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ORIGINAL PAPER

Syntheses, X-ray Crystal Structures and Intermolecular Interaction Patterns of Hydrazone Derivatives with 1,2,3-Triazole Entity at 100 K

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Abstract Five new hydrazone derivatives, (*E*)-*N*′-(4-fluorobenzylidene)-5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide, (*E*)-*N*′-(4-chlorobenzylidene)-5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide, (*E*)-*N*′-(4-bromobenzylidene)-5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide, (*E*)-*N*′-(4-hydroxy-3-methoxybenzylidene)-5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide and (*E*)-*N*′-(1-(4-bromophenyl)ethylidene)-5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide (denoted as **A-E**), were prepared and their molecular structures were characterized by single crystal X-ray diffraction. Compound **A** crystallizes in monoclinic $P2_1/c$, $a = 6.8057(1)$ Å, $b = 12.7447(3)$ Å, $c = 18.6936(3)$ Å, $\beta = 105.356(1)°$, **B** crystallizes in monoclinic $P2_1/c$, $a = 8.3815(2)$ Å, $b = 20.8298(4)$ Å, $c = 9.5932(2)$ Å, $\beta = 99.612(1)°$, **C** crystallizes in monoclinic $P2_1/c$, $a = 8.4213(8)$ Å, $b = 21.077(2)$ Å, $c = 9.5899(10)$ Å, $\beta = 99.979(2)°$, **D** crystallizes in monoclinic $P2_1/c$, $a = 11.1644(10)$ Å, $b = 16.3508(15)$ Å, $c = 9.7313(9)$ Å, $\beta = 105.757(1)°$ and **E** crystallizes in triclinic $P\bar{1}$, $a = 8.7415(7)$ Å, $b = 10.1032(8)$ Å, $c = 11.6852(9)$ Å, $\alpha = 68.306(1)°$, $\beta = 84.894(1)°$, $\gamma = 68.289(1)°$. All of the five compounds with close molecular conformations adopt a *trans* configuration with respect to the hydrazone C = N double bond and weak non-classical intermolecular C–H···O hydrogen bonds are observed in the crystal. Isomorphous substitution between compounds **B** and **C** with simple replacement of chlorine atom to bromine atom is giving rise to similar molecular geometries, unit cell parameters and intermolecular interaction pattern of three-dimensional network.

Keywords Hydrazone · Triazole · Crystal structure · Hydrogen bond · Isomorphous substitution

Introduction

Hydrazones, a class of organic compounds which containing an azomethine –NHN=CH– group are formed by the condensation of substituted hydrazines with aldehydes or ketones. Hydrazones can also be synthesized through the coupling of aryldiazonium salts with active hydrogen compounds [1] and this is also one of the oldest methods for the synthesis of arylhydrazones as mentioned by Belskaya et al. [2]. These compounds exhibit efficient nonlinear optical property in their crystalline states [3], complex formation with metal ions and pharmacological properties like antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antiplatelet, antitubercular, anticancer and antitumor activities [4–11].

1,2,3-Triazoles have occupied an important role both in organic and pharmaceutical chemistry [12]. These 1,2,3-traizoles are obtained by the 1,3-dipolar cycloaddition reaction of organoazide with appropriate dipolarophile. 1,2,3-Triazoles with high aromatic stabilization remain stable under basic and acid hydrolysis and reductive and oxidative conditions [13, 14]. Moreover, this heterocycle has a high dipole moment and made it favorable in the

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binding of biomolecular targets through hydrogen bonding [15].

Prompted by these observations, a new series of hydrazone derivatives were synthesized and subjected to single crystal X-ray structure determination studies.

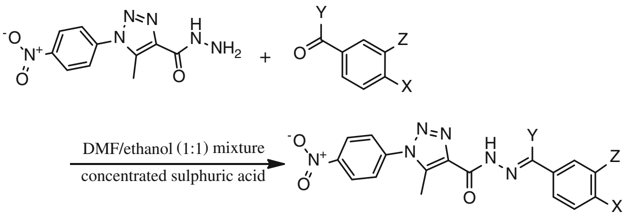
Experimental

General Procedure for Synthesis

A series of five hydrazone derivatives possessing 5-methyl-1-(4-nitrophenyl)-1,2,3-triazole moiety were prepared by the reaction of 5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide with suitably substituted aryl aldehydes. To a solution of 5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide (0.01 mol) in a 1:1 mixture of DMF and ethanol (10 mL), 0.01 mol of 4-flurobenzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde or 4-bromoacetophenone was added. Concentrated sulphuric acid (0.5 mL) was added to this reaction mixture and the contents were refluxed. The solid product separated was collected by filtration, dried and recrystallized from ethanol. Single crystals suitable for X-ray analysis were obtained by slow evaporation method (Scheme 1).

*Preparation of (E)-N′-(4-Fluorobenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**A**)*

Reflux time: 1–2 h. Solvent used for slow evaporation: ethanol-*N*,*N*-dimethylformamide (DMF) (3:1) solution. Yield: 90 %. Elemental analyses test for $C_{17}H_{13}FN_6O_3$: Anal. Calcd.: C, 55.44; H, 3.56; N, 22.82 %. Found: C, 55.48; H, 3.80; N, 22.60 %. IR (KBr, cm^{-1}): 3352.28 (N–H), 1683.86 (C=O), 1584 (C=N stretch), 1554.63 (Asym. N=O), 1324.7 (Sym. N=O).



