

Crystal Structures of 1-Aryl-1*H*- and 2-Aryl-2*H*-1,2,3-triazolyl Hydrazones. Conformational Consequences of Different Classical Hydrogen Bonds

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The crystal structures of (*Z*)-1-phenyl-4-[(2-phenylhydrazono)methyl]-1*H*-1,2,3-triazole, (*Z*)-4-[(2-(2,4-dimethylphenyl)hydrazono)methyl]-2-phenyl-2*H*-1,2,3-triazole, (*E*)-4-[(2-(2,4-dinitrophenyl)hydrazono)methyl]-2-phenyl-2*H*-1,2,3-triazole, and (*E*)-*N*-((2-phenyl-2*H*-1,2,3-triazol-4-yl)methylene)isonicotinohydrazide dihydrate are reported. The formations of (*Z*)- configurations about the C=N bonds in the first two compounds arise from the stabilizing presence of intramolecular N–H...N hydrogen bonds, while in the third compound, the presence of intramolecular N–H...O hydrogen bonds promotes an (*E*) geometry. The arrangement about the CONHC=N fragment in the hydrated acylhydrazone is $E_{C(O)NH}/E_{C=N}$. Also present in (*E*)-*N*-((2-phenyl-2*H*-1,2,3-triazol-4-yl)methylene)isonicotinohydrazide is an interesting $R^4_4(8)$ ring formed from hydrogen bonds generated from four water molecules. Significant $\pi\cdots\pi$ stacking interactions are exhibited in three compounds, but not in the least planar first compound, in which the dominant intermolecular interactions are C–H... π interactions. Other intermolecular interactions in one of the compounds are C–H... π interactions, in another compound are C–H...O hydrogen bonds and N–O... π interactions, and in the last compound are O–H...X (X = O and N), N–H...O and C–H...O hydrogen bonds.

Keywords: benzotriazoles, hydrazones, acylhydrazones, hydrates, intermolecular interactions

Introduction

1,2,3-Triazole derivatives have found applications in many areas.¹⁻³ Particularly important uses have been in the medical field, including as antiviral,⁴⁻⁶ antimalarial,⁷ antitubercular,⁸⁻¹⁰ antifungal,¹¹⁻¹³ anti-HIV,¹⁴ β -lactamase inhibition,¹⁵ anti-epileptic,¹⁶ anti-HSV,¹⁷ anti-inflammatory,¹⁸ antimicrobial^{19,20} and α -glycosidase inhibition agents.²¹⁻²⁴ A recent α -glycosidase inhibition study involved a number of different 1-phenyl-1*H*- and 2-phenyl-2*H*-1,2,3-triazolyl derivatives.²⁴ See Figure 1 for the tautomeric forms of the parent compounds: 1*H*-1,2,3-triazole and 2*H*-1,2,3-triazole.

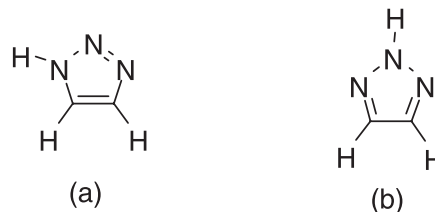
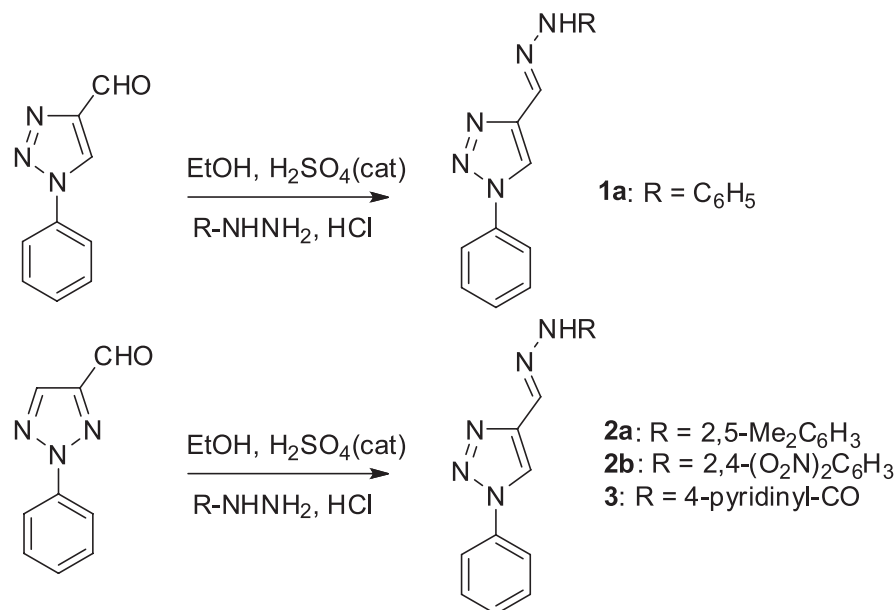


Figure 1. (a) 1*H*-1,2,3-triazole; (b) 2*H*-1,2,3-triazole.

The crystal structures of four of the moderately active hydrazonyl derivatives in the glycosidase inhibition study²⁴ have been determined, namely of (*Z*)-1-phenyl-4-[(2-phenylhydrazono)methyl]-1*H*-1,2,3-triazole (**1a**), (*Z*)-4-[(2-(2,4-dimethylphenyl)hydrazono)methyl]-2-phenyl-2*H*-1,2,3-triazole (**2a**), (*E*)-4-[(2-(2,4-dinitrophenyl)hydrazono)methyl]-2-phenyl-2*H*-1,2,3-triazole (**2b**),

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Scheme 1. Preparation of compounds.

and (*E*)-*N*-((2-phenyl-2*H*-1,2,3-triazol-4-yl)methylene)isonicotinohydrazide dihydrate, (**3**·2H₂O), see Scheme 1.

An antifungal activity study of related 1*H*-1,2,3-triazolyl hydrazones was also published very recently.¹³ The crystal structure of one of the compounds, (*E*)-4-[2-C₆H₄-NH-N=CH]-1-(2-C₆H₄)-1*H*-1,2,3-triazole (**1b**), was reported and has been deposited in the Cambridge Crystallographic Data Centre (CCDC No. 976935; ref code: FONZAL), but only the molecular configuration had been reported in the article.¹³ In this article, we report the crystal structures of **1a**, **2a**, **2b** and (**3**·2H₂O), and make comparisons with that of **1b**.

Experimental

X-Ray crystallography

Data for compounds **1a**, **2a** and (**3**·2H₂O) were obtained at 100(2) K, while data for compound **2b** were collected at 120(2) K. All with Mo K α radiation by means of a Rigaku Saturn 724+ (2 × 2 bin mode) instrument of the National Crystallography Service (NCS), University of Southampton. Data collection, data reduction and unit cell refinement were achieved with the DENZO²⁵ and COLLECT²⁶ programs. Correction for absorption was achieved in each case by a semi-empirical method based upon the variation of equivalent reflections with the Rigaku version of the program SADABS 2007/2.²⁷ The program, MERCURY²⁸ was used in the preparation of the Figures. SHELXL97²⁹ and PLATON³⁰ were used in the calculation of molecular geometry. The structures were solved by

direct methods by SHELXT and fully refined by means of the SHELXL using OSCAIL.³¹ Difference map provided position for the N–H hydrogen atoms in all four compounds and for the water hydrogen atoms in (**3**·2H₂O). All other hydrogen atoms were placed in calculated positions. Crystal data and structure refinement details are listed in Table 1.

