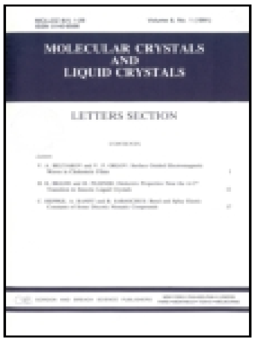

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Synthesis and X-Ray Crystal Structures of Tetrahalogeno-4,4′-bi-1,2,4-triazoles

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*Two novel tetrahalogeno-4,4′-bi-1,2,4-triazoles, tetrachloro-4,4′-bi-1,2,4-triazole (**1**, TCBTr) and tetrabromo-4,4′-bi-1,2,4-triazole (**2**, TBBTr) were successfully synthesized through halogenation of 4,4′-bi-1,2,4-triazole (BTr) and structurally characterized by elemental analysis, IR, ^{13}C NMR and MS spectra. The single crystals of title compounds were cultivated and determined with X-ray diffraction, and the test results reveal that the aromatic $\pi \ldots \pi$ stacking interactions between molecules and the tetrahalogeno-4,4′-bi-1,2,4-triazoles with the two triazole rings being perpendicular are well observed in the crystal structure of (**1**) and (**2**).*

Keywords single crystals; synthesis; tetrahalogeno-4,4′-bi-1,2,4-triazoles; X-ray diffraction

Introduction

In recent years, substituted triazoles have emerged as an important heterocyclic class with a growing number of applications in medicinal chemistry and materials science due to its unique chemical and structural properties [1–5]. 4,4′-Bi-1,2,4-triazole (BTr) with two vertical *N,N′*-linked triazole rings was first reported in 1967 by Bartlett [6], and then a series of coordination compounds from BTr as ligand were synthesized and had made remarkable achievements in the field of coordination chemistry and material science [7–12]. Theoretical study shows that tetranitro-4,4′-bi-1,2,4-triazole (TNBT) might be an ideal energetic material with high density (1.99 g/cm^3), detonation velocity (9.50 km/s) and CJ pressure (42.2 GPa), but it is still not be successfully synthesized [13]. Moreover, the other derivatives from the basic skeleton of BTr were also rarely reported [14].

Generally, halogenated azoles are considered to be very important intermediates in heterocyclic chemistry for the ability of halogen group in carbon–carbon, carbon–nitrogen and carbon–oxygen bonds formation [15–21]. So, tetrahalogeno-4,4′-bi-1,2,4-triazoles as key intermediates might not only lead to TNBT and its analogs through nitrolysis, but produce many valuable derivatives of BTr as pharmaceuticals or pesticides. Furthermore, these new compounds could contribute to chemistry of bifunctional tectons for supramolecular chemistry making accessible families of functionalized bitriazoles.

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In our previous work, we have reported the synthesis and crystal structure of tetraiodo-bi-4,4′-triazole (TIBTr) [22]. Herein, we report the synthesis of the other two tetrahalogenated-BTrs, namely tetrachloro-4,4′-triazole (**1**, TCBTr) and tetrabromo-4,4′-triazole (**2**, TBBTr), together with their interesting crystal structures. The research on the nitration and other derivatization reactions are under way and will be reported later.

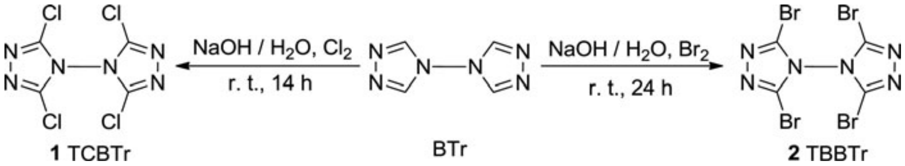
Experimental

Materials and Instruments

The Cl_2 gas was prepared *via* the reaction of hydrogen peroxide with concentrated hydrochloric acid. The other chemicals and solvents were commercial available. Elemental analysis was carried out on an Elemental Vario EL cube. Melting points were determined using an Optimelt OPM100 and are uncorrected. The FT-IR spectrum was obtained on Nicolet Nexus 870 FTIR Spectrophotometer (KBr pellets). MS spectra were recorded at a Varian 325 mass spectrometer. The ^{13}C NMR spectra were measured with AV 600 spectrometer (600 MHz). Powder X-ray diffraction patterns were obtained using a Bruker Smart APEX II CCD operating with a point focused Mo Kα radiation.