(A - E)

A	X = F	; Y = H	; Z = H
B	X = Cl	; Y = H	; Z = H
C	X = Br	; Y = H	; Z = H
D	X = OH	; Y = H	; Z = OCH_3
E	X = Br	; Y = CH_3	; Z = H

Scheme 1 The chemical syntheses of five compounds (**A**–**E**) described in this paper

*Preparation of (E)-N′-(4-Chlorobenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**B**)*

Reflux time: 1–2 h. Solvent used for slow evaporation: ethanol. Yield: 87 %. Elemental analyses test for $C_{17}H_{13}ClN_6O_3$: Anal. Calcd.: C, 53.07; H, 3.41; N, 21.84 %. Found: C, 53.12; H, 3.42; N, 21.82 %. IR (KBr, cm^{-1}): 3321.42 (N–H), 1693.50 (C=O), 1573.91 (C=N stretch), 1548.5 (Asym. N=O), 1329.7 (Sym. N=O).

*Preparation of (E)-N′-(4-Bromobenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**C**)*

Reflux time: 1–2 h. Solvent used for slow evaporation: ethanol-*N*,*N*-dimethylformamide (DMF) (3:1) solution. Yield: 87 %. Elemental analyses test for $C_{17}H_{13}BrN_6O_3$: Anal. Calcd.: C, 47.57; H, 3.05; N, 19.58 %. Found: C, 47.59; H, 3.10; N, 19.46 %. IR (KBr, cm^{-1}): 3321.42 (N–H), 1685.79 (C=O), 1588 (C=N stretch), 1544.98 (Asym. N=O), 1371.39 (Sym. N=O).

*Preparation of (E)-N′-(4-Hydroxy-3-methoxybenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**D**)*

Reflux time: 1–2 h. Solvent used for slow evaporation: ethanol. Yield: 87 %. Elemental analyses test for $C_{18}H_{16}N_6O_5$: Anal. Calcd: C, 54.54; H, 4.07; N, 21.20 %. Found: C, 54.56; H, 4.02; N, 21.20 %. IR (KBr, cm^{-1}): 3356.14 (N–H), 1670.35 (C=O), 1593.20 (C=N stretch), 1544.12 (Asym. N=O), 1384.89 (Sym. N=O).

*Preparation of (E)-N′-(1-(4-Bromophenyl)ethylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**E**)*

Refluxed time: 3–4 h. Solvent used for slow evaporation: ethanol-*N*,*N*-dimethylformamide (DMF) (3:1) solution. Yield: 87 %. Elemental analyses test for $C_{18}H_{15}BrN_6O_3$: Anal. Calcd.: C, 48.77; H, 3.41; N, 18.96 %. Found: C, 48.72; H, 3.46; N, 18.98 %. IR (KBr, cm^{-1}): 3309.6 (N–H), 1682.9 (C=O), 1577.5 (C=N stretch), 1560.4 (Asym. N=O), 1343.6 (Sym. N=O).

X-ray Data Collection

Single crystals suitable for X-ray analysis were performed on Bruker SMART APEXII CCD and Bruker APEX Duo CCD area-detector diffractometers using Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed by using the *APEX2* software [16], whereas the cell refinement and data reduction were performed under the *SAINT* software [16]. All five complete crystallographic data were collected