Results and Discussion

The compounds were prepared as previously reported²⁴ from the corresponding aldehydes, see Scheme 1. Samples used in the structure determinations were grown by slow evaporation of solutions in methanol for **1a** and **2a**, in 2-methoxyethanol for **2b**, and in ethyl acetate for **3**. The cell dimensions for a sample of **2b**, recrystallized from methanol, indicated the same phase as obtained from 2-methoxyethanol. The crystals obtained from recrystallisation of **3** from ethyl acetate were of the dihydrate (**3**·2H₂O).

Molecular conformations

The asymmetric unit in each of **1a**, **2a** and **2b** consists of a single molecule, that of (**3**·2H₂O) a molecule of **3** and two molecules of water. Figure 2 illustrates the numbering schemes for all the molecules. Selected bond lengths and angles are listed in Table 2. Comparison of the bond lengths in the triazolyl rings in the 1*H*-1,2,3-triazole, compound **1a**, and the 2*H*-1,2,3-triazole compounds, **2a**, **2b** and (**3**·2H₂O), indicate that the major differences are found in the C4–C5 and C5–N1 bond lengths. The bond lengths in the

Table 1. Crystal data and structure refinement

	1a	2a	2b	(3·2H₂O)
Empirical formula	C ₁₅ H ₁₃ N ₅	C ₁₇ H ₁₇ N ₅	C ₁₅ H ₁₁ N ₇ O ₄	C ₁₅ H ₁₆ N ₆ O ₃
Formula weight	263.30	291.38	353.31	328.34
Temperature / K	100(2)	100(2)	120(2)	100(2)
Crystal system, space group	triclinic, <i>P</i> -1	monoclinic, <i>P</i> ₂ /n	triclinic, <i>P</i> -1	monoclinic, <i>P</i> ₂ /c
Unit cell dimensions				
<i>a</i> / Å	5.7096(4)	15.139(7)	9.2315(3)	9.2332(6)
<i>b</i> / Å	7.2055(5)	5.5315(17)	9.5903(5)	11.9186(7)
<i>c</i> / Å	15.7986(11)	17.352(8)	9.6938(6)	14.0316(9)
α / degree	98.715(10)	90	89.796(6)	90
β / degree	99.437(10)	94.300(4)	65.000(8)	95.041(7)
γ / degree	90.9490(10)	90	85.248(7)	90
Volume / Å ³	633.19(8)	1448.9(10)	774.67(7)	1538.16(17)
<i>Z</i>	2	4	2	4
Density (calculated) / (mg m ⁻³)	1.381	1.336	1.515	1.418
Absorption coefficient / mm ⁻¹	0.088	0.084	0.115	0.103
F(000)	276	616	364	688
Crystal size / mm	0.11 × 0.07 × 0.03	0.24 × 0.04 × 0.04	0.96 × 0.53 × 0.23	0.16 × 0.096 × 0.06
θ range for data collection / degree	2.65 to 27.48	3.45 to 27.62	3.10 to 27.43	3.06 to 27.48
Index ranges	-6 ≤ <i>h</i> ≤ 7; -9 ≤ <i>k</i> ≤ 9; -20 ≤ <i>l</i> ≤ 20	-16 ≤ <i>h</i> ≤ 19; -7 ≤ <i>k</i> ≤ 4; -22 ≤ <i>l</i> ≤ 21	-11 ≤ <i>h</i> ≤ 11; -12 ≤ <i>k</i> ≤ 12; -12 ≤ <i>l</i> ≤ 12	-8 ≤ <i>h</i> ≤ 11; -15 ≤ <i>k</i> ≤ 11; -18 ≤ <i>l</i> ≤ 18
Reflections collected	7812	8351	9903	9099
Independent reflections	2856 (<i>R</i> _{int} = 0.0398)	3306 (<i>R</i> _{int} = 0.0218)	3511 (<i>R</i> _{int} = 0.0205)	3511 (<i>R</i> _{int} = 0.0438)
Reflections observed (> 2sigma)	1959	2891	2982	2481
Data completeness	0.98	0.98	1.00	1.00
Data/restraints/parameters	2856 / 0 / 184	3306 / 0 / 204	3511 / 0 / 238	3511 / 0 / 232
Goodness-of-fit on F ²	0.89	1.06	1.10	1.02
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> ₁ = 0.042 w <i>R</i> ₂ = 0.102	<i>R</i> ₁ = 0.053 w <i>R</i> ₂ = 0.116	<i>R</i> ₁ = 0.035 w <i>R</i> ₂ = 0.097	<i>R</i> ₁ = 0.043 w <i>R</i> ₂ = 0.101
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.071 w <i>R</i> ₂ = 0.114	<i>R</i> ₁ = 0.062 w <i>R</i> ₂ = 0.122	<i>R</i> ₁ = 0.041 w <i>R</i> ₂ = 0.105	<i>R</i> ₁ = 0.066 w <i>R</i> ₂ = 0.108
Largest diff. peak and hole / (e Å ⁻³)	0.26 and -0.28	0.21 and -0.22	0.24 and -0.23	0.26 and -0.27
CCDC No.	1434781	1434786	1434776	1434783

hydrazonyl linker, C13–N5–N4–C6–C4, in compounds **1a**, **1b** and **2a**, indicate that electron delocalization occurs within the link, as do the bond lengths in the acylhydrazonyl linker, C14–C13(O1)–N5–N4–C6–C4, in molecule **3**.

The most significant conformational result is that compounds **1a** and **2a** have (*Z*) geometries about the C=N bond, in contrast to the (*E*)-configuration in **2b** and (**3·2H₂O**) (Figure 2); compound **1b**¹³ also has the (*E*)-configuration (Figure 3a). Generally in the absence of special circumstances, (*Z*)-isomers are thermodynamically less stable than (*E*)-isomers. The special circumstances in **1a** and **2a** must be the formations of the classical and strong N5–HN5...N3 intramolecular hydrogen bonds, which enhance the stability of the (*Z*)-isomers. On the other hand, the (*E*)-configuration in the 2,4-dinitrophenyl derivative, **2b** does permit the formation of strong classical N4–HN5...O1 intermolecular hydrogen bonds, involving

an oxygen atom of the *ortho*-nitro group. Such a strong N4–HN5...O1 intermolecular hydrogen bond in **2b** must further enhance the stability of the (*E*)-configuration of **1b** over that of the (*Z*)-isomer. For compound **1b**, it is argued that the *ortho*-chloro substituent prevents the formation of a (*Z*)-configuration, due to the potential steric hindrance between chlorine and adjacent atoms (see Figure 3b). In Figure 3b are drawn the two possibilities for (*Z*)-(**1b**), arising from the two possible positions of the chloro group in the phenyl ring. The chlorine atom would be uncomfortably close in (*i*) to the N–H bond and in (*ii*) to a nitrogen atom.