Synthetic Procedures

The synthetic routes of the title compounds (**1**) and (**2**) are presented in Scheme 1.



Scheme 1. Synthesis of compounds (**1**) and (**2**).

Synthesis of Tetrachloro-4,4′-bi-1,2,4-triazole (1)

Saturated chlorine water (300 mL) was added to a stirred solution of BTr (1.36 g, 10.0 mmol) in 2.0 mol/L sodium hydroxide solution (50 mL) at r.t., and then chlorine gas was continuously fed into the mixture and stirred for 14 h at r.t.. The mixture was neutralized with a diluted basic solution. The white precipitates were filtered, washed with water (30 mL × 2) and dried under vacuum. Recrystallization from tetrahydrofuran afforded colorless crystals. Yield: 70 %. Mp: 248∼249°C. MS: *m/z* 274.2 (M^+). IR (KBr pellet, cm^{-1}) ν: 1483, 1470, 1325, 1309, 1292, 962, 659. Anal. Calcd. (%) for $C_4N_6Cl_4$: C, 17.54; N, 30.68. Found (%): C, 17.48; N, 30.78. ^{13}C NMR (DMSO-d_6, 600 MHz): 142.73 ppm.

Synthesis of Tetrabromo-4,4′-bi-1,2,4-triazole (2)

Bromine (7.99 g, 50.0 mmol) was added to a stirred solution of BTr (1.36 g, 10.0 mmol) in 2.0 mol/L sodium hydroxide solution (50 mL) at r.t.. The mixture was stirred for 24 h at r.t.. The white precipitates were filtered, washed with water (30 mL × 2) and dried under vacuum. Recrystallization from tetrahydrofuran afforded colorless crystals. Yield: 83%. Mp: 271 ∼ 272°C. MS: *m/z* 452.8 (M^+). IR (KBr pellet, cm^{-1}) ν: 1473, 1454, 1287, 1258, 941, 644. Anal. Calcd. (%) for $C_4N_6Br_4$: C, 10.64; N, 18.61. Found (%): C, 10.54; N, 18.84. ^{13}C NMR (DMSO-d_6, 600 MHz): 132.72 ppm.

Single-Crystal X-ray Diffraction

Single crystals of the title compounds (**1**) and (**2**) suitable for X-ray diffraction analyses were grown by slow evaporation of tetrahydrofuran or Methanol at room temperature. The two single crystals with dimensions of 0.24 mm × 0.22 mm × 0.16 mm for (**1**) and 0.22 mm × 0.20 mm × 0.18 mm for (**2**) were performed on a Bruker SMART APEXII diffractometer equipped with a charge-coupled device (CCD) area detector with a graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collection were performed with Mo*K* radiation (λ=0.71073 Å) by the ω scan mode at 293(2) K for compound (**1**) and 113(2) K for compound (**2**).

All structures were solved by direct methods and refined by full-matrix least-squares on F^2. The structures were solved by direct methods using the Bruker SHELXS-97 for compound (**1**) and (**2**) [23], and refined with using full-matrix least-squares procedures SHELXS-2013 for compounds (**1**) and (**2**) [24]. The crystallographic details for the structure determination of the compounds are presented in Table 1. The selected bond lengths and angles are shown in Table 2.

Results and Discussion

Spectral Analyses

The as-prepared compounds were fully characterized by FT-IR, MS and ^{13}C NMR spectra. Their structures were determined using X-ray diffraction analysis. The elemental analysis, MS and NMR spectra have been in well agreement with the formulae proposed by the X-ray crystallography for (**1**) and (**2**), respectively.