Table 1 Crystal data, data collection and structure refinement details

Compound	**A**	**B**	**C**	**D**	**E**
Crystal data					
CCDC no.	894705	894704	894703	894706	894707
Chemical formula	$C_{17}H_{13}FN_6O_3$	$C_{17}H_{13}ClN_6O_3$	$C_{17}H_{13}BrN_6O_3$	$C_{18}H_{16}N_6O_5$	$C_{18}H_{15}BrN_6O_3$
Formula weight	368.33	384.78	429.24	396.37	443.27
Temperature (K)	100	100	100	100	100
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions					
a (Å)	6.8057(1)	8.3815(2)	8.4213(8)	11.1644(10)	8.7415(7)
b (Å)	12.7447(3)	20.8298(4)	21.077(2)	16.3508(15)	10.1032(8)
c (Å)	18.6936(3)	9.5932(2)	9.5899(10)	9.7313(9)	11.6852(9)
α (°)	90	90	90	90	68.306(1)
β (°)	105.356(1)	99.612(1)	99.979(2)	105.757(1)	84.894(1)
γ (°)	90	90	90	90	68.289(1)
Volume ($Å^3$)	1563.53(5)	1651.32(6)	1676.4(3)	1709.7(3)	889.52(12)
Z, D_x (Mg/m^3)	4, 1.565	4, 1.548	4, 1.701	4, 1.540	2, 1.655
μ (mm^{-1})	0.12	0.27	2.49	0.12	2.35
$F(000)$	760	792	864	824	448
Crystal size, mm^3	0.28 × 0.11 × 0.08	0.49 × 0.14 × 0.08	0.37 × 0.21 × 0.05	0.42 × 0.23 × 0.08	0.39 × 0.11 × 0.06
Color, shape	Yellow, block	Colorless, plate	Colorless, plate	Yellow, plate	Yellow, plate
Data collection					
θ_{max}, θ_{min} (°)	27.5, 2.0	27.5, 2.0	27.5, 2.4	27.5, 1.9	27.5, 1.9
Method	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans
hkl range	$-8 \leq h \leq 8$	$-10 \leq h \leq 10$	$-10 \leq h \leq 10$	$-14 \leq h \leq 14$	$-11 \leq h \leq 10$
	$-14 \leq k \leq 16$	$-26 \leq k \leq 27$	$-27 \leq k \leq 22$	$-21 \leq k \leq 20$	$-13 \leq k \leq 12$
	$-24 \leq l \leq 24$	$-12 \leq l \leq 12$	$-12 \leq l \leq 12$	$-12 \leq l \leq 12$	$-15 \leq l \leq 15$
Measured reflections	15,319	27,361	15,733	16,130	15,542
Independent reflections	3,590	3,790	3,819	3,914	4,055
Reflections with $I > 2\sigma(I)$	2,578	3,152	3,361	3,327	3,721
R_{int}	0.048	0.048	0.029	0.026	0.028
Completeness (%)	99.9	100	99.5	99.4	99.1
T_{min}, T_{max}	0.968, 0.991	0.881, 0.979	0.460, 0.886	0.953, 0.991	0.465, 0.864
Refinement					
Parameters/restraints	296/0	296/0	296/0	326/0	313/0
$R[F^2 > 2\sigma(F^2)]$	0.052	0.039	0.027	0.034	0.024
$wR(F^2)$	0.122	0.093	0.066	0.090	0.060
Goodness of fit	1.04	1.03	1.05	1.04	1.07
w: A, B	0.0578, 0.3767	0.0375, 0.834	0.0293, 1.2374	0.0393, 0.7467	0.0286, 0.3466
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.26, −0.39	0.24, −0.27	0.38, −0.42	0.32, −0.25	0.40, −0.34

Weighting scheme, $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$ where $P = (F_o^2 + 2F_c^2)/3$

at 100 (1) K using the Oxford Cryosystem Cobra low temperature attachment [17] and these crystallographic data are showed in Table 1. The crystal structures were solved by direct method and refined against F^2 by full-matrix least-squares refinement using *SHELXTL* package [18]. The non-hydrogen atoms were refined anisotropically, whereby the hydrogen atoms were located in difference Fourier maps [O–H = 0.84(2) Å, N–H = 0.83(2)–