The arrangement about the C(O)–NH–N=CH-aryl fragment in **3** is designated as *E*_{C(O)NH}/*E*_{C=N}. As reported for many acylhydrazones, such as **3**, there are two potential configurations about the C(O)–NH bond (*E*_{C(O)NH} and *Z*_{C(O)NH}), as well as the two geometric isomers about the C=N

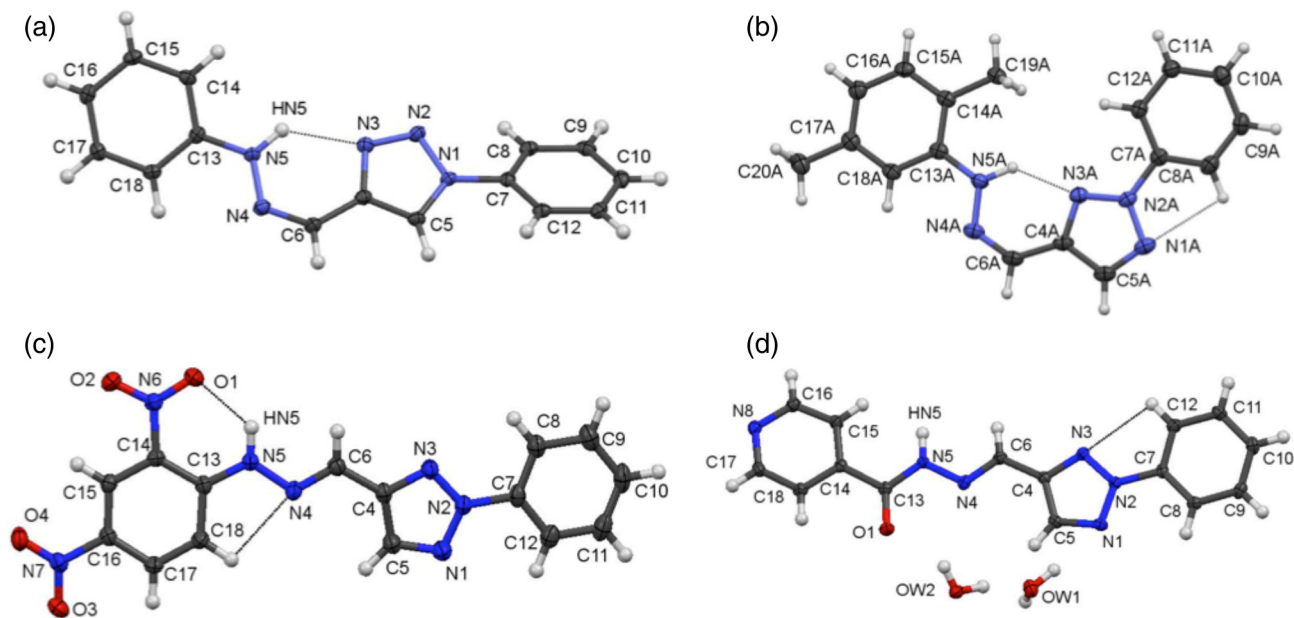


Figure 2. Atom arrangements and numbering schemes for (a) **1a**, (b) **2a**, (c) **2b**, and (d) **(3.2H₂O)**. Ellipsoids are drawn at the 50% level. Hydrogen atoms are drawn as spheres of arbitrary radius. Intramolecular hydrogen bonds are drawn as thin dashed lines.

Table 2. Selected bond lengths (Å) and angles (degree)

	1a	2a	2b	(3.2H₂O)
C13–N5	1.4005(18)	1.395(2)	1.3524(14)	1.3519(13)
N5–N4	1.3626(18)	1.3502(18)	1.3757(13)	1.3772(15)
N4–C6	1.2940(19)	1.295(3)	1.2812(14)	1.2769(18)
C6–C4	1.455(2)	1.446(3)	1.4551(15)	1.4494(18)
C4–C5	1.377(2)	1.403(3)	1.4031(16)	1.397(2)
C5–N1	1.3466(19)	1.323(3)	1.3245(16)	1.3245(16)
N1–N2	1.3600(17)	1.3452(17)	1.3449(13)	1.3429(16)
N2–N3	1.3155(17)	1.339(2)	1.3550(13)	1.3318(15)
N3–C4	1.375(2)	1.346(2)	1.3384(14)	1.3342(18)
C13–N5–N4	118.14(12)	119.79(14)	118.97(9)	117.58(12)
N5–N4–C6	118.39(15)	118.44(15)	115.19(10)	116.68(12)
N4–C6–C4	129.14(15)	129.27(15)	118.73(10)	118.03(13)
C18–C13–N5–N4	21.9(2)	1.3(2)	8.82(17)	
C15–C14–C13–N5				8.2(2)
C18–C14–C13–N5				173.02(13)
C15–C14–C13–O1				171.29(13)
C18–C14–C13–O1				7.5(2)
C14–C13–N5–N4	159.39(14)	179.36(15)	172.05(11)	179.94(11)
C13–N5–N4–C6	177.85(13)	179.16(16)	177.03(11)	175.48(13)
N5–N4–C6–C4	1.4(2)	0.2(3)	176.56(11)	179.05(12)
N4–C6–C4–N3	1.8(3)	2.4(3)	179.51(12)	176.87(13)
N4–C6–C4–C5	178.51(15)	176.1(2)	0.7(2)	1.1(2)

bond ($E_{C=N}$ and $Z_{C=N}$), making four possible arrangements in all about the C(O)–NH–N=CH–aryl fragment.^{32–35}

While the triazolyl ring is planar in all compounds, none of the compounds is planar overall. The deviation from planarity is relatively small for the *2H*-1,2,3-triazolyl compounds, **2a**, **2b** and **3**, as shown by the angles between

the aryl rings in Table 3, and very much larger for **1a** and **1b** (see Figure 4). The increased deviation from planarity of the triazole and its attached phenyl ring in a *H*-1,2,3-triazolyl may arise from steric repulsions between the *ortho* C–H bonds in the triazole ring and the phenyl ring. Of interest, the sums of the dihedral angles between the

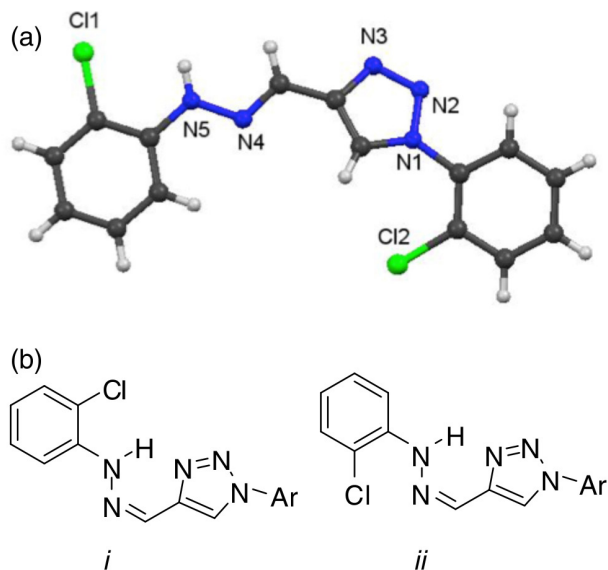


Figure 3. (a) The (*E*)-geometric form determined for **1b** in the solid state;¹³ (b) potential (*Z*)-forms of **1b**. Ar = 2-chlorophenyl.

phenyl groups and the triazolyl ring are very similar to the single dihedral angle between the two phenyl rings in each of **1a**, **2a**, **2b** and **3**, which indicates that the deviation from planarity can be considered to have arisen from rotations about the C13–N5 and C7–N2 bonds occurring in the same sense. This is not the case in the 1*H*-1,2,3-triazolyl compound, **1b**. For **1b**, the dihedral angles point to rotations about the C13–N5 and C7–N2 bonds occurring in the opposite senses, with the result that the two phenyl groups have a small dihedral angle of ca. 6°, compared to ca. 51° in **1a**. If rotations about these C13–N5 and C7–N2 bonds did occur in the same sense, it would place either Cl1 too close to N5, or Cl2 too close to N2.

