### ARTICLE



# Novel *tris*(5-aryl-1*H*-tetrazol-1-yl)methanes and 2-dichloromethyl-5-aryl-2*H*-tetrazoles and noncovalent interactions in their crystal structure

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# **1** | INTRODUCTION

Polydentate (polynuclear) systems containing several heterocyclic fragments (azoles or azines) bonded with one central atom are promising selective ligands for coordination chemistry.<sup>[1-3]</sup> Carbon, boron, or phosphorus can be considered as such central atom. In particular, the use of chelating ligands with large, sterically demanding substituent groups will often allow for the preparation of metal complexes of low coordination number. The numerous examples of such systems are known for pyrazoles, imidazoles, and some other heterocycles<sup>[1-3]</sup> (Figure 1).

Such ligands have found widespread application in coordination chemistry, forming stable chelate-type or sandwich-type complexes with the majority of metal centers [Mn(II), Rh(III), Re(I), Ru(II), Ag(I), Pd(II), Cu(I), Fe(II), and Hg(II)] (Figure 2).<sup>[4–7]</sup>

It should be noted that such polynuclear systems based on high-nitrogen heterocycles may be considered not only as perspective ligands for the construction of

#### Abstract

A series of *tris*(5-aryl-1*H*-tetrazol-1-yl)methanes (**3a-3g**) and 2-dichloromethyl-5-aryl-2*H*-tetrazoles (**4a-4d**) were synthesized by reaction of 5-aryl-NHtetrazoles with trichloromethane in strong aqueous basic condition. The compounds obtained were fully characterized by means of HRESI-MS, <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectroscopies, as well as by single-crystal X-ray diffraction (for **3a**, **3b**, **4d**). Inspection of the X-ray diffraction data and Hirshfeld surface analysis for *tris*(5-aryl-1*H*-tetrazol-1-yl)methanes **3a,b** and 2-dichloromethyl-5-aryl-2*H*tetrazole **4d** showed the presence of noncovalent  $\pi$ -hole•••lone pair and  $\pi$ -hole••• $\pi$  interactions involving electrophilic tetrazole carbon atom.

metal ions complexes, but also as high-energy compounds.<sup>[8–10]</sup> However, data on the synthesis and properties of polyazolylalkanes containing triazole or tetrazole moieties are very limited. Earlier, one of us described the synthesis of the first example of tristetrazolylalkanes—*tris*(5-phenyl-1*H*-tetrazol-1-yl) methane.<sup>[8]</sup> This compound was synthesized from 5-phenyltetrazolide and trichloromethane in strong basic medium.

In the present work, under the reaction of a series of 5-aryl-NH-tetrazoles (**1a-g**), that exist in aqueous basic solutions as tetrazolides (**2a-g**), with trichlorolmethane corresponding *tris*(5-aryl-*1H*-tetrazol-1-yl)methanes (**3a-g**) and 2-dichloromethyl-5-aryl-2*H*-tetrazoles (**4a-d**) were synthesized. The compounds obtained were characterized by HRESI-MS, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies, and X-ray diffraction analysis (for **3a,b** and **4d**). According to the X-ray diffraction (XRD) data for compounds **3a,b** and **4d** some specific noncovalent  $\pi$ - $\pi$  and  $\pi$ -lone pair interactions involving tetrazole moieties were determined.





**SCHEME1** Synthesis of tris(5-aryl-1H-tetrazol-1-yl)methanes (3a-g) and 2-dichloromethyl-5-aryl-2H-tetrazoles (4a-d)

#### 2 **RESULTS AND DISCUSSION**

#### 2.1 Synthesis of tetrazoles 3a-g and 4a-d

A series of 5-aryl-NH-tetrazoles (1a-g) containing electrondonating or electron-withdrawing substituents (CH<sub>3</sub>, CF<sub>3</sub>, NO<sub>2</sub>, Cl, OH) in different positions of the benzene ring were chosen as model compounds. As a result of reaction of 5-aryl-NH-tetrazoles (1a-g) with trichloromethane two main products are formed: poorly soluble tris(5-aryl-1Htetrazol-1-yl)methanes (3a-g) and soluble in organic layer 2-dichloromethyltetrazoles (2a-g).