Synthesis of Title Compounds

In numerous synthetic methods of halogenated azoles, the title compounds could be achieved from the reaction of halogen and BTr in aqueous alkaline solution [25, 26]. Through this method, (**1**) and (**2**) were successfully prepared at room temperature with the yields of 70 % and 83 %, respectively.

Compounds (**2**) was easily synthesized from BTr with Br_2 in aqueous solution of NaOH. However, compound (**1**) could not be achieved directly by the similar method that Cl_2 gas was fed into alkaline solution of BTr, a by-product as yellow foam was only obtained. After many experiments, compound (**1**) could be realized by the procedure that saturated aqueous solution of chlorine was added firstly and then Cl_2 gas was continuously fed into the mixture for 14 h in good yields.

Crystal Structure Description of Title Compound (1)

As depicted in Fig. 1, the molecule in (**1**) consists of two *N,N′*-linked 1,2,4-triazole rings and two C–Cl bonds in each triazole ring. The distances of the bonds C1–Cl1 and C2–Cl2 are 1.676(2) Å and 1.687(2) Å, respectively, together with the distance of the two triazole

Table 1. Crystallographic data and date collection parameters for (**1**) and (**2**)

Compounds	(**1**)	(**2**)
Empirical formula	$C_4N_6Cl_4$	$C_4N_6Br_4$
Formula weight	273.90	451.74
Temperature (K)	293 (2)	113 (2)
Wavelength (Å)	0.71705	0.71705
Crystal system	Monoclinic	Monoclinic
Space group	*C* 2/*c*	*P* 2(1)/*c*
Unit cell dimensions (Å, °)	$a = 11.791$ (2), $\alpha = 90$, $b = 7.617$ (6), $\beta = 104.601$ (9), $c = 11.277$ (17), $\gamma = 90$	$a = 7.3532$ (10), $\alpha = 90$, $b = 12.1288$ (15), $\beta =95.132$ (14), $c = 11.5886$ (14), $\gamma = 90$
Volume (Å^3), *Z*	980.2 (8), 4	1029.4 (2), 4
Calculated density (g • cm^{-3})	1.856	2.915
Absorption coefficient μ (mm^{-1})	1.174	15.607
θ range for data collection (°)	3.22–27.94	2.44–30.05
F(000)	536	824
Crystal size (mm^3)	0.24 × 0.22 × 0.16	0.22 × 0.20 × 0.18
Reflection collected	5473	12020
Independent reflection	5473/1165 ($R_{\text{int}} = 0.0401$)	12020/2994 ($R_{\text{int}} = 0.1108$)
Completeness to θ max (%)	99.4	99.8
Data/restrain/parameters	1165/0/65	2994/0/128
Goodness-of-fit on *F*2	1.021	0.916
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0368$, $wR_2 = 0.0995$	$R_1 = 0.0501$, $wR_2 = 0.1082$
R indices [all data]	$R_1 = 0.0496$, $wR_2 = 0.1048$	$R_1 = 0.0939$, $wR_2 = 0.1222$
Largest diff.e peak and hole (e A^{-3})	0.419 and −0.456	1.461 and −1.155

Table 2. selected bond lengths (Å) and bond angles (°) of compounds (**1**) and (**2**)