Dihedral angles between aryl and triazolyl rings in 1-aryl-1*H*- and 2-aryl-2*H*-1,2,3-triazole compounds have been shown to vary considerably, for example, such angles are 0.34(17) and 87.1(2)°, respectively, in 4-(difluoromethyl)-1*H*-1,2,3-triazole,³⁶ and in one independent molecule of 1-[5-methyl-1-(4-nitrophenyl)methyl-1-(4-methylphenyl)-1*H*-1,2,3-triazol-4-yl] ethanone.³⁷ The aryl group substituents and crystal packing effects have major influences on such dihedral angles. The

Table 3. Angles between the best planes through the aryl rings

Compound	Angle between free phenyl and triazole / degree	Angle between free phenyl and phenyl on triazole / degree	Angle between triazole and attached phenyl / degree
1a	23.72(8)	51.15(7)	28.54(8)
2a	2.58(9)	7.13(8)	4.64(9)
2b	14.06(7)	8.66(6)	6.92(7)
(32H ₂ O)	6.35(7)	11.19(7)	5.28(7)
1b ¹³	23.34(8)	6.57(8)	27.67(8)

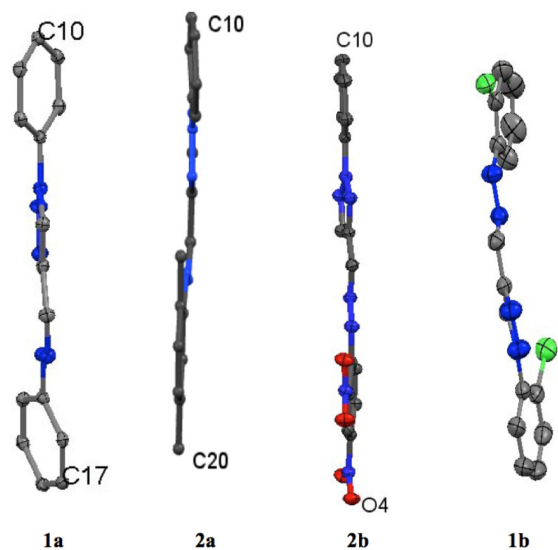


Figure 4. Molecular conformations. Hydrogen atoms have been omitted.

dihedral angles in **2a** between the phenyl group and (i) the attached *ortho*-nitro group, O2–N6–O1, and (ii) *para*-nitro group, O3–N7–O4, are 3.93 and 13.69°, respectively. The small angle between the phenyl and its *ortho*-nitro group facilitates the formation of the N5–HN5...O1 intramolecular hydrogen bond.

Crystal structures

Compound **1a**

The only classical hydrogen bond present in **1a** is the intramolecular N5–HN5...N3 hydrogen bond (Figure 2a). The intermolecular interactions in **1a** are four C–H... π interactions (Table 4).³⁸

The combination of the C–H... π interactions, C9–H9... π (phenyl-*b*), C12–H12... π (phenyl-*b*), C15–H15... π (phenyl-*a*) and C18–H18... π (phenyl-*a*), provides sheets of molecules in the *ab* plane, as shown in Figure 5. Phenyl-*a* and phenyl-*b* are the phenyl groups with atoms C7–C12 and C13–C18, respectively. The triazole ring is not involved in C–H... π interactions. The PLATON analysis³¹ indicates the possibility of π (triazolyl)... π (triazolyl) stacking interactions.³⁹ However,

Table 4. Geometric parameters (Å, degree) for intra- and intermolecular interactions