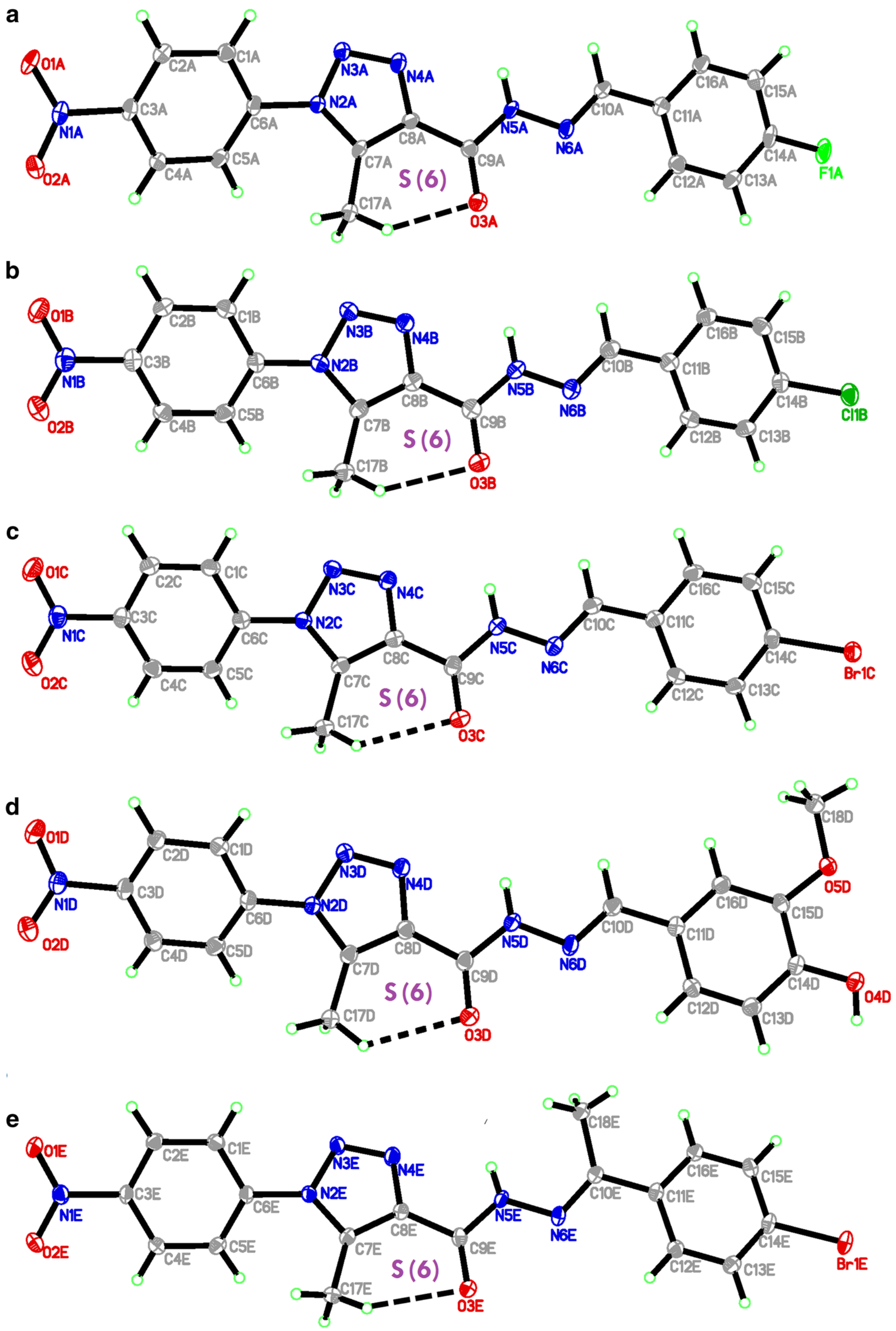


Fig. 1 The molecular structures of compounds **A** to **E**, (**a**–**e**) with atom numbering schemes and 50 % probability displacement ellipsoids. The *dashed lines* represent the intramolecular hydrogen bond interactions (Color figure online)

0.883(16) Å and C–H = 0.92(3)–1.006(17) Å]. The final refinement converged well. Absorption correction was applied to the final crystal data by using the *SADABS* software [16]. PLATON [19] was used to prepare material for publication. The overlay diagrams were drawn using Olex2 software [20].

Results and Discussion

General Molecular Structure Descriptions

In all of the five compounds (**A–E;** Fig. 1), each molecule consists of a 5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole

Table 2 Dihedral angle between two moeties

Moeities	Dihedral angle, °				
	Molecule **A**	Molecule **B**	Molecule **C**	Molecule **D**	Molecule **E**
I, II	34.53(10)	25.16(9)	24.63(9)	22.55(6)	33.49(9)
I, III	13.72(10)	11.11(8)	10.67(9)	13.16(6)	7.57(9)
II, III	25.03(9)	15.90(8)	15.93(8)	33.41(6)	27.52(8)
IV, II	18.50(12)	15.4(3)	14.3(3)	18.77(1)	11.8(3)
I, V	6.77(6)	9.59(11)	9.29(13)	6.54(11)	6.43(10)
III, V	6.96(4)	4.01(11)	3.66(13)	6.67(9)	7.59(10)

Moeties I–V are N1-N3/C7/C8, C1-C6, C11-C16 rings, N1/O1/O2 nitro-group and O3/N5/N6/C9/C10 bridge, respectively

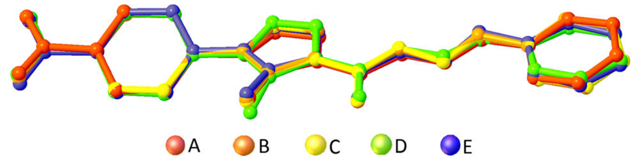


Fig. 2 The overlay diagram of compounds **A** to **E** shows close similarity in their molecular geometries. Only non-H atoms common to all five compounds are shown (Color figure online)

group connected to a substituted benzene ring through C9(=O3)–N5–N6=C10 connecting bridge. The 1,2,3-triazole ring is essentially planar with *r.m.s.* deviations from 0.003 to 0.005 Å. The least squares planes formed by C(=O)–NH–N=C bridge in compounds **A** to **E** are nearly planar as indicated by the *r.m.s.* deviations of 0.026, 0.04, 0.038, 0.04 and 0.088 Å. The hydrazone N6=C10 double bond with lengths of 1.285(2), 1.279(2), 1.279(3), 1.284(2) and 1.291(2) Å, respectively in **A** to **E** are in agreement with the typical C_{sp2}=N double bond length of 1.279(8) Å [21]. The dihedral angles between the least squares planes formed by two moieties are summarized in Table 2. Fig. 2 shows the overlay diagram of all five compounds with similarities in their molecular conformations. A weak intramolecular C17–H17B···O3 hydrogen bond (Table 3) was observed in all compounds and it features an *S*(6) ring motif [22] as shown in Fig. 1.

*Crystal Structure of (E)-N′-(4-Fluorobenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**A**)*

In the crystal, molecules are linked by intermolecular C13*A*–H13*A*···O1*A*(nitro) hydrogen bond into head-to-tail chains running along the *c* axis. The [001] chains are then connected by C10*A*–H10*A*···O3*A* and C16*A*–H16*A*···O3*A* hydrogen bonds, with atom O3*A* as the same acceptor, into sheets parallel to (010) plane with $R_2^1(6)$ ring motifs [22] as shown in Fig. 3.