A principal scheme of formation of tris(5-aryl-1Htetrazol-1-yl)methanes (3a-g) and 2-dichloromethyl-5-aryl-2H-tetrazoles (4a-d) may includes the following successive stages (Scheme 1). First, taking into account the acidic properties of the N-unsubstituted tetrazoles  $(pK_a < 5)$ <sup>[9]</sup> in the basic media 5-aryl-NH-tetrazoles (1a-g) dissociate to give corresponding anions-tetrazolides 2a-g. In accordance with the generally accepted mechanism,<sup>[10]</sup> the highly reactive dichlorocarbene may formed from trichloromethane in strong sodium hydroxide solutions. It should be noted that this reaction does not proceed under moderate basic conditions what additionally proves the carbene mechanism of the one. Obviously, under the interaction between dichlorocarbene and tetrazolides 2a-g two isomeric Nsubstituted tetrazoles may formed: 1-dichloromethyl-1H-5-aryltetrazoles and 2-dichloromethyl-2H-5-aryltetrazoles (**4a-d**) (Scheme 1). Further, 1-dichloromethyl-1H-5-aryltetrazoles react with the base to give corresponding tetrazolylchlorocarbenes which interact with another molecule of tetrazolate to give intermediate bis(5-aryl-1H-tetrazol-1-yl)chloromethanes and at the third similar stage the formation of tristetrazolylmethanes (3a-g) is occurred. However, 2-dichloromethyl-2H-5-aryltetrazoles (4a-d) remain unchanged and the formation of corresponding tris(5-aryl2*H*-tetrazol-2-yl)methanes is not detected. As it was shown earlier by means of DFT calculation 1*H*-isomer **3a** is more thermodynamically stable comparing with hypothetical isomer—*tris*(5-phenyl-2*H*-tetrazol-2-yl)methane<sup>[8]</sup> what may be the explanation for the observed composition of the reaction products. An increasing of the concentration of sodium hydroxide up to 40% mas. leads to higher yields of 2-dichloromethyltetrazoles **4a-d** (up to 20%) while the formation of tris-products **3a-g** was not detected at all.

# 2.2 | Characterization of tetrazoles 3a-g and 4a-d

The compounds obtained were characterized by means of HRESI-MS, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies. In addition, solid-state structures of three compounds (**3a**, **3b**,

**4d**) were elucidated by single-crystal XRD (SC XRD). The HRMS-ESI spectra display fragmentation patterns corresponding to  $[M + H/Na/Ag]^+$  in positive mode and  $[M-H]^-$  in negative mode with the characteristic isotopic distribution.

In the <sup>1</sup>H NMR spectrum of *tris*(5-aryl-1*H*-tetrazol-1-yl)methanes **3a-g** a characteristic signal of central CHproton is observed at 9.29 to 9.47 ppm. The signal of the protons of the CHCl<sub>2</sub>-group in 2*H*-tetrazoles **4a-d** manifested at the range of 8.17 to 8.86 ppm. There is characteristic signal of carbon atom of the tetrazole ring at 155 to 156 ppm (for 1*H*-tetrazoles **3a-g**) and 165 to 167 ppm (for 2*H*-tetrazoles **4a-d**) in the <sup>13</sup>C {<sup>1</sup>H} NMR spectra. It should be noted that the tristetrazoles are very limited soluble which makes it difficult to analyze.