Intramolecular hydrogen bonds							
Compound	D–H...A	D–H	H...A	D...A	D–H...A		
1a	N5–HN5...N3	0.949(17)	2.067(17)	2.7829(18)	131.0(14)		
2a	N5–HN5...N3	0.929(17)	2.042(17)	2.768(2)	133.9(15)		
2a	C8H8...N1	0.95	2.49	2.808(3)	100		
2b	N5–HN5...O1	0.898(14)	1.975(14)	2.6342(14)	129.1(14)		
2b	N5–HN5...N6	0.898(14)	2.621(16)	2.9512(15)	102.7(11)		
2b	C18–H18...N4	0.95	2.40	2.7320(16)	100		
(3·2H ₂ O)	C12–H12...N3	0.93	2.50	2.8069(18)	100		
Intermolecular hydrogen bonds							
Compound	D–H...A	D–H	H...A	D...A	D–H...A		
2b	N5–HN5...O1 ⁱ	0.898(14)	2.520(15)	3.3218(14)	149.0(14)		
2b	C5–H5...O3 ⁱⁱ	0.95	2.53	3.3984(18)	152		
2b	C6–H6...O3 ⁱⁱⁱ	0.95	2.60	3.0389(15)	109		
2b	C6–H6...O2 ^j	0.95	2.60	3.5082(15)	160		
2b	C11–H11...O4 ^{iv}	0.95	2.52	3.2179(18)	130		
(3·2H ₂ O)	OW2–HW1A...O1	0.836(18)	2.072(18)	2.8281(150)	150.2(17)		
(3·2H ₂ O)	OW2–HW1A...N4	0.836(18)	2.562(19)	3.2512(16)	140.6(15)		
(3·2H ₂ O)	OW2–HW1B...OW1	0.959(18)	1.773(18)	2.7198(16)	168.5(16)		
(3·2H ₂ O)	N5–HN5...OW2 ^v	0.869(18)	2.048(18)	2.8974(17)	165.6(14)		
(3·2H ₂ O)	OW1–HW2A...OW2 ^{vi}	0.787(18)	2.119(18)	2.8742(16)	161.0(18)		
(3·2H ₂ O)	OW1–HW2B...N8 ^{vii}	0.886(18)	1.9759(17)	2.8457(17)	167.2(16)		
(3·2H ₂ O)	C6–H6...OW2 ^v	0.93	2.55	3.3076(18)	138		
(3·2H ₂ O)	C9–H9...OW1 ^{viii}	0.93	2.56	3.4728(19)	169		
(3·2H ₂ O)	C15–H15...OW2 ^v	0.93	2.52	3.3985(18)	158		
Symmetry codes: <i>i</i> = 1 – <i>x</i> , 1 – <i>y</i> , –1 – <i>z</i> ; <i>ii</i> = 1 – <i>x</i> , 2 – <i>y</i> , – <i>z</i> ; <i>iii</i> = <i>x</i> , <i>y</i> , –1 + <i>z</i> ; <i>iv</i> = –1 + <i>x</i> , 1 + <i>y</i> , –1 + <i>z</i> ; <i>v</i> = – <i>x</i> , –½ + <i>y</i> , ½ + <i>z</i> ; <i>vi</i> = – <i>x</i> , 1 – <i>y</i> , 1 – <i>x</i> ; <i>vii</i> = 1 + <i>x</i> , ½ – <i>y</i> , ½ + <i>z</i> ; <i>viii</i> = 1 – <i>x</i> , <i>y</i> , <i>z</i> .							
Y–X...π interactions ^a							
Compound	Y–X...Cg ^a	X...Cg	X _{perp}	γ	Y–X...Cg	Y...Cg	
1a	C9–H9...Cg3 ⁱ	2.68	2.67	5.81	131	3.3796(17)	
1a	C12–H12...Cg3 ⁱⁱ	2.63	2.62	6.29	131	3.3403(16)	
1a	C15–H15...Cg2 ⁱⁱⁱ	2.78	2.75	8.72	131	3.4822(17)	
1a	C18–H18...Cg2 ^{iv}	2.76	2.72	10.36	129	3.4370(16)	
2a	C19–H19B...Cg2 ^v	2.81	2.68	17.59	150	3.692(2)	
2b	N7–O4...Cg2 ^{vi}	3.7402(11)	3.37	25.73	74.54(6)	3.6125(12)	
Symmetry codes: <i>i</i> = – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i> ; <i>ii</i> = 1 – <i>x</i> , 2 – <i>y</i> , 1 – <i>z</i> ; <i>iii</i> = – <i>x</i> , 2 – <i>y</i> , 1 – <i>x</i> ; <i>iv</i> = 1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i> ; <i>v</i> = <i>x</i> , 1 + <i>y</i> , <i>z</i> ; <i>vi</i> = 1 – <i>x</i> , 2 – <i>y</i> , –1 – <i>z</i> .							
π...π interactions ^a							
Compound	Cg(I)...Cg(J)	Cg...Cg	α	β	γ	CgI _{perp}	CgJ _{perp}
1a	Cg1...Cg1 ⁱ	4.2304(9)	0.02	34.8	34.8	3.48	3.475
2a	Cg1...Cg2 ⁱⁱ	3.726(2)	4.58(9)	27.4	22.8	3.4350(7)	3.3089(6)
2a	Cg2...Cg1 ⁱⁱ	3.726(2)	4.58(9)	22.8	27.4	3.3089(6)	3.4350(7)
2a	Cg3...Cg1 ⁱⁱⁱ	4.065(2)	2.64(9)	33.3	30.7	3.493597	3.3986(7)
2b	Cg1...Cg1 ^{iv}	3.8953(8)	0.03	32.4	32.4	3.27	3.265
2b	Cg2...Cg3 ^v	4.0523(9)	8.66	30.4	36.7	3.25	3.294
2b	Cg3...Cg1 ^v	3.8968(7)	14.05	26.6	26.2	3.50	3.484
(3·2H ₂ O)	Cg1...Cg2 ^{vi}	3.5089(8)	5.28	12.6	7.5	3.48	3.425
(3·2H ₂ O)	Cg1...Cg2 ^{vii}	3.9188(8)	8.00	32.3	36.0	3.17	3.314
(3·2H ₂ O)	Cg3...Cg2 ^{vii}	3.9611(8)	14.12	44.0	23.8	3.63	3.246
Symmetry operation: <i>i</i> = 1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i> ; <i>ii</i> = 1 – <i>x</i> , – <i>y</i> , 1 – <i>z</i> ; <i>iii</i> = <i>x</i> , 1 + <i>y</i> , <i>z</i> ; <i>iv</i> = – <i>x</i> , 2 – <i>y</i> , –1 – <i>z</i> ; <i>v</i> = 1 – <i>x</i> , 2 – <i>y</i> , –1 – <i>z</i> ; <i>vi</i> = 1 + <i>x</i> , <i>y</i> , <i>z</i> ; <i>vii</i> = 1 + <i>x</i> , ½ – <i>y</i> , ½ + <i>z</i> .							

^aIn compounds **1a** and **2b**, Cg1, Cg2 and Cg3 are the centroids of the ring containing N2, C10 and C16, respectively; in compound **3**, Cg1, Cg2 and Cg3 are the centroids of the ring containing N2, C16 and C10, respectively; in compound **2a**, Cg1, Cg2, Cg3, Cg4, Cg5 and Cg6 are the centroids of the ring containing N2A, C10A, C16A, N2B, C10B and C16B, respectively; β is the angle between the vectors Cg...Cg and CgI_{perp}, where CgI_{perp} is the perpendicular distance of CgI from the plane of ring J. Similarly, γ is the angle between the vectors Cg...Cg and CgJ_{perp}. CgJ_{perp} is the perpendicular distance of CgJ from the plane of ring I.

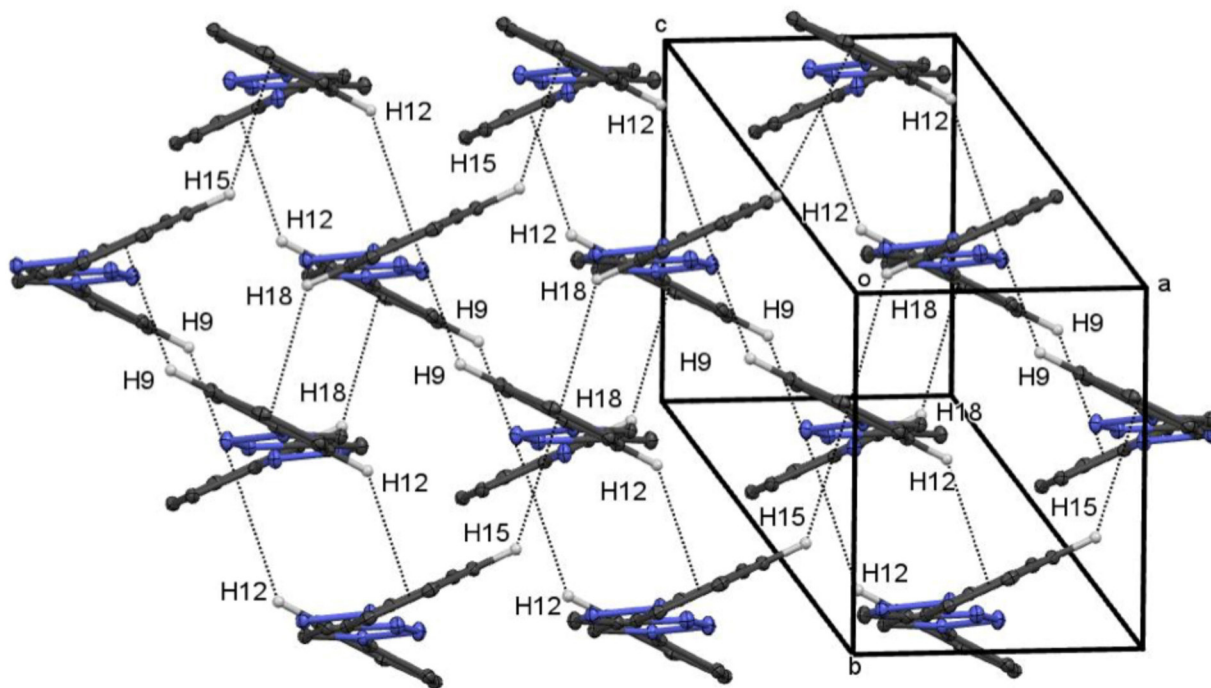


Figure 5. Compound **1a**. Part of the sheet of molecules obtained from C9–H9... π (phenyl-*a*), C12–H12... π (phenyl-*a*), C15–H15... π (phenyl-*b*) and C18–H18... π (phenyl-*b*) in the *ab* plane; phenyl-*a* and phenyl-*b* are the free and triazole-bound phenyl, respectively.

although the perpendicular distance between parallel triazole rings is only 3.475 Å, the C_g...C_g distance is large at 4.2304(9) Å, resulting in ring offsets of 2.413 Å, which indicates that the triazole rings do not overlap.