Compound (**1**)					
N1-C2	1.373 (2)	N1-N1A	1.364 (3)	Cl1-C1	1.687 (2)
N2-C1	1.281 (2)	N2-N3	1.400 (2)	Cl2-C2	1.676 (2)
N3-N2	1.285 (2)	C1-N2-N3	107.45 (15)	N3-C2-N1	110.80 (17)
N1A-N1-C2	128.25 (15)	C2-N1-C1	103.89 (15)	N2-C1-N1	110.69 (17)
N1A-N1-C1	127.78 (15)	C2-N3-N2	107.18 (15)	N3-C2-Cl2	127.77 (15)
N1-C1-Cl1	121.19 (14)	N2-C1-Cl1	128.10 (15)	N2-N3-C2-Cl2	−179.96 (15)
N1-C2-Cl2	121.43 (14)	N2-N3-C2-N1	−0.2 (2)	N3-N2-C1-N1	0.1 (2)
N1A-N1-C1-Cl1	4.0 (3)	N1A-N1-C2-Cl2	−3.0 (3)	C1-N2-N3-C2	0.1 (2)
N1A-N1-C2-N3	177.24 (16)	C1-N1-N1A-C2A	82.3 (2)	C1-N1-N1A-C1A	−93.9 (2)
Compound (**2**)					
N1-C1	1.382 (8)	N2-C1	1.281 (7)	Br2-C(1)	1.852 (6)
N1-C2	1.375 (8)	N3-C2	1.295 (7)	Br1-C(2)	1.834 (6)
N1-N4	1.365 (6)	N2-N3	1.410 (7)	N5-C3-Br3	127.8 (5)
N1-N4-C3	127.7 (5)	N4-N1-C2	127.9 (5)	C1-N2-N3	106.9 (6)
N1-C1-Br2	122.3 (4)	N3-C2-Br1	126.5 (5)	C4-N6-N5	107.5 (5)
N2-C1-Br2	126.9 (5)	C4-N4-C3	102.5 (5)	N5-N6-C4-Br4	179.6 (5)
N1-N4-C3-Br3	5.8 (9)	C1-N2-N3-C2	−0.2 (8)	N6-N5-C3-Br3	−179.2 (5)
N2-N3-C2-N1	0.0 (7)	C3-N5-N6-C4	2.3 (7)	N4-N1-C2-N3	−178.5 (6)
N3-N2-C1-N1	0.4 (8)	C1-N1-N4-C3	79.1 (8)	C1-N1-N4-C4	−91.4 (8)

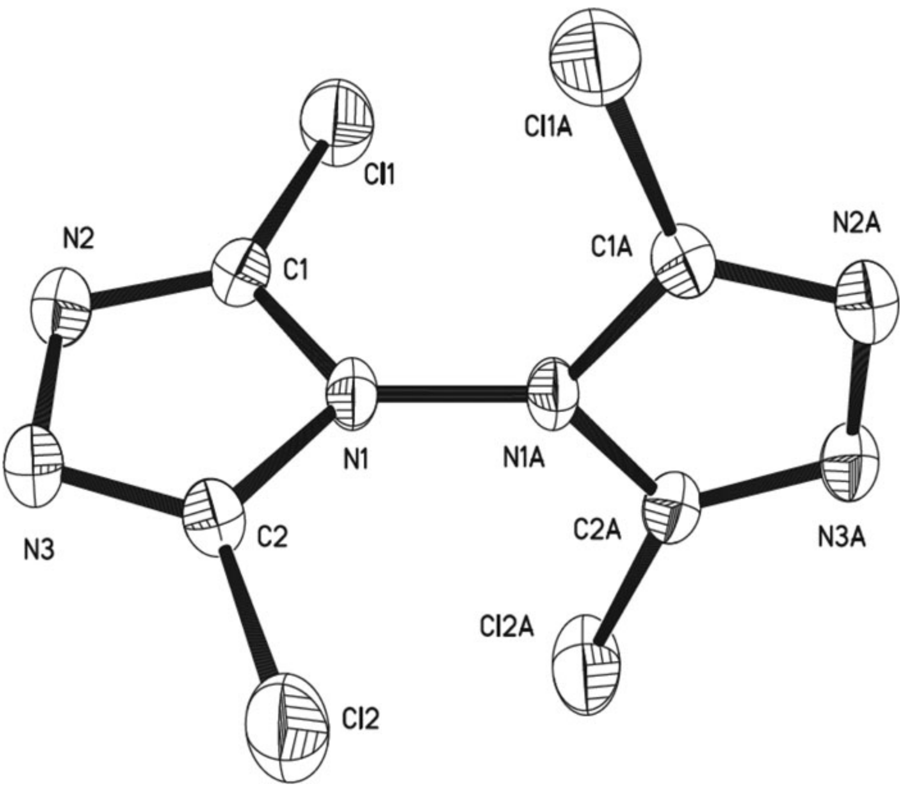


Figure 1. Crystal structure of (**1**) with 30% probability thermal ellipsoids.