Tetrazole cycle is a high-energy fragment that decomposes exothermically with an evolving of two molecules



**FIGURE 3** Views of XRD structures **3a**, A, **3b**, B, and **4d**, C, with numbering schemes. Thermal ellipsoids are drawn at the 50% probability level. XRD, X-ray diffraction

of nitrogen.<sup>[11,12]</sup> Compounds containing several tetrazole fragments, as in the case of tristetrazolylmethanes **3a-g**, are potential energy-rich molecules.

### 2.3 | XRD structures

The crystals of 3a and 4d were grown from methanol solutions, whereas for the crystallization of 3b acetatemethanol system was used. The crystals of 3a and 3b have monoclinic syngony (P21/c and P21/n space groups) while the syngony for **4d** crystal is orthorhombic (Pnma). In all cases, crystallographically independent part of crystal contains only one tetrazole molecule without any solvates. The plots of the XRD structure of 3a, 3b, and 4d is given on Figure 3. In all cases, the tetrazole ring is a planar conjugated system. The bonds lengths and angles of the heterocycle fragments in the compounds 3a, 3b, and 4d corresponds to known data for 1H- and 2Htetrazoles.<sup>[12,13]</sup> Whereas the rotation of the 5-aryltetrazolyl moieties in compounds 3a, 3b is strongly hindered the central carbon atom can be asymmetrical.

**TABLE 1**Results of the Hirshfeld surface analysis for the X-<br/>ray structures of 3a, 3b, and 4d

Structure	Contributions of different intermolecular contacts to the molecular Hirshfeld surface
3a	N•••H 46.2% H•••H 25.9% C•••H 12.9% N•••N 4.5% C•••N 10.5%
3b	N•••H 46.3% H•••H 28.1% C•••H 19.0% N•••N 5.5% C•••N 1.1%
4d	Cl•••H 33.6% Cl•••N 16.9% N•••H 13.3% H•••H 11.1% Cl•••Cl 8.5% C•••H 4.6% C•••N 2.6% C•••Cl >1%

We carried out the Hirshfeld surface analysis for the XRD structures of **3a**, **3b**, and **4d** to understand what kind of intermolecular contacts gives the largest contributions in crystal packing (Table 1). The molecular Hirshfeld surface represents an area where molecules come into contacts, and its analysis gives the possibility of an additional insight into the nature of intermolecular interactions in the crystal state. For the visualization, we have used a mapping of the normalized contact distance  $(d_{\text{norm}})$ ; its negative value enables identification of molecular regions of substantial importance for detection of short contacts. Figure 4 depicts the Hirshfeld surfaces for **3a**, **3b**, and **4d**. In these Hirshfeld surfaces, regions of shortest intermolecular contacts visualized by red circle areas.

The Hirshfeld surface analysis for the XRD structures of 3a, 3b, and 4d indicates the domination of the contacts that involve hydrogen atoms, specifically, N•••H, H•••H, C•••H (76%-85%) in case of 3a and 3b and Cl•••H, N•••H, H•••H, C•••N (80%) for 4d. These contacts provide the largest contributions to the molecular Hirshfeld surfaces, because the fraction of hydrogen atoms is maximal and the Hirshfeld surfaces analysis does not disclose the attractive or repulsive nature of these contacts. Apart from the contacts that involve H atoms, 3a and 3b exhibit the N•••N and C•••N contacts, whereas crystal of 4d contains Cl···N, Cl···Cl, C···N. The N···N and C···N Cl···N contacts are responsible for  $\pi$ - $\pi$  and lone pair(lp)- $\pi$  interactions. Introduction of the halogen substituent in the substituent leads to appearance of Hal-Hal contacts which could be interpreted as type II halogen bonding.

