*-1, with  $a = 6.2824(13) \text{ \AA}$ ,  $b = 7.7173(15) \text{ \AA}$ ,  $c = 10.443(2) \text{ \AA}$ ,  $\alpha = 89.16(3)^\circ$ ,  $\beta = 88.20(3)^\circ$ ,  $\gamma = 89.10(3)^\circ$ ,  $V = 505.94(18) \text{ \AA}^3$ ,  $Z = 2$ ,  $M_r = 301.92$ ,  $D_c = 1.982 \text{ mg} \cdot \text{m}^{-3}$ ,  $F(000) = 296$  and  $\mu(\text{MoK}\alpha) = 1.152 \text{ mm}^{-1}$ , the final  $R = 0.0498$  and  $wR = 0.1139$ . X-ray analysis reveals that a stronger  $\pi$  interaction of the triazole units with the tetrazene moiety.

**Key words:** organic chemistry; nitrogen-rich compound; 2,2',5,5'-tetrachloro-1,1'-azo-1,3,4-triazole; synthesis; crystal structure

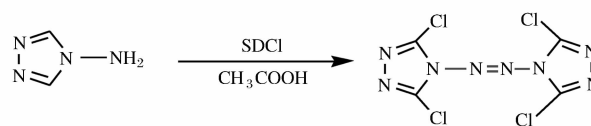
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### 1 Introduction

Nitrogen-rich compounds as energetic materials have currently attracted significant attention due to higher heats of formation, density, and oxygen balance than those of their carbocyclic analogues. Their high heats of formation is directly attributable to the large number of inherently energetic N—N and C—N bonds than from the overall heats of combustion. Many of the reported nitrogen-rich compounds are based on C/N heteroaromatic cycles, including pyrimidine<sup>[1]</sup>, triazole<sup>[2-4]</sup>, tetrazole<sup>[5-7]</sup>, triazine<sup>[8-9]</sup>, tetrazine<sup>[10-11]</sup>, and heptazine<sup>[12]</sup>. In particular, heteroaromatic rings linked by an azo group have recently been extensively studied<sup>[3-6,8-9,11]</sup> because the azo linkage not only desensitizes but also dramatically increases heats of formation of high-nitrogen compounds<sup>[8]</sup>. These compounds contain C—N=N—C structure. However, to the best of our knowledge, nitrogen-rich heterocycle compounds containing tetrazene (N—N=N—N) structure are not much reported. Although Bottaro<sup>[13]</sup> reported the preparation of a series of 1,1'-azo-1,2,4-triazole derivatives, no physical properties or crystal structure were available.

On the basis of these findings, we felt that tetrazene-linked bitriazole would not only provide more substitutive positions, but also enhance nitrogen content relative to the simple 1,2,4-triazole system. In our previous studies<sup>[14-15]</sup>, a series of triazole derivatives containing tetrazene (N—N=N—N) structure were synthesized. As a useful intermediate for the synthesis of energetic materials containing polyazido or polynitro, the synthesis and crystal structure of 2,2',5,5'-tetrachloro-1,1'-azo-1,3,4-triazole are reported in this paper (Scheme 1).



Scheme 1

### 2 Experimental

#### 2.1 Materials and instrument

All materials were commercially available and used as received. Melting points were determined using XT4 microscope melting point apparatus and were uncorrected. Infrared (IR) spectra were recorded on a Nicolet Magna IR 560 spectrophotometer and were run as KBr pellets. <sup>13</sup>C NMR spectroscopy (DMSO-*d*<sub>6</sub>) were recorded on ARX400 instrument with TMS as an internal standard. Mass spectra were recorded on a ZAB-HS mass spectrometer in EI. Elemental analyses were performed on an Elementar Vario EL.

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**Corresponding author:** PANG Si-ping, e-mail: pangsp@bit.edu.cn

## 2.2 Synthesis of the title compound

Sodium dichloroisocyanurate (SDCI) (79.20 g, 360 mmol) was dissolved in 400 mL water, 80 mL AcOH was added. After 1 h, 4-amino-1,2,4-triazole (6 g, 72 mmol) was added. The reaction mixture was stirred for 3 h at 50 °C. After cooled to room temperature, the solution was neutralized with NaHCO<sub>3</sub> to pH 7 and extracted with AcOEt. The extract was washed with water and dried with MgSO<sub>4</sub>. The solvent was evaporated to dryness in vacuo. The residue was purified by column chromatography (silica gel, 1 : 3 EtOAc/CHCl<sub>3</sub>), and the title compound was obtained with yield of 3.2 g, 30% as a colorless crystal. Single crystal of the title compound was obtained by slow evaporation from acetone at room temperature.

m. p. 197–199 °C, <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 139.6. EIMS *m/z*(%): 302 (M<sup>+</sup>, 0.5), 164 (23), 136(7), 108 (12), 96 (23), 75 (45), 47 (100). Anal. Calcd for C<sub>4</sub>Cl<sub>4</sub>N<sub>8</sub> (302): C 15.89, N 37.09; found: C 16.04, N 37.38.