rings is 1.364(3) Å. The angles of selected bonds in the triazole rings of compound (**1**) range from 103.89(15)° to 128.25(15)°. The torsion angles of the bond C1-N1-N1A-C2A and C1-N1-N1A-C1A are −93.9(2)° and 82.3(2)°, respectively. The other torsion angles in one tirazole ring indicate that all atoms are almost coplane.

As shown in Fig. 2, single-crystal X-ray studies indicate the compound (**1**) crystallized in monoclinic system with space group *C* 2/*c*. The crystal packing of (**1**) is stabilized by the weak supramolecular interactions, particular for Cl··· N and Cl··· π. Apart from the weak supramolecular interactions, there are also weak aromatic $\pi \cdots \pi$ packing interactions involving four triazole rings of the two adjacent molecules, in which the triazole rings are parallel to each other with the centroid-to-centroid separation of 4.120 Å. As a result, the intermolecular interactions link the molecule into an infinite three-dimensional network (Fig. 2).

Crystal Structure Description of Title Compound (2)

As depicted in Fig. 3, the molecule in (**2**) consists of two *N,N′*-linked 1,2,4-triazole rings and two C-Br bonds in each triazole ring, with the distances of four C-Br bonds range from 1.834(6) Å to 1.852(6) Å in length, and the distance of the two triazole rings is 1.365(6) Å. The angles of the selected bonds in the triazole rings of compounds (**2**) range from 102.5(5)° to 129.3(5)°, and the torsion angle of the bond C1-N1-N4-C4 is −91.4(8)° while

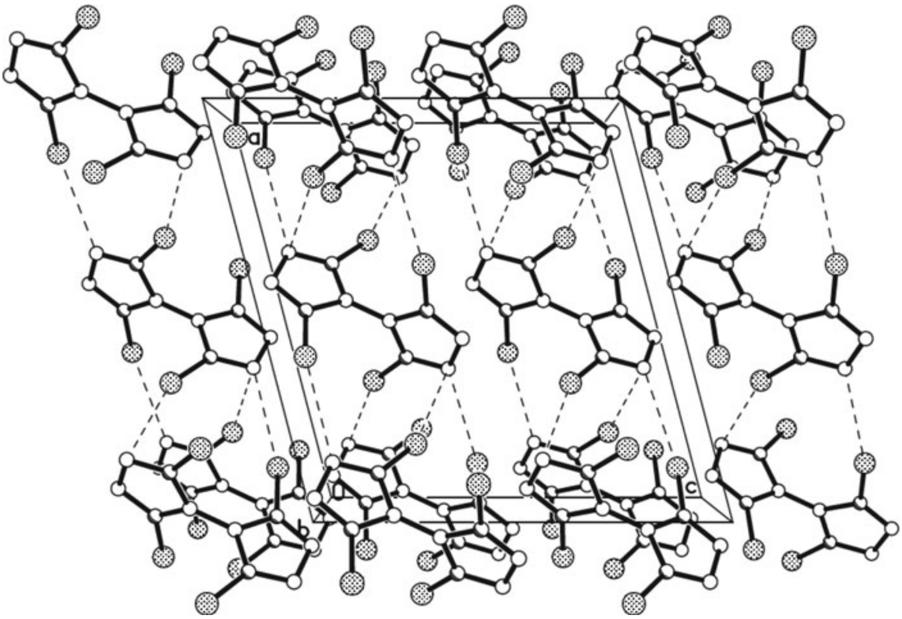


Figure 2. Crystal packing diagram of (**1**) along the *b*-axis.