The inspection of XRD data and Hirshfeld surface analysis for compounds **3a,b** and **4d** indicates the presence of several nontrivial types of intermolecular noncovalent contacts involving tetrazole moieties which determine the crystal packing in every case (Figure 5):



FIGURE 4 Hirshfeld surfaces for 3a, A, 3b, B, 4d, C. Thermal ellipsoids are drawn at the 50% probability level



**FIGURE 5** Noncovalent interactions involving tetrazole moieties in **3a**,**b** and **4d**: A,  $\pi$ - $\pi$  interactions in **3a** (left) and **3b** (right); B,  $\pi$ (C) **•••**lp(N) interactions in **3a** (left) and **3b** (right); C,  $\pi$ - $\pi$  interactions and  $\pi$ (C)**•••**lp(Cl) interactions in **4d** 

**TABLE 2**Geometrical parameters for intermolecular noncovalent interactions involving tetrazole moieties in crystal structure of 3a,**3b**, 4d

					ΣvdW radii (Å)		
Compound	Contact	Distance (Å)	∠R–X•••¥ (°)	∠X••••Y−R (°)	Bondi	Rowland	Alvarez
3a	N1•••N3	3.230(2)	88.7(1)	91.1(1)	3.10	3.28	3.32
	C5•••N2	3.292(2)	83.6(1)	88.9(1)	3.25	3.41	3.43
	C5B•••N1	3.446(2)	85.9(1)	161.6(1)	3.25	3.41	3.43
3b	N2•••N3	3.151(2)	93.7(1)	95.8(1)	3.10	3.28	3.32
	C5B•••N1	3.201(2)	80.7(1)	148.0(1)	3.25	3.41	3.43
4d	C10•••C5	3.488(1)	89.1(1)	89.0(1)	3.40	3.54	3.54
	N4•••Cl1	3.415(1)	89.7(1)	95.4(1)	3.30	3.40	3.48

the  $\pi$ - $\pi$  (N•••N and C•••N) interactions between two symmetrically located tetrazole rings and  $\pi$ (C)•••lp (N) interactions in case of **3a** and **3b**, whereas **4d** displays  $\pi$ (C)••• $\pi$ <sub>phenyl</sub>(C) and  $\pi$ (N)•••lp(Cl) interactions. The

geometric parameters for these interactions are given in Table 2.

In all cases the distances for the  $\pi$ - $\pi$  contacts involving tetrazole moieties are slightly larger than sum of Bondi's vdW radii<sup>[14]</sup> but shorter then sums of Rowland's and Alvarez's radii.<sup>[15]</sup> The corresponding angles between the shortest contacts and the planes of  $\pi$ -systems are almost 90° what is characteristic for interactions between  $\pi$ -systems.<sup>[16]</sup> The distances for tertrazole(C)•••lp contacts are less or on the border of sums Alvarez radii. In these cases, the angle between the contact and tetrazole plane is close to 90° indicating the involvement of tetrazole  $\pi$ -system in these interactions. The second angle in case of C•••N contacts is in range of 140° to 165°, whereas for N•••Cl it close to 90°. These values are in agreement with the suggestion of involvement of the lone pairs of the tetrazole nitrogen (**3a,b**) and the chlorine substituent (**4d**) in the contacts with tetrazole carbon atom.

The  $\pi$ - $\pi$  contacts between tetrazole moieties due to symmetrical disposition should be considered as classical  $\pi$ - $\pi$ stacking interaction which have mostly dispersion nature.<sup>[17]</sup> In the same time the contacts with tertrazole carbon could also have contribution of so called  $\pi$ -hole interaction. A  $\pi$ -hole is usually defined as the region of positive electrostatic potential in place of an empty antibonding  $\pi^*$ -orbital, typically located perpendicularly to a framework.<sup>[18]</sup> According to the known data one may conclude that for the tetrazoles the  $\pi^*$ -orbital should be concentrated more on C atom rather than N atoms what makes the C atom to be more electrophilic and to act as  $\pi$ -hole.<sup>[12,13,19,20]</sup> The relevant habit for carbon atom previously was showed for other heteroatomic  $\pi$ -systems like acyl compound,<sup>[21]</sup> azines.<sup>[22,23]</sup> isocyanides,<sup>[24,25]</sup> nitriles,<sup>[26]</sup> and carbon monoxide.<sup>[27,28]</sup> However, to the best our knowledge the  $\pi$ -hole donor ability for tetrazoles was not reported earlier.