Compound **2a**

The major intermolecular interactions in **2a** are π ... π stacking interactions. Dimers are generated from pairs of π (triazole)... π (phenyl-*a*) interactions. These dimeric units are further linked by π (triazole)... π (phenyl-*b*) and by C–H... π (phenyl-*a*) interactions into two molecule wide columns, where phenyl-*a* and phenyl-*b* refer to the phenyl group attached to the triazole and the other phenyl group, respectively (Figure 6a). These two-molecule wide columns are free standing and so **2a** has a one-dimensional structure. As shown in Figure 6b, such columns of molecules are propagated in different directions, with angles between the best planes of ca. 76°.

Compound **2b**

As well as the classical intramolecular N–H...O hydrogen bond, there is also a classical intermolecular N–H...O hydrogen bond, and weaker intermolecular C–H...O hydrogen bonds, π ... π stacking and N–O... π interactions (Table 4).^{40,41} In the following discussion, the overall structure is broken down into three sub-structures. Firstly, pairs of the classical intermolecular N5–HN5...O1 and weaker C11–H11...O4 hydrogen bonds form

centrosymmetric dimers, as shown in Figure 7a. Included within these dimers are intramolecular N5–HN5...O1 hydrogen bonds: together, these hydrogen bonds generate a set of R²₂(8), R²₂(4) and R²₂(8) rings. The O1...O1 distance in the O1–NH5–O1–NH5 ring is short. Secondly, ladders of molecules, containing R²₂(24) and R⁴₂(24) rings,⁴² are generated from the combination of C5–H5...O3 and C6–H6...O3 hydrogen bonds: in these ladders, the C5–H5...O3 hydrogen bonds form the rings of the ladder and the C6–H6...O3 form the sides (see Figure 7b). The third sub-structure is a sheet of molecules generated from π (triazole)... π (nitrophenyl), π (phenyl)... π (nitrophenyl) and π (triazole)... π (triazole) stacking interactions, N7–O4... π (phenyl) and C11–H11...O4 hydrogen bonds. The π (triazole)... π (nitrophenyl), π (phenyl)... π (nitrophenyl) and N7–O4... π (phenyl) interactions generate dimeric units, which are linked into single-molecule wide columns by the π (triazole)... π (triazole) interactions. These single-molecule wide columns are further linked into bi-molecule wide columns by the C11–H11...O4 hydrogen bonds (see Figure 7c). Overall, a three-dimensional array is produced.

Compound (**3**·2H₂O)

The intermolecular interactions in compound (**3**·2H₂O) are π ... π stacking interactions and O–H...X (X = O and N), N–H...O and C–H...O hydrogen bonds (Table 4). As expected, the two water molecules are strongly involved in the supramolecular arrangements. A sheet containing

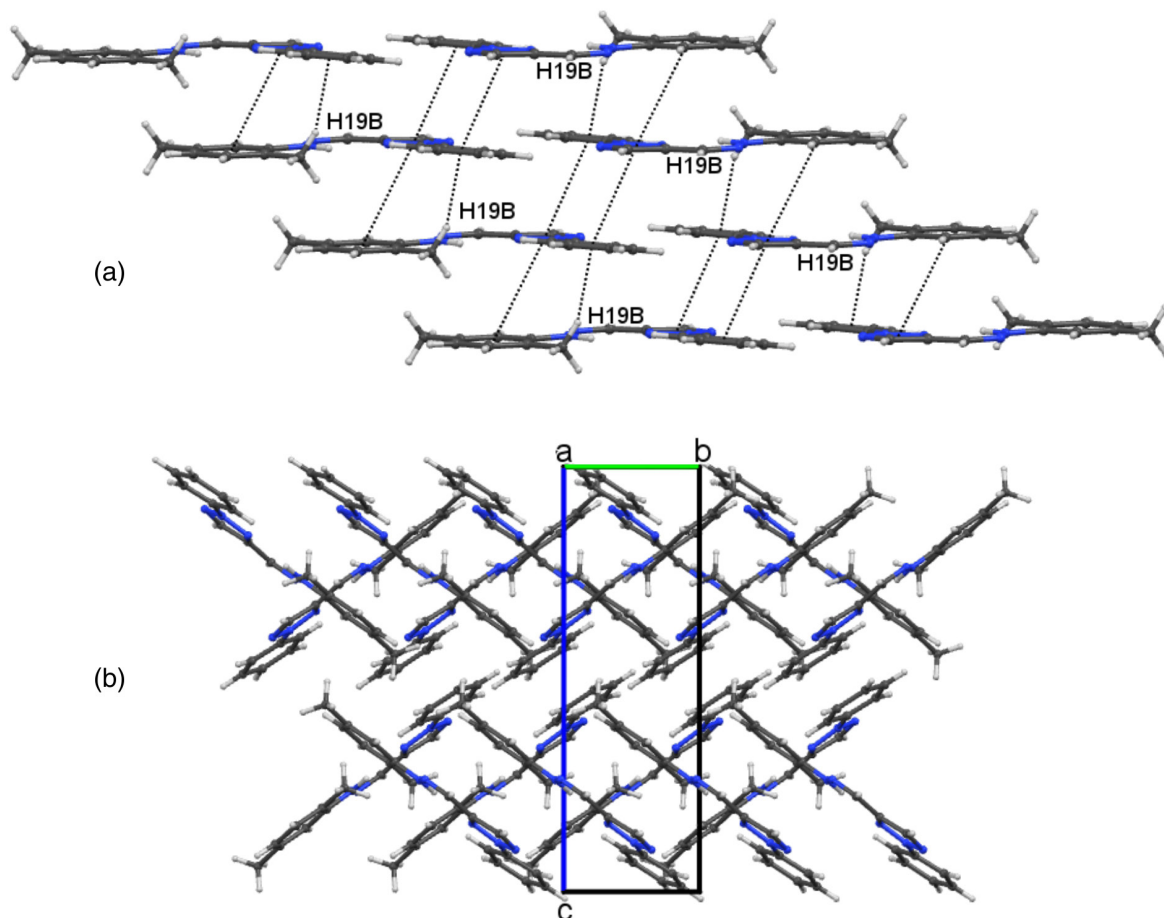


Figure 6. Compound **2a**. (a) Part of a two-molecular wide column of molecules of **2a** generated from $\pi(\text{triazole})\cdots\pi(\text{phenyl-}a)$, $\pi(\text{triazole})\cdots\pi(\text{phenyl-}b)$ and by $\text{C-H}\cdots\pi(\text{phenyl-}a)$ interactions, where phenyl-*a* and phenyl-*b* refer to the phenyl group attached to the triazole and the other phenyl group, respectively; (b) a view, looking down the *a*-axis of the orientations of the different columns passing through the unit cell.