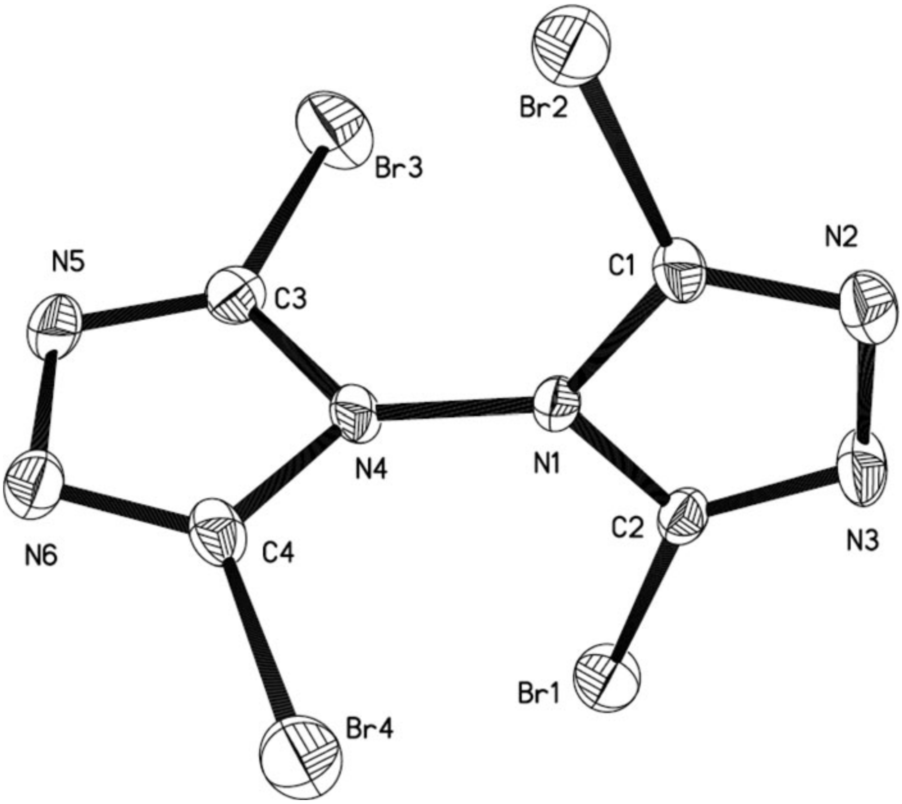


Figure 3. Crystal structure of (**2**) with 30% probality thermal ellipsoids.