The CCDC search based on Bondi vdW radii allows the verification of approximately 390 examples  $\pi$ -hole••• $\pi$ and  $\pi$ -hole•••lp interactions involving tetrazole carbon what indicates the involvement of tetrazole species in  $\pi$ -hole interactions is a relatively common phenomenon.

## 3 | CONCLUSION

5-Aryltetrazolates interact with chloroform in aqueous strongly basic medium to give *tris*(5-aryl-1*H*-tetrazol-1-yl) methanes **3a-g** and 2-dichloromethyl-5-aryl-2*H*-tetrazoles **4a-d**. The reaction obviously proceeds with the formation of carbene intermediates. Inspection of the X-ray diffraction data and Hirshfeld surface analysis for tris(5-aryl-1*H*-tetrazol-1-yl)methanes **3a,b** and 2-dichloromethyl-5-aryl-2*H*-tetrazole **4d** indicates the presence of several nontrivial types of intermolecular noncovalent contacts with tetrazole moieties which can be considered as  $\pi$ -hole•••lone pair and  $\pi$ -hole••• $\pi$  interactions involving electrophilic tetrazole carbon atom. The CCDC search

based on the contacts with tetrazole fragment indicates that the involvement of tetrazole species in  $\pi$ -hole interactions by carbon atom is a relatively common phenomenon. Compounds **3a-g** may be of interest as promising ligands for complexation with transition metal ions and energy-rich compounds.

#### 4 | EXPERIMENTAL

#### 4.1 | General

All solvents and reagents were purchased from commercial sources and used without further purification. 5-Aryl-NH-tetrazoles **1a-g** were synthesized using previously reported procedures.<sup>[11,12,29]</sup>

Mass-spectra were recorded on Bruker MicroTOF spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were recorded with Bruker 400 MHz WB Avance III spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} chemical shifts were determined using residual signals of the deuterated solvents (CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub>) at 298 K and were referenced to that of SiMe<sub>4</sub> ( $\delta = 0$ ).

# 4.2 | General procedure of synthesis of compounds 3a-g and 4a-d

About 50 mmol of 5-aryl-1*H*-tetrazole (**1a-g**) was dissolved in 100 mL of 10% aqueous solution of NaOH and 35 mL of chloroform was added to this solution over 1 hour with vigorous stirring at 45°C. The reaction was carried out for 6 hours at the same temperature. After cooling, the mixture was poured into 200 mL of ice-water and treated with 200 mL of diethyl ether. The precipitate appeared at the interface between organic and aqueous phases was filtered off, washed with water and ether and dried to give very low soluble compounds (**3a-g**). The organic layer was dried and evaporated at vacuum. Compounds (**4a-d**) was separated by means of the column chromatography (eluent CHCl<sub>3</sub>: MeOH, 9.5:0.5).

# 4.3 | Characterization data for the tetrazole derivatives

*Tris*(*5*-*phenyl*-1*H*-*tetazol*-1-*yl*)*methane* (*3a*). Yield 0.37 g (5%), colorless crystals, m.p. 155°C. HRESI<sup>+</sup>-MS, m/z: 449.1664  $[M + H]^+$  (calc. for C<sub>22</sub>H<sub>17</sub>N<sub>12</sub>: 449.1699). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>), δ: 7.37 to 7.62 (m, 15H, Ar), 9.25 (s, 1H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>), δ: 72.9 (CH); 121.6, 129.1, 129.3, 132.1 (Ar); 155.0 (CN<sub>4</sub>). (Correspond to literary data<sup>[8]</sup>).