*Crystal Structure of (E)-N′-(4-Chlorobenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**B**)*

In the crystal, simple replacement of fluorine atom by chlorine atom in the molecule changes the crystal packing from two-dimensional networks in compound **A** to a three dimensional network with an additional C–H···Cl interaction (Table 3). Fig. 4a shows that atom O3*B* accepts two hydrogen from atoms C13*B* and C17*B* to link the molecules into two molecular-thick chains with $R_2^2(12)$ and $R_2^2(18)$ ring motifs [22], running along the *c* axis. The [001] two molecular-thick chains are cross-linked by intermolecular C16*B*–H16*B*···Cl1*B* hydrogen bonds into two-dimensional planes (Fig. 4b) parallel to (100) and the adjacent planes are further connected into a three-dimensional network (Fig. 4c) via weak intermolecular C15*B*–H15*B*···O1*B* interactions. The crystal packing is further stabilized by π-π interactions, involving the centroids of triazole ring and chloro-substituted benzene ring [centroid to centroid distance = 3.5972(9) Å; symmetry code = *x*, *y*, 1 + *z*].

*Crystal Structure of (E)-N′-(4-Bromobenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**C**)*

The space group and unit cell parameters of the crystal structure of **C** are similar to those found in compound **B** (Table 1) after the simple substitution of chlorine atom with bromine atom, which is also known as isomorphous substitution. In the crystal, three intermolecular C–H···O hydrogen bonds and one C–H···Br hydrogen bonds (Table 3) were observed, involving the atoms C13, C15, C16, C17, O1 and O3 which are equivalent to those atoms involved in the hydrogen bonding in compound **B.** This interesting observation is due to the uniqueness of space group (both are in space group $P2_1/c$) and also the similarity in the unit cell parameters and molecular geometries between compounds **B** and **C** as shown in Fig. 5. The torsion angles formed between two moieties (nitro group,

Table 3 Hydrogen bond geometries in compounds **A–E**

D–H···*A*	*D*–H/Å	H···*A*/Å	*D*···*A*/Å	∠*D*–H···*A*/°	Symmetry code
A					
C10*A*–H10*A*···O3*A*	0.98(2)	2.42(2)	3.305(3)	149.7(17)	*x* − 1, *y*, *z*
C13*A*–H13*A*···O1*A*	0.98(3)	2.34(2)	3.231(2)	150(2)	*x*, *y*, *z* + 1
C16*A*–H16*A*···O3*A*	0.93(2)	2.48(2)	3.298(2)	147(2)	*x* − 1, *y*, *z*
C17*A*–H17*B*···O3*A*	0.96(2)	2.54(2)	3.042(2)	112.9(16)	
B					
C13*B*–H13*B*···O3*B*	0.944(18)	2.288(18)	3.115(2)	146.0(14)	−*x* + 1, −*y*+1, −*z*
C15*B*–H15*B*···O1*B*	0.931(17)	2.483(17)	3.359(2)	156.8(14)	*x* + 1, −*y*+1/2, *z* − 3/2
C16*B*–H16*B*···Cl1*B*	0.96(2)	2.78(2)	3.6695(17)	155.0(14)	*x*, −*y*+1/2, *z* + 1/2
C17*B*–H17*B*···O3*B*	0.964(19)	2.513(18)	3.105(2)	119.6(13)	
C17*B*–H17*C*···O3*B*	0.97(2)	2.523(17)	3.350(2)	143.1(15)	−*x* + 1, −*y*+1, −*z*+1
C					
C13*C*–H13*C*···O3*C*	0.95(2)	2.29(2)	3.132(2)	148(2)	−*x* + 1, −*y*+1, −*z*+1
C15*C*–H15*C*···O1*C*	0.94(2)	2.52(2)	3.392(3)	155.9(19)	*x* − 1, −*y*+1/2, *z* + 3/2
C16*C*–H16*C*···Br1*C*	0.95(2)	2.86(2)	3.710(2)	149.8(17)	*x*, −*y*+1/2, *z* − 1/2
C17*C*–H17*B*···O3*C*	0.96(3)	2.49(3)	3.098(3)	121.5(19)	
C17*C*–H17*C*···O3*C*	0.99(3)	2.49(3)	3.324(3)	142(2)	−*x* + 1, −*y*+1, −*z*
D					
O4*D*–H1O*D*···O3*D*	0.84(2)	1.93(2)	2.7658(14)	177.5(19)	−*x* + 2, −*y*, −*z*+1
C2*D*–H2*D*···N3*D*	0.969(15)	2.485(16)	3.1804(16)	128.6(12)	*x*, −*y*+1/2, *z* − 1/2
C17*D*–H17*B*···O3*D*	0.990(16)	2.425(16)	3.1087(17)	125.7(12)	
E					
C2*E*–H2*E*···O3*E*	0.94(2)	2.45(2)	3.148(2)	131.3(15)	*x*, *y* + 1, *z*
C5*E*–H5*E*···O3*E*	0.94(2)	2.530(19)	3.320(2)	141.6(16)	−*x* + 2, −*y*+1, −*z*+1
C17*E*–H17*B*···O3*E*	0.98(2)	2.53(3)	3.120(2)	118.4(19)	