## 2.3 X-ray crystallography

A single crystal with dimensions of 0.50 mm × 0.30 mm × 0.05 mm was selected for X-ray diffraction analysis. The data were collected on a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. A total of 3890 reflections were collected in the range of  $2.64^\circ \leq \theta \leq 27.48^\circ$  by using an  $\omega$ -2 $\theta$  scan mode, of which 2185 were unique with  $R_{\text{int}} = 0.0447$  and 1321 observed reflections ( $I > 2\sigma(I)$ ) were used in the succeeding refinements.

The structure was solved by direct methods with SHELXS-97<sup>[16]</sup> and expanded by the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were determined with theoretical calculations and refined isotropically. A fullmatrix least-squares refinement gave the final  $R = 0.0498$  and  $wR = 0.1139$  ( $w = 1/[\sigma^2(F_o)^2 + (0.0600P)^2 + 0.0000P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ),  $S = 1.018$ . The maximum peak in the final difference Fourier map was 0.464 e/Å<sup>3</sup> and the minimum peak -0.529 e/Å<sup>3</sup>. In the final circle of refinement the largest parameter shift  $(\Delta/\sigma)_{\text{max}}$  is 0.000.

## 3 Results and discussion

The atomic coordinates and thermal parameters for the title compound are listed in Table 1, and the selected bond lengths and bond angles in Table 2. The molecular structure is shown in Fig. 1, and the packing diagram in a unit cell in Fig. 2.

As seen from Fig. 1, the molecule of the title adopts a planar and symmetry molecule structure, with two triazole rings and a tetrazene chain. The least-square plane equation is  $1.0058x - 2.0110y + 0.5136z = -0.9948$ , with the largest deviation of  $-0.0048(2)$  Å(N(4)). The sum of N(4)—N(3)—C(1), N(4)—N(3)—C(2), C(1)—N(3)—C(2) bond angle is 360°, indicating that the N(3) and N(3A) atoms are *sp*<sup>2</sup> hybridized with their lone pair electrons in pure *p* atomic orbital.

Moreover, there are significant differences between the title compound and N<sub>4</sub>H<sub>4</sub> (NH<sub>2</sub>—N=N—NH<sub>2</sub>)<sup>[17-18]</sup> with respect to the bond lengths. The bond length between the N atoms of the azo group (N4=N4A) increases considerably from 1.205 Å in N<sub>4</sub>H<sub>4</sub> to 1.222(2) Å in the title compound. On the other hand, the bond lengths of the formal N—N single bonds decrease from 1.429 Å (N<sub>4</sub>H<sub>4</sub>) to 1.382(2) Å (N3—N4, Table 2), which indicates a stronger delocalization of the azo  $\pi$  bond along the tetrazene moiety within the title compound.

Surprisingly, most of the bond length in the title compound are between single bond and double bonds (Table 2). For example, the N(3)—C(1) and N(3)—C(2) bond lengths are 1.377(4) and 1.390(4) Å respectively, which are slightly shorter than the normal C—N bond length (1.470 Å)<sup>[19]</sup>. However, the bond lengths of N(1)—C(1) and N(2)—C(2) are 1.286(5) and 1.284(4) Å respectively, closed to the C=N double bond (1.270 Å)<sup>[19]</sup>. This indicates a stronger  $\pi$  interaction of the triazole units with the tetrazene moiety in the title compound, leading to a  $\pi$ -system which is strongly delocalized over the whole molecule. The presence of the delocalised  $\pi$ -system probably accounts for the remarkable stability of this type of tetrazene.

**Table 1 Atomic coordinates and thermal parameters**

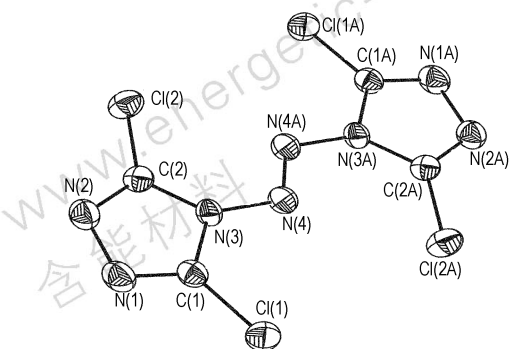
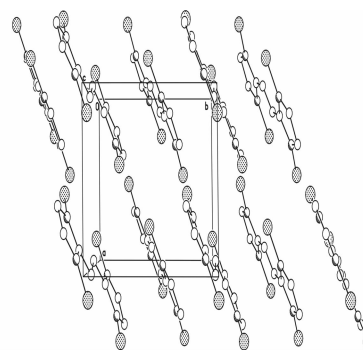
atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U_{eq} (\text{\AA}^2 \times 10^3)$
Cl(1)	4716(2)	7432(1)	453(1)	48(1)
Cl(2)	-2195(2)	4540(1)	2710(1)	48(1)
Cl(3)	-5850(2)	2247(2)	5055(1)	52(1)
Cl(4)	-11427(2)	-87(2)	1713(1)	54(1)
N(1)	2927(5)	7132(5)	2789(3)	47(1)
N(2)	1122(5)	6363(4)	3370(3)	44(1)
N(3)	1142(4)	5854(4)	1300(3)	33(1)
N(4)	811(4)	5419(4)	43(3)	38(1)
N(5)	-6445(5)	2341(5)	2569(3)	46(1)
N(6)	-7884(5)	1737(5)	1686(3)	47(1)
N(7)	-8929(4)	867(4)	3616(3)	35(1)
N(8)	-10345(5)	34(4)	4473(3)	39(1)
C(1)	2904(5)	6796(5)	1586(3)	38(1)
C(2)	101(5)	5633(5)	2483(3)	35(1)
C(3)	-7085(5)	1814(5)	3698(4)	38(1)
C(4)	-9305(6)	886(5)	2332(3)	37(1)