*Tris*(*5*-(*m*-*tolyl*)-1*H*-*tetrazol*-1-*yl*)*methane* (3b). Yield 0.90 g (11%), colorless crystals, m.p. 157°C. HRESI<sup>+</sup>-MS, *m/z*: 513.1948  $[M + Na]^+$  (calc. for C<sub>25</sub>H<sub>22</sub>N<sub>12</sub>Na: 513.1983). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>), δ: 2.26 (s, 9H, CH<sub>3</sub>), 7.14 to 7.44 (m, 12H, Ar), 9.39 (s, 1H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>), δ: 21.2 (CH<sub>3</sub>), 74.0 (CH), 121.8, 126.6, 129.5, 133.4, 139.4 (Ar), 155.5 (CN<sub>4</sub>).

*Tris*(*5*-(*2*-chlorophenyl)-1H-tetrazol-1-yl)methane (*3c*). Yield 0.71 g (7%), light yellow crystals, m.p. 169°C. 1H NMR (400 MHz, DMSO-d6), δ: 7.46 to 8.01 (m, 12H, Ar), 9.43 (s, 1H, CH).

*Tris*(5-(4-chlorophenyl)-1H-tetrazol-1-yl)methane (3d). Yield 0.71 g (7%), light yellow crystals, m. p. 165°C. HRESI<sup>-</sup>-MS, m/z: 549.0383 [M-H]<sup>-</sup> (calc. for  $C_{22}H_{12}Cl_3N_{12}$ : 549.0368). <sup>1</sup>H NMR (400 MHz, DMSO $d_6$ ), δ: 7.68 to 8.17 (m, 12H, Ar), 9.47 (s, 1H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO- $d_6$ ), δ: 77.0 (CH), 124.9, 129.2, 129.3, 130.3, 136.9 (Ar), 165.3 (CN<sub>4</sub>).

*Tris*(5-(3-(*trifluoromethyl*)*phenyl*)-1*H*-*tetrazol*-1-*yl*) *methane* (3e). Yield 0.87 g (8%), colorless crystals, m. p. 162°C. HRESI<sup>+</sup>-MS, m/z: 675.1135  $[M + Na]^+$  (calc. for  $C_{25}H_{13}F_9N_{12}Na$ : 675.1124). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> $d_6$ ),  $\delta$ : 7.74 to 7.96 (m, 12H, Ar), 9.23 (s, 1H, CH). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>- $d_6$ ),  $\delta$ : 63.22 (s, 9F, CF<sub>3</sub>).

*Tris*(*5*-(*4*-*hydroxyphenyl*)-1*H*-*tetrazol*-1-*yl*)*methane* (3f). Yield 0.516 g (6%), white crystals, m.p. 183°C. HRESI<sup>-</sup>-MS, m/z: 495.1396  $[M-H]^-$  (calc. for C<sub>22</sub>H<sub>16</sub>N<sub>12</sub>O<sub>3</sub>: 495.1396). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ: 6.75 to 7.97 (m, 12H, Ar), 9.29 (s, 1H, CH).

*Tris*(*5*-(*3*-*nitro*-*4*-*hydroxyphenyl*)-1*H*-*tetrazol*-1-*yl*) *methane* (3g). Yield 0.70 g (9%), red crystals, m. p. 189°C. HRESI<sup>+</sup>-MS, m/z: 654.0913  $[M + Na]^+$  (calc. for C<sub>22</sub>H<sub>13</sub>N<sub>15</sub>O<sub>3</sub>Na: 654.0890). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$ : 7.57 (s, 1H, CH), 7.75 to 8.31 (m, 9H, Ar).

**2-Dichloromethyl-5-phenyl-2H-tetrazole** (4a). Yield 2.62 g (23%), cream-colored crystals, m.p.  $93^{\circ}$ C. HRESI<sup>+</sup>-MS, m/z:  $[M + Ag]^+$  334.9015 (calc. for  $C_8H_6Cl_2N_4Ag$ : 334.9026). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$ : 7.21 to 7.63 (5H, m, Ph), 8.84 (1H, s, CH) (correspond to literary data<sup>[8]</sup>).