molecules of **3** and water, with oxygen atom, OW1, is generated from combinations of $\pi(\text{triazolyl})\cdots\pi(\text{phenyl})$, $\pi(\text{triazolyl})\cdots\pi(\text{pyridinyl})$ and $\pi(\text{phenyl})\cdots\pi(\text{pyridinyl})$ interactions, and $\text{C9-H9}\cdots\text{OW1}$ and $\text{OW1-HW2B}\cdots\text{N8}$ hydrogen bonds, as illustrated in Figure 8a. Molecules in each layer of the sheet are linked by $\text{C9-H9}\cdots\text{OW1}$ and $\text{OW1-HW2B}\cdots\text{N8}$ hydrogen bonds, and layers are linked by the three different $\pi\cdots\pi$ interactions. The two water molecules make very different connections to other molecules, as shown in Figures 8b and 8c. There are seven short contacts to the water molecule, HW1A-OW2-HW2A (Figure 8b), but there are only four short contacts to the other water molecule, HW2A-OW1-HW2B (Figure 8c). Such contacts to the water molecules generate various rings of atoms. However, the most interesting ring present in $(\mathbf{3}\cdot 2\text{H}_2\text{O})$ is the $\text{R}^4_4(8)$ ring generated from four water molecules, two of each HW1A-OW2-HW2A and HW2A-OW1-HW2B , see Figure 8d. As shown in Figure 8d, the water molecules in the tetrameric rings make short contacts with various atoms in **3**. Overall, a three-dimension array is formed, see Figure 8e.

The hydrogen bonding interactions between the water molecules and molecule of **3** clearly stabilize the $E_{\text{C(O)NH}}/E_{\text{C=N}}$ arrangement about the C(O)-NH-N=CH-aryl fragment in $(\mathbf{3}\cdot 2\text{H}_2\text{O})$.

Conclusions

The significance of the classical intramolecular hydrogen bonds in the molecular conformations is very pronounced in this study. The formations of (*Z*)-configurations about the C=N bonds in **1a** and **2a** arise from the stabilizing presence of intramolecular $\text{N5-HN5}\cdots\text{N3}$ hydrogen bonds, while in **2b** the presence of intramolecular $\text{N5-HN5}\cdots\text{O1}$ hydrogen bonds, *in lieu* of potential $\text{N5-HN5}\cdots\text{N3}$ hydrogen bonds, reinforces the (*E*)-geometry. An $E_{\text{C(O)NH}}/E_{\text{C=N}}$ arrangement about the C(O)-NH-C=N fragment, and an interesting $\text{R}^4_4(8)$ ring composed of four hydrate molecules, are features of the crystal structure of the hydrated acylhydrazone, $(\mathbf{3}\cdot 2\text{H}_2\text{O})$.

As found in this study, significant $\pi\cdots\pi$ interactions are exhibited by compounds **2a** and **2b**, but not by the

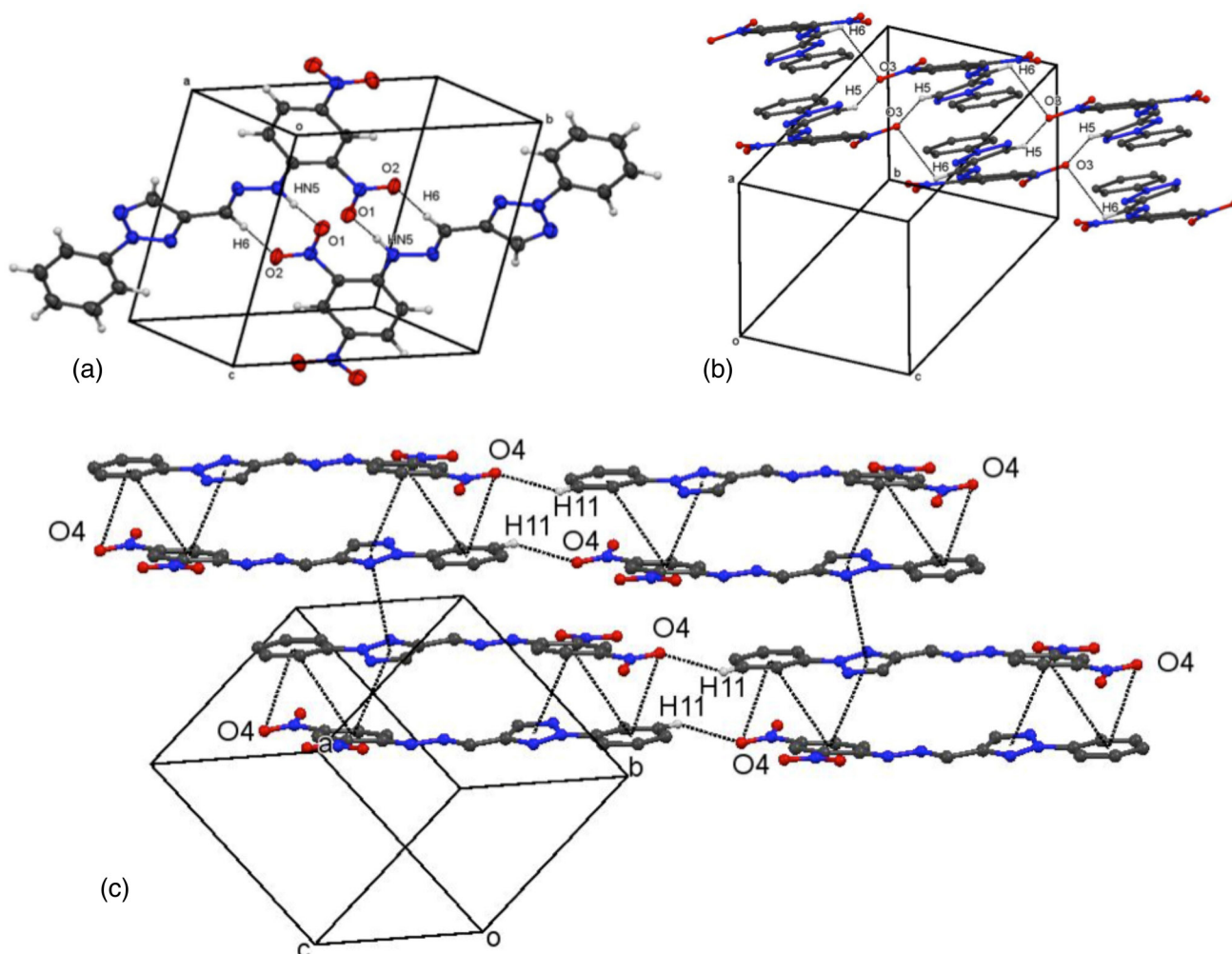


Figure 7. Compound **2b**. (a) A centrosymmetric dimer generated from pairs of N5–HN5...O1 and C6–H6...O2 intermolecular hydrogen bonds; also indicated are intramolecular N5–HN5...O1 hydrogen bonds, together these hydrogen bonds generate a set of $R^2_2(8)$, $R^2_2(4)$ and $R^2_2(8)$ rings; (b) ladders of molecules, containing $R^2_2(24)$ and $R^4_2(24)$ rings, are generated from the combination of C5–H5...O3 and C6–H6...O3 intermolecular hydrogen bonds; (c) part of a sheet of molecules generated from $\pi(\text{triazole})\cdots\pi(\text{nitrophenyl})$, $\pi(\text{phenyl})\cdots\pi(\text{nitrophenyl})$, $\pi(\text{triazole})\cdots\pi(\text{triazole})$ and N7–O4... $\pi(\text{phenyl})$ interactions and C11–H11...O4 intermolecular hydrogen bonds. Intermolecular interactions are drawn as thin dashed lines. Symmetry operations are listed in Table 4.

least planar molecule, **1a**. In contrast, the only important intermolecular interactions in **1a** are C–H... π interactions. Are these differences between **1a**, on one hand, and **2a** and **2b**, on the other, consequences of compound **1a** being an 1*H*-1,2,3-triazole compound, while **2a** and **2b** are 2*H*-1,2,3-triazole derivatives? To effectively answer these questions, further structures of related hydrazonyl derivatives of 1,2,3-triazoles need to be determined.