**Table 2 Bond lengths and angles for the title compound**

bond	bond lengths/\AA
Cl(1)—C(1)	1.689(4)
N(1)—N(2)	1.405(4)
N(3)—N(4)	1.382(4)
Cl(2)—C(2)	1.691(4)
N(2)—C(2)	1.284(4)
N(3)—C(2)	1.390(4)
N(1)—C(1)	1.286(5)
N(3)—C(1)	1.377(4)
N(4)—N(4A)	1.222(5)

bond	bond angles/(°)
C(1)—N(1)—N(2)	107.2(3)
C(1)—N(3)—C(2)	103.3(3)
N(1)—C(1)—N(3)	111.3(3)
N(2)—C(2)—N(3)	110.8(3)
C(2)—N(2)—N(1)	107.4(3)
N(4)—N(3)—C(2)	137.2(3)
N(1)—C(1)—Cl(1)	126.4(3)
N(2)—C(2)—Cl(2)	125.1(3)
C(1)—N(3)—N(4)	119.5(3)
N(4)—N(4)—N(3)	111.2(4)
N(3)—C(1)—Cl(1)	122.3(3)
N(3)—C(2)—Cl(2)	124.0(3)

**Fig. 1** Molecular structure of the title compound**Fig. 2** Packing diagram in a unit cell

## 4 Conclusions

In conclusion, we synthesized new triazole derivative containing tetrazene ( $\text{N}=\text{N}=\text{N}-\text{N}$ ) structure. X-ray analysis reveals that a stronger  $\pi$  interaction of the triazole units with the tetrazene moiety in the compound.

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## 2,2',5,5'-四氯-1,1'-偶氮-1,3,4-三唑的合成与晶体结构

李生华<sup>1,2</sup>, 施宏刚<sup>1</sup>, 孙成辉<sup>2</sup>, 李小童<sup>1,2</sup>, 庞思平<sup>1</sup>, 于永忠<sup>1</sup>, 赵信岐<sup>1</sup>

(1. 北京理工大学生命科学与技术学院, 北京 100081;

2. 北京理工大学材料科学与工程学院, 北京 100081)

**摘要:** 4-氨基-1,2,4-三唑与二氯异氰尿酸钠反应合成了 2,2',5,5'-四氯-1,1'-偶氮-1,3,4-三唑, 利用 X 射线衍射分析方法测定了它的晶体结构。该化合物的晶体结构属三斜晶系, 空间群 *P*-1,  $a = 6.2824(13) \text{ \AA}$ ,  $b = 7.7173(15) \text{ \AA}$ ,  $c = 10.443(2) \text{ \AA}$ ,  $\alpha = 89.16(3)^\circ$ ,  $\beta = 88.20(3)^\circ$ ,  $\gamma = 89.10(3)^\circ$ ,  $V = 505.94(18) \text{ \AA}^3$ ,  $Z = 2$ ,  $M_r = 287.22$ ,  $D_c = 1.982 \text{ mg} \cdot \text{m}^{-3}$ ,  $F(000) = 296$  和  $\mu(\text{MoK}\alpha) = 1.152 \text{ mm}^{-1}$ , 最终偏离因子  $R = 0.0498$ ,  $wR = 0.1139$ , 结构分析表明在三唑环和四氮烯键中有强的  $\pi$  电子共轭作用。

**关键词:** 有机化学; 富氮化合物; 2,2',5,5'-四氯-1,1'-偶氮-1,3,4-三唑; 合成; 晶体结构

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**文献标识码:** A

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## Synthesis Technique of 2-Methyl-6-nitroaniline

QI Lei<sup>1</sup>, PANG Si-ping<sup>1</sup>, SUN Cheng-hui<sup>2</sup>

(1. School of Life Science and Technology, Beijing Institute of Technology, Beijing 100081, China;

2. School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China)

**Abstract:** The synthesis technique of 2-methyl-6-nitroaniline was studied. In previous method, acetylation and nitration of 2-methylaniline were completed in one pot, but the nitration reaction temperature was difficult to be controlled. To improve the method, the acetylation and nitration were detached into two parts. The structure of the product, its by-product and its intermediate were characterized by IR, NMR and MS. The results show that the temperature of nitration process can be controlled easily, and the yield is 59.4% and the purity is up to 99.68%.

**Key words:** organic chemistry; 2-methyl-6-nitroaniline; 2-methyl-4-nitroaniline; synthesis