**2-Dichloromethyl-5-m-tolyl-2H-tetrazole (4b)**. Yield 3.03 g (25%), white crystals, m.p. 98°C. HRESI<sup>+</sup>-MS, m/z: 350.9164  $[M + Ag]^+$  (calc. for C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>4</sub>Ag: 350.9158). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.48 (3H, s, CH<sub>3</sub>), 7.36 to 8.07 (5H, m, Ar), 8.17 (1H, s, CH).

5-(2-chlorophenyl)-2-dichloromethyl-2H-tetrazole (4c). Yield 2.74 g (21%), white crystals, m.p. 91°C. HRESI<sup>+</sup>-MS, m/z: 284.9472 [M + Na]<sup>+</sup> (calc. for C<sub>8</sub>H<sub>5</sub>Cl<sub>3</sub>N<sub>4</sub>Na: 284.9485). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ: 7.53 to 7.55, 8.16 to 8.20 (5H, m, Ar), 8.40 (1H, s, CH).

5-(4-chlorophenyl)-2-(dichloromethyl)-2H-tetrazole (4d). Yield 3.00 g (23%), cream-colored crystals, m. p. 95°C. HRESI<sup>+</sup>-MS, m/z: 284.9472  $[M + Na]^+$  (calc. for  $C_8H_5Cl_3N_4Na:$  284.9479). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta:$  7.47 to 7.61, 8.05 to 8.07 (5H, m, Ar), 8.30 (1H, s, CH).

X-ray diffraction. Single crystals of 3a, 3b, and 4d were selected for data collection under optical microscope, encased in an oil-based cryoprotectant (to avoid deterioration under contact with the atmosphere) and mounted on cryoloops. Diffraction data were collected at 125 K (3a), 115 K (3b), and 270.87 K (4d) using a Rigaku Oxford Diffraction XtaLAB SuperNova diffractometer equipped with an HyPix3000 CCD area detector operated with monochromated microfocused CuK $\alpha$  radiation ( $\lambda$ [CuK $_{\alpha}$ ] = 1.54184 Å (**3a**, **3b**),  $\lambda$ [CuK<sub> $\alpha$ </sub>] = 0.71073 Å (**4d**)). All the data were integrated and corrected for background, Lorentz, and polarization effects by means of the CrysAlisPro program complex. Analytical numeric absorption correction (3b) and empirical absorption correction (3a, 4d) were applied using multifaceted crystal model and spherical harmonics, respectively. The unit-cell parameters were refined by the least-squares techniques. The structures were solved by direct methods and refined using the SHELX program incorporated in the OLEX2 program package.<sup>[30]</sup> The final models included coordinates and anisotropic displacements parameters for all atoms. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the "riding" model approximation, with Uiso(H) set to 1.5Ueg(C) and a C-H bond length of 0.98 Å for the CH<sub>3</sub> groups, and with Uiso(H) set to 1.2Ueq(C) and a C-H bond length of 0.95 Å for the for CH groups in cyclic moieties.<sup>[30]</sup> Crystal data and refinement details for 3a, 3b, and 4d are given in Table 3.

#### 4.4 | Details of Hirshfeld surface analysis

The Hirshfeld molecular surfaces were generated by CrystalExplorer 3.1 program.<sup>[31,32]</sup> The normalized contact distances,  $d_{\text{norm}}$ ,<sup>[33]</sup> based on Bondi's van der Waals radii,<sup>[14]</sup> were mapped into the Hirshfeld surface. In the color scale, negative values of  $d_{\text{norm}}$  are visualized by the red color indicating contacts shorter than the sum of van der Waals radii. The white color denotes intermolecular distances that are close to van der Waals contacts with  $d_{\text{norm}}$  equal to zero. In turn, contacts longer than the sum of van der Waals radii with positive  $d_{\text{norm}}$  values are colored with blue.