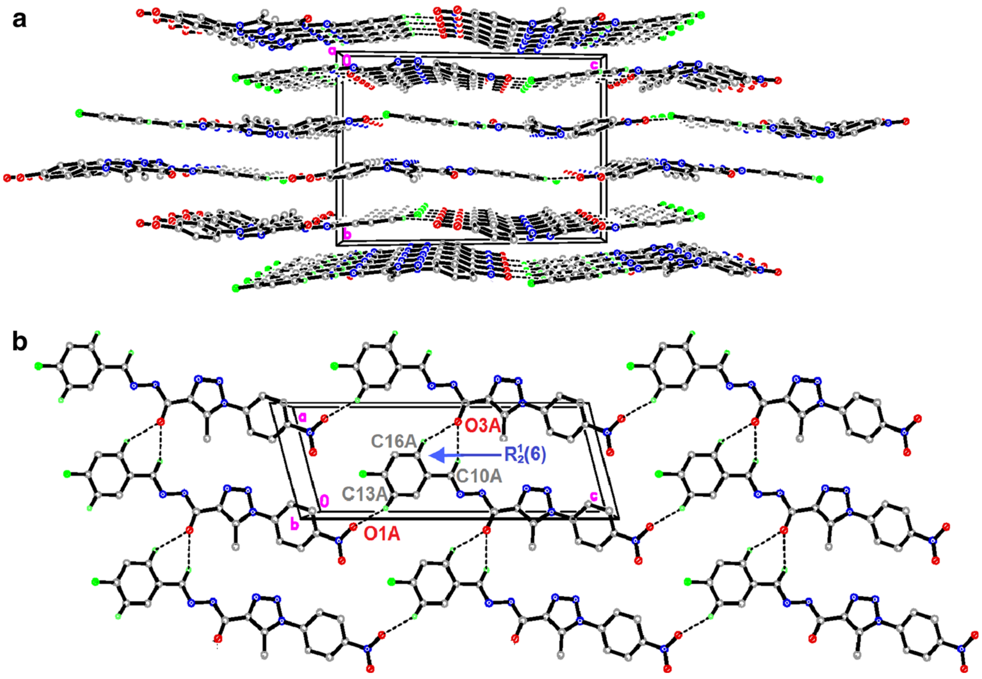


Fig. 3 The crystal packing in compound **A** viewed along the **a** *a* and **b** *b* axes. The *dashed lines* represent the hydrogen bonds. For clarity sake, hydrogen atoms not involved in hydrogen bonding have been omitted (Color figure online)

benzene rings, triazole ring or connecting bridge) in **B** and **C** are highly similar as tabulated in Table 2. Because of the above factors, the molecules in compound **C** are connected by intermolecular hydrogen bonds into a three-dimensional network which is similar to the crystal packing in compound **B**. π-π stacking interactions are also observed with a