Moreover, there appears to be no obvious reason why **1a** cannot adopt a near planar configuration. Other points to be considered are the influences of steric effects or the position of substituents. Compound **1a** has no substituents in either the two phenyl rings, while both **2a** and **2b** have *ortho*- and *para*-substituents in the phenyl ring (C13–C18). The other 1*H*-1,2,3-triazole compound mentioned in this article, **1b**,¹³ has *ortho* chloro substituents in both phenyl rings, and does exhibit a much smaller dihedral angle between the two phenyl

rings than does **1a**, but is still not planar (Table 3). As in **1a**, no $\pi\cdots\pi$ interactions are exhibited by **1b**, but the number of different C–H... π intermolecular interactions is reduced to one. The most important intermolecular interaction in **1b** is the classical intermolecular N(hydrazine)–H...N(triazole) hydrogen bonds, with less important interactions being C–H...Cl and N(hydrazine)–H...Cl hydrogen bonds. This prompts the question: does the presence of substituents in the phenyl rings reduce or even prevent C–H... π interactions in **2a** and **2b**, which thus results in different sets of intermolecular interactions being taken up? The answer awaits further study.

Supplementary Information

Full details of the crystal structure determinations in cif format are available in the online version as Supplementary

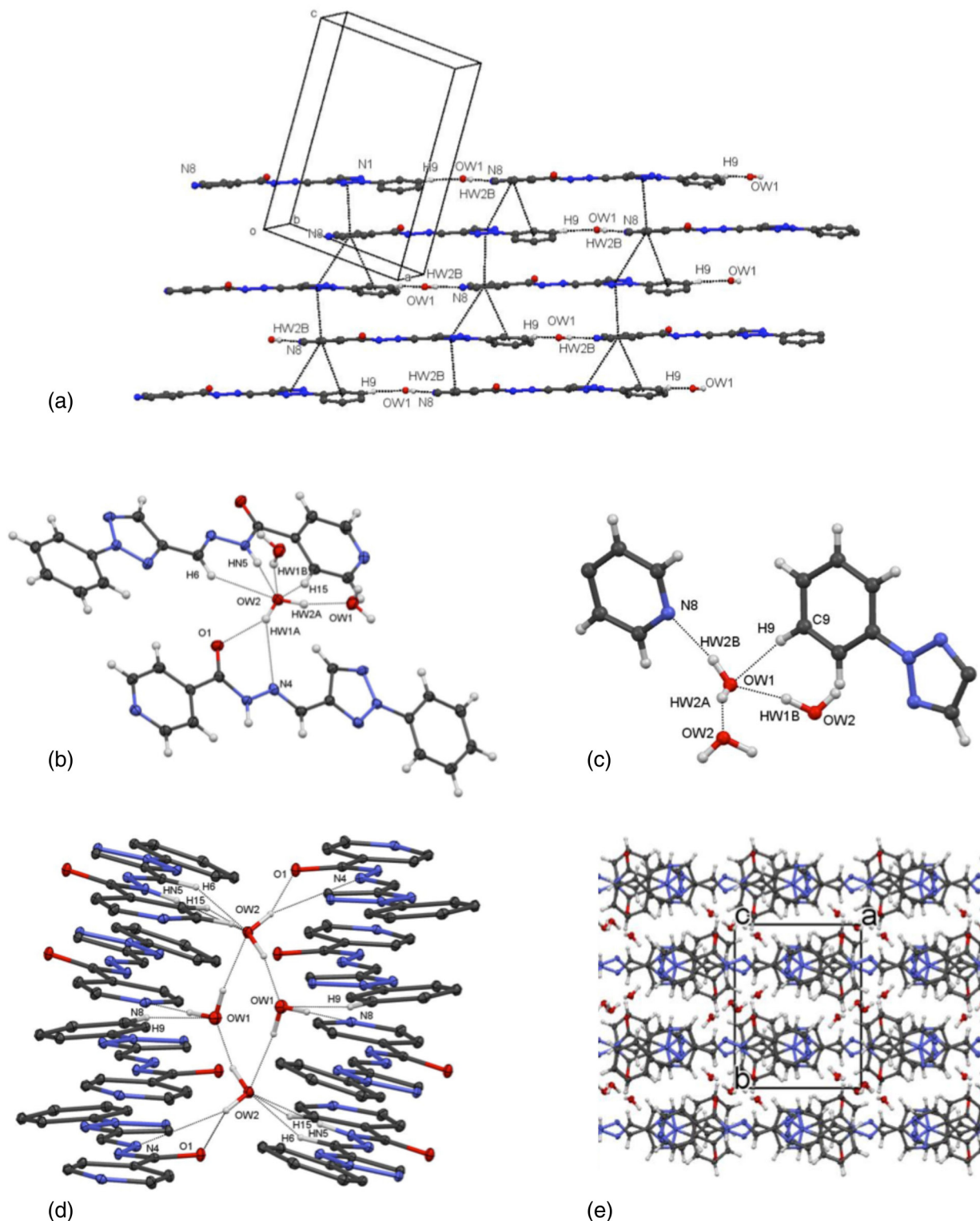


Figure 8. Compound ($3 \cdot 2\text{H}_2\text{O}$). (a) A sheet of **3** and hydrate molecules (with OW1) is generated from combinations of π (triazolyli)- π (phenyl), π (triazolyli)- π (pyridinyl) and π (phenyl)- π (pyridinyl) interactions, and C9-H9...OW1 and OW1-HW2B...N8 hydrogen bonds; (b) and (c) short contacts to the hydrate molecules, HW1A-OW2-HW2A and HW2A-OW1-HW2B, respectively; (d) a $R^2_1(8)$ ring generated from four hydrate molecules, showing contacts with molecules **3**; (e) packing of the molecules looking down the c-axis. Table 4 lists the symmetry operations. The intermolecular interactions are drawn as thin dashed lines.

Information, at <http://jbc.sbg.org.br>, and have also been deposited with the Cambridge Crystallographic Data Centre

with deposition numbers, 1434781, 1434786, 1434776 and 1434783 for **1a**, **2a**, **2b** and ($3 \cdot 2\text{H}_2\text{O}$), respectively. Copies of

these can be obtained free of charge on written application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033); on request by e-mail to deposit@ccdc.cam.ac.uk or by access to <http://www.ccdc.cam.ac.uk>.

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