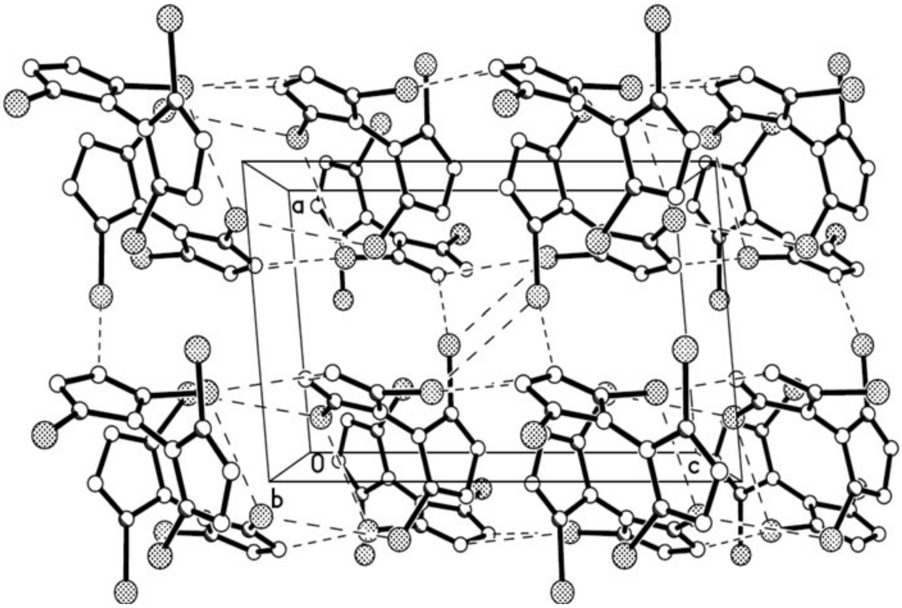


Figure 4. Crystal packing diagram of (**2**) along the *b*-axis.

the bond C1–N1–N4–C3 is 79.1(8)°. The other torsion angles in one tirazole ring indicate that all atoms are almost coplane, as well.

As shown in Fig. 4, the single-crystal X-ray studies indicate that the compound (**2**) crystallized in monoclinic system with group $P\ 2_1/c$. The aromatic $\pi \cdots \pi$ stacking interactions are observed in the crystal packing of (**2**), together with the weak supramolecular interactions of Br$\cdots$N, Br$\cdots$Br and Br$\cdots\pi$ contacts. The adjacent molecules are packing via weak aromatic $\pi \cdots \pi$ stacking intercations of the parallel adjacent triazole rings the centroid-to-centroid separation of 6.2338 Å.

Compared with the crystal data of tetraiodo-4,4′-bi-1,2,4-triazole [22], the bonds of C–X (C–Cl, C–Br and C–I) are gradually increasing from 1.676(2) Å to 2.063(6) Å. The distance of the two triazoles in BTr is about 1.37 Å, whenever Btr is in halogeno-4,4′-bi-1,2,4-triazoles or coordination compounds [7–12, 27]. Not only the angle between the two triazole rings is in the range 50° to 90° when the BTr was treated as ligands in coordination compounds [7–12, 28], but the two triazole rings in the title compounds are also perpendicular. That may be because the halogeno-4,4′-bi-1,2,4-triazoles are nearly orthogonal, overlap of the aromatic $\pi \cdots$ orbital is approximate zero and changing the angle between the rings is quite easy. On the other hand, the lone pair electrons on the two N atoms repel each other, forcing N–N′ bond twists a certain angle so that the molecules are in a stable state.

Single-crystal X-ray studies indicate the compounds crystallized in monoclinic system with space group $C\ 2/c$ of compound (**1**) and $P\ 2(1)/c$ of compounds (**2**) and tetraiodo-4,4′-bi-1,2,4-triazole. That may be because the atomic radius and deformations are gradually increasing from Cl to I, leading to the differents stacking in the cells of these compounds.

Conclusion

In summary, two tetrahlageno-4,4′-bi-1,2,4-triazoles were prepared and structurally characterized, the single crystals of these compounds were also obtained. The molecular structure is featured with two triazoles rings in a molecule and packing *via* weak suparmolecular interactions for halogeno–N, halogeno–halogeno, halogeno–π and aromatic $\pi \cdots \pi$ between adjacent molecules. The distance and angle of the two triazole rings indicate that BTr has its own character which can predicate that the two triazole ring in the derivatives of BTrs are almost perpendicular and in the lengths of about 1.37 Å. The lengths of the C–X bonds (C–Cl, C–Br and C–I) are gradually increasing from 1.676 Å to 2.062 Å. These tetrahlageno-4,4′-bi-1,2,4-triazoles are versatile intermediates to achieve various derivatives of 4,4′-bi-1,2,4-triazole and will make richer on the types and quantities of heterocyclic compounds.

Acknowledgments

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Supplementary Material

Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre and assigned the following deposition numbers: CCDC-971635 and CCDC-967884 for (**1**) and (**2**), respectively. Copies of the data can be obtained free of charge via e-mail: deposit@ccdc.ccdc.cam.ac.uk or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033).

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