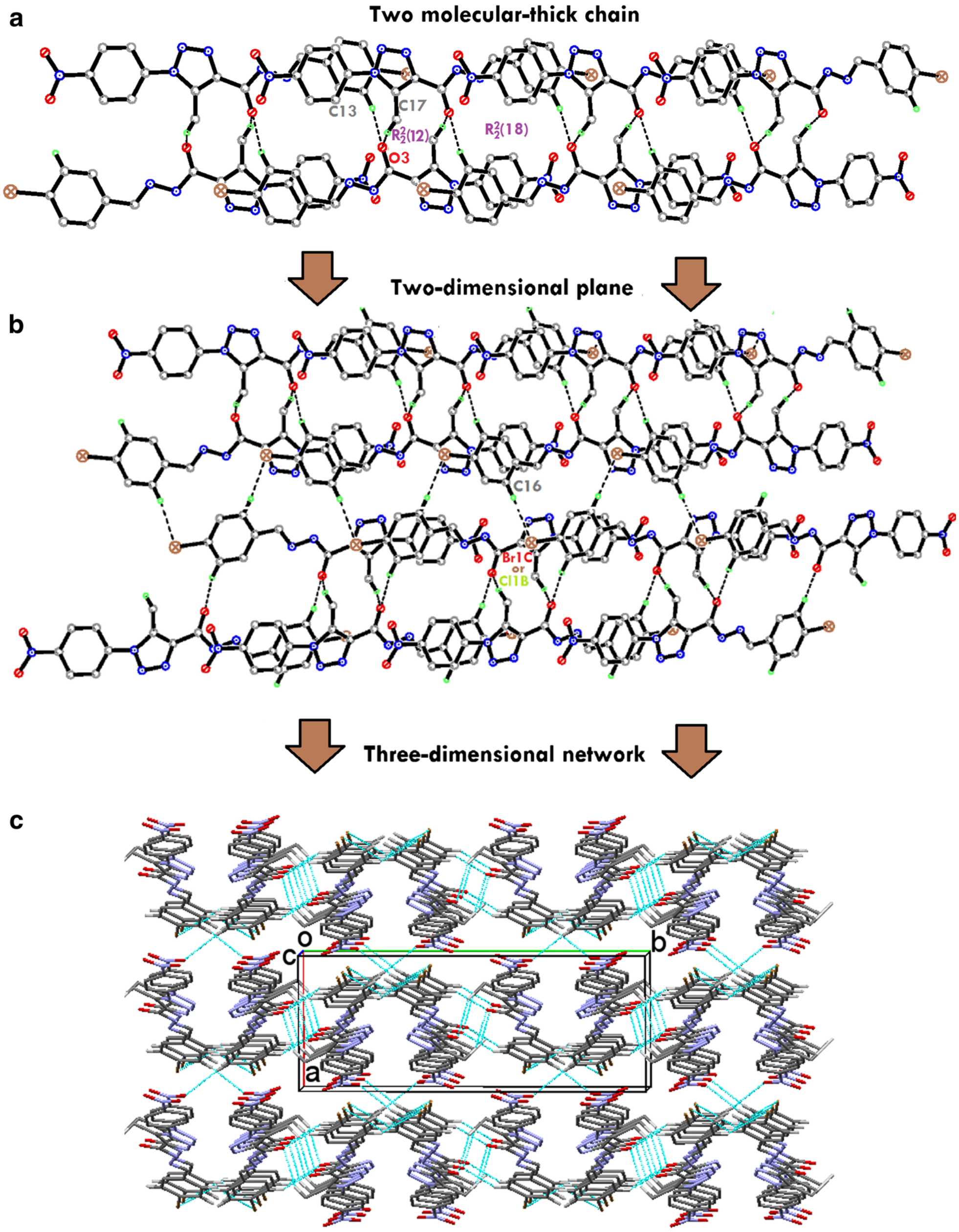


Fig. 4 Development of hydrogen bond interactions in the crystal packing of compound **B** from **a** two molecular thick chain to **b** two-dimensional plane and further established into **c** three-dimensional network. *Dashed lines* show the intermolecular hydrogen bonds. H atoms not involved in hydrogen bonding are omitted for clarity (Color figure online)

centroid–centroid distance of 3.5745(11) Å, involving the centroids of triazole ring and bromo-substituted benzene rings [symmetry code = x, y, $-1 + z$]. Since the crystal packing is similar to that of compound **B**, (Fig. 4), the packing diagrams are not shown.

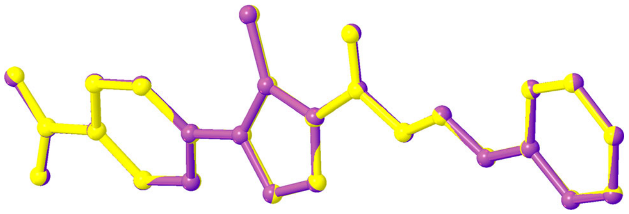


Fig. 5 The overlay diagram of compounds **B** (*purple*) to **C** (*yellow*) shows high similarity in their molecular structures with good fitting. Only non-H atoms common to both compounds are shown (Color figure online)

*Crystal Structure of (E)-N′-(4-Hydroxy-3-methoxybenzylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**D**)*

In the crystal (Fig. 6), the hydroxyl group which is attached to the benzene ring acts as a good electron donor and a strong intermolecular O4*D*–H1O*D*···O3*D* hydrogen bond is formed. This OH(hydroxyl)···O=C hydrogen bond links the molecules into inversion dimers [symmetry code = $2-x$, $-y$, $1-z$], generating $R_2^2(22)$ graph-set motifs [22] and they

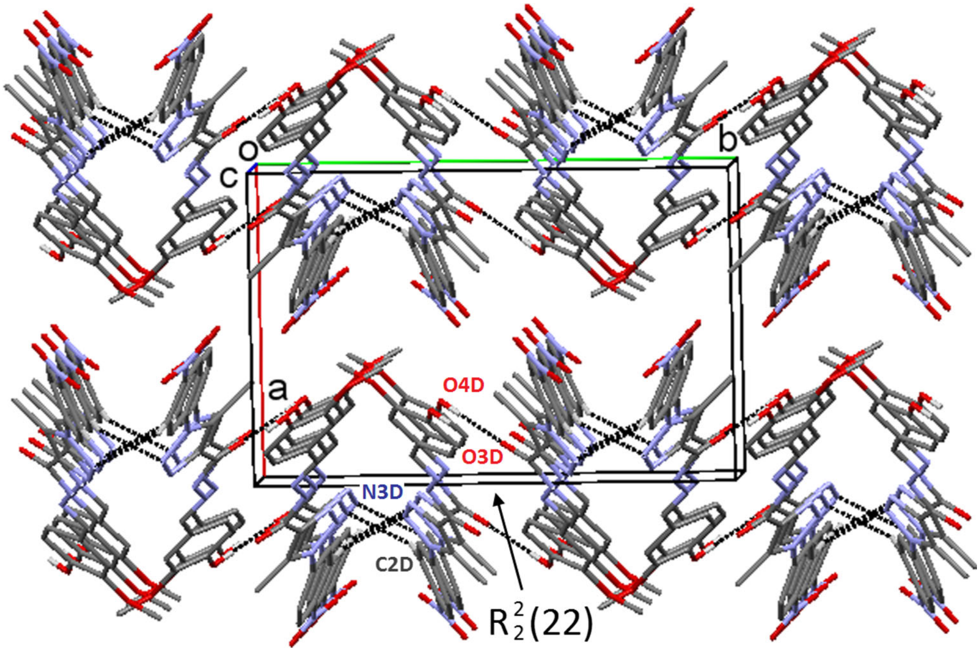


Fig. 6 *Dashed lines* show the intermolecular hydrogen bond interactions which linked the molecules of compound **D** into 2-dimensional sheets parallel to *bc* plane (Color figure online)