### 4.5 | Processing of CCDC

Processing of the Cambridge Structure Database (v 5.39) was performed using the ConQuest module (v 1.20). The analysis for the (tetrazole)…lp and (tetrazole)… $\pi$  interactions was based on three parameters: viz. distance C…X (d1), and angles N1-C…X (a1) and N2-C…X (a2) (Figure 6). The distances were restricted by sum of Bond

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**TABLE 3** Crystallographic data and structure refinement parameters for 3a, 3b, 4d

Compound	3a	3b	4d
CCDC code	1 910 559	1 897 088	1 910 560
Empirical formula	$C_{22}H_{16}N_{12}$	$C_{25}H_{22}N_{12}$	$C_8H_5Cl_3N_4$
Formula weight	448.47	490.54	263.51
Temperature/K	125	115	271
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_{1}/c$	$P2_1/n$	Pnma
a/Å	9.63737(13)	12.5835(2)	10.3614(2)
b/Å	15.53047(19)	14.5238(3)	6.79914(15)
c/Å	13.91431(19)	13.1292(2)	14.7801(3)
$lpha/^{\circ}$	90	90	90
$eta/^\circ$	93.4940(11)	92.8858(15)	90
$\gamma/^{\circ}$	90	90	90
Volume/Å <sup>3</sup>	2078.72(5)	2396.46(7)	1041.24(4)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.433	1.360	1.681
$\mu/mm^1$	0.782	0.724	0.848
F(000)	928.0	1024.0	528.0
Crystal size/mm <sup>3</sup>	$0.33 \times 0.12 \times 0.1$	$0.093 \times 0.08 \times 0.038$	$0.1\times0.1\times0.1$
Radiation	$CuK_{\alpha}$ ( $\lambda = 1.54184$ )	$CuK_{\alpha} (\lambda = 1.54184)$	$MoK_{\alpha}$ ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/°	8.542 to 147.894	9.086 to 145.402	5.512 to 54.998
Index ranges	$-12 \le h \le 11,$ $-19 \le k \le 19, -17 \le l \le 17$	$-15 \le h \le 13,$ $-17 \le k \le 17, -15 \le l \le 16$	$-13 \le h \le 13,$ $-8 \le k \le 8, -19 \le l \le 19$
Reflections collected	37 761	11 925	14 359
Independent reflections	4191 ( $R_{int} = 0.1208$ , $R_{sigma} = 0.0558$ )	4719 ( $R_{int} = 0.0268$ , $R_{sigma} = 0.0329$ )	1296 ( $R_{int} = 0.0271$ , $R_{sigma} = 0.0123$ )
Data/restraints/parameters	4191/0/307	4719/0/338	1296/0/88
Goodness-of-fit on $F^2$	1.024	1.027	1.044
Final R indexes $(I > = 2\sigma [I])$	$R_1 = 0.0850, wR_2 = 0.1176$	$R_1 = 0.0384, wR_2 = 0.0994$	$R_1 = 0.0214$ , w $R_2 = 0.0528$
Final R indexes (all data)	$R_1 = 0.0996, wR_2 = 0.1227$	$R_1 = 0.0475, wR_2 = 0.1047$	$R_1 = 0.0238, wR_2 = 0.0542$
Largest diff. peak/hole/e $\text{\AA}^{-3}$	0.21/-0.32	0.27/-0.22	0.38/-0.28



FIGURE 6 Parameters taken for processing CCDC data

vdW radii and a1-2 angularity was restricted to in a range from  $65^{\circ}$  to  $115^{\circ}$ , whereas X was any atom except hydrogen. In case of several contacts, the shortest contact was selected. Only structures with determined 3D and with no error were included in the search query. In addition to this, powder structures were excluded from the search. To ensure that we have only high-quality structures, Rfactor—which represents the agreement between the obtained crystallographic model and the experimental diffraction data—was kept below 0.1.

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