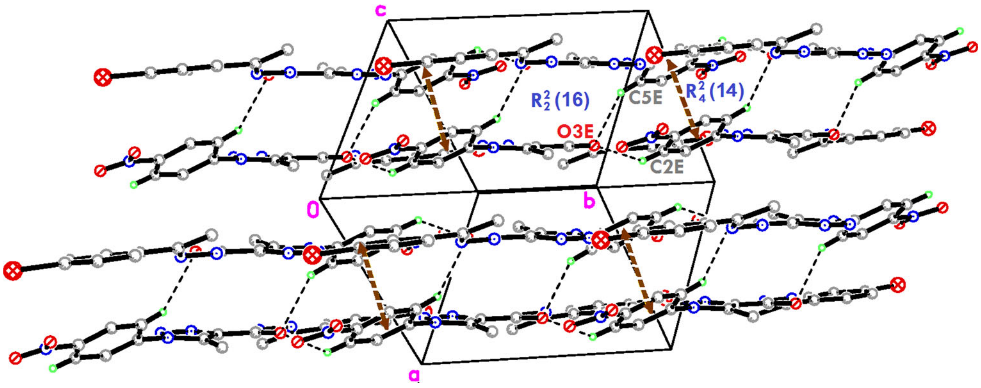


Fig. 7 The crystal packing in compound **E** showing distorted ladder-like chains, propagating along the *b*-axis, with H atoms not involved in intermolecular interactions being omitted. The *simple dashed lines* and *dashed lines* with *double arrows* represent the intermolecular hydrogen bonds and π-π stacking interactions, respectively (Color figure online)

are further inter-linked by C2*D*–H2*D*···N3*D* into sheets parallel to *bc* plane.

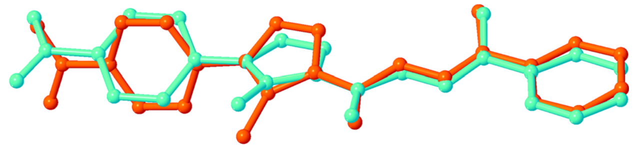


Fig. 8 Overlay diagram of compound **E** (*light green*) and reported compound XEBGAO (*red*). Only non-H atoms common to both compounds are shown (Color figure online)

*Crystal Structure of (E)-N′-(1-(4-Bromophenyl) ethylidene)-5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carbohydrazide (**E**)*

In comparison to compound **C** (monoclinic $P2_1/c$), a simple substitution of H atom attached to atom C10 with methyl group results in the crystallization of **E** in triclinic $P\bar{1}$. In the crystal, non-classical intermolecular C–H···O hydrogen bonds produce a crystal packing which is different from those observed in compound **C**. The intermolecular C2*E*–H2*E*···O3*E* hydrogen bond links the molecules into chains, propagating along the *b* axis. Each pair of anti-parallel [010] chains is inter-connected by C5*E*–H5*E*···O3*E* hydrogen bond into a [010] distorted ladder-like chain (Fig. 7) which comprised of $R_4^2(14)$ and $R_2^2(16)$ ring motifs [22]. The crystal packing is further consolidated by the π-π stacking interactions between the inversion-related C1*E*-C6*E* rings within each [010] distorted ladder-like chain as represented by the dashed lines with double arrows as shown in Fig. 7 [centroid to centroid distance = 3.6988(11) Å and symmetry code = $-x + 2$, $-y + 2$, $-z + 1$].

Unlike the isomorphous chlorine-bromine substitution in compounds **B** and **C** which is resulting in similar molecular conformation, unit cell parameters and crystal packing, compound **E** and its chlorine derivative (ref. code XEBGAO [23], space group $P\bar{1}$, $a = 8.6603$ (1) Å, $b = 10.2844$ (1) Å, $c = 10.4033$ (1) Å, $\alpha = 83.816$ (1)°, $\beta = 81.402$ (1)°, $\gamma = 76.373$ (1)°) do not exhibit the same similarity as shown in former after the simple substitution of bromine atom to chlorine atom. The differences in between their molecular conformations are displayed in the overlay diagram (Fig. 8).

Conclusion

Five new hydrazone derivatives are synthesized with (*E*)-*N*′-benzylidene-5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carbohydrazide moiety as the main body and different functional groups (F, Cl, Br, OH, OCH_3) are substituted at the terminal benzene ring. A weak intramolecular C–H···O hydrogen bond is observed in each compounds, featuring an *S*(6) ring motif. Strong intermolecular O–H···O = C hydrogen bond is formed in the crystal structure of **D**, whereas for the rest of the compounds, only weak intermolecular C–H···Cl, C–H···Br and C–H···O hydrogen bonds are observed. Isomorphous chlorine-bromine substitution has taken place in compounds **B** and **C** in which they are both crystallize in space group $P2_1/c$ with similar unit cell parameters.

Supplementary Materials

The crystallographic data for compounds **A-E** have been deposited with the Cambridge Crystallographic Data Center No. CCDC 894703–894707. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033.

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