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PAPER

The differing influence of halides upon supramolecular aggregation through C–X···π interactions in the crystal structures of (5-methyl-1-(4-X-arylamino)-1*H*-1,2,3-triazol-4-yl)methanol derivatives, X = H, F and Cl

Alessandro K. Jordão,[a] Vitor F. Ferreira,[a] Anna C. Cunha,[a] James L. Wardell,[bc] Solange M. S. V. Wardell*[d] and Edward R. T. Tiekink*[e]

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The presence of localised C–X···π [or C–X···π(C=C)] interactions are shown to be pivotal in the crystal structures of (5-methyl-1-(4-X-arylamino)-1*H*-1,2,3-triazol-4-yl)methanol derivatives, X = H (**1**), F (**2**) and Cl (**3**). In the absence of halide (**1**), molecules aggregate into supramolecular chains *via* alternating ten-membered $\{\cdots HOC_2N\}_2$ and 14-membered $\{\cdots HN_2C_3O\}_2$ synthons. Molecules assemble into a three-dimensional architecture *via* edge-to-face C–H···π(arene) interactions occurring between the phenyl rings. In the presence of halide (*i.e.* F (**2**) and Cl (**3**) in the 4-position of the phenyl ring), two-dimensional arrays are formed by interconnected ten-membered $\{\cdots HOC_2N\}_2$ (as seen in **1**) and 24-membered $\{\cdots HO\cdots NC_2OH\cdots N_4H\}_2$ hydrogen bonded synthons. The latter arrangement allows for the close approach of halide to the 1,2,3-triazole ring and the formation of C–X···π interactions which appear to be particularly significant in the case of Cl (**3**), as evidenced by systematic changes (*i.e.* elongation) in the geometric parameters within the five-membered ring. In this series of structures, the presence of C–X···π interactions is shown to moderate the supramolecular aggregation based on conventional hydrogen bonding.

Introduction

Directional and persistent conventional hydrogen bonding interactions occurring between hydrogen atoms connected to electronegative elements remains as the mainstay of supramolecular recognition, in particular in crystal engineering endeavours of both organic and metal-organic molecules.[1–3] However, it is also known that such hydrogen bonding interactions may be usurped by less conventional interactions as, for example, reported recently for the structure of ethyl (*Z*)-2-cyano-3-[(4-alkoxyphenyl)amino]prop-2-enoate.[4] In the crystal structure of this compound, rather than putative N–H···O hydrogen bonds, supramolecular aggregation occurs through N···π and O···π interactions. While rare, the N···π interactions in this crystal structure were related to the well established cation···π interactions.[5] Analogous interactions but involving a lone pair interacting with a π-system, *i.e.* element(lone pair)···π, are attracting increasing attention. An early and prominent example amongst these is the cytidine-O(lone pair)···π (guanine) interaction that is thought responsible for stabilising the structure of the left-handed Z-DNA duplex.[6] It turns out that such interactions are well documented in macromolecular chemistry[7] but less well established in molecular crystallography.[8,9] A focus of recent studies of element(lone pair)···π(arene) interaction interactions has been upon the supramolecular aggregation patterns they stabilise, for example in the crystal structures of transition metal carbonyls[10a] as well as for heavier elements such as arsenic,[10b] selenium,[10c] tellurium[10d] and lead.[10e] Halogen atoms are also known to form C–X···π(arene) interactions,[11] including in the realm of protein and protein/drugs structure,[12] observations which complements the propensity of halides to form $X^-\cdots\pi$ interactions.[13] Based on surveys of the Cambridge Structural Database,[14] both C–X···π(arene) and $X^-\cdots\pi$(arene) interactions are directional,[15] and are the subject of increasing theoretical investigations.[16] However, in terms of crystal engineering endeavours, the systematic utilisation of C–X···π interactions as supramolecular

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[a] *Universidade Federal Fluminense, Departamento de Química Orgânica, Instituto de Química, Outeiro de São João Baptista, Niterói, RJ, 24020-141, Brazil*
[b] *FioCruz-Fundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos-FarManguinhos, Rua Sizenando Nabuco, 100, Manguinhos, Rio de Janeiro, RJ, 21041-250, Brazil. Fax: 55 21 2552-0435; Tel: 55 21 2552-0435*
[c] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB24 3UE, UK*
[d] *Centro de Desenvolvimento Tecnológico em Saúde (CDTS), Fundação Oswaldo Cruz (FIOCRUZ), Casa Amarela, Campus de Manguinhos, Av. Brasil 4365, 21040-900, Rio de Janeiro, RJ, Brazil. E-mail: solangewardell@yahoo.co.uk*
[e] *Department of Chemistry, University of Malaya, Kuala Lumpur, 50603, Malaysia. E-mail: Edward.Tiekink@gmail.com; Fax: +60 3 7967 4193; Tel: +60 3 7697 6775*

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synthons, operating in isolation of other supramolecular synthons, is still in its infancy.[17]

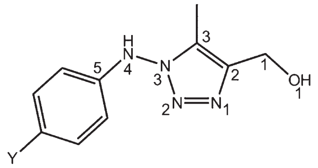
The under-utilisation of the C–X···π synthon in crystal engineering, in part, reflects a certain lack of understanding of such interactions owing to a deficiency of systematic studies. This deficiency clearly contradicts the first paradigm of crystal engineering suggested by Desiraju,[2] *i.e.* a pillar of crystal engineering is the systematic evaluation of closely related structures designed to ascertain the influence upon crystal packing patterns in response to small modifications to molecular structure - how and why molecules pack as they do. In this spirit, herein, the crystal and molecular structures of three compounds which differ only in the substituent at the 4-position of the phenyl ring, Scheme 1, are described. It will be demonstrated that a discernible influence upon crystal packing is related to the formation of C–X···π interactions in the halogen derivatives to complement previous studies in this area showing that these interactions can be manifested in the absence of supporting synthons.[17] These new compounds became available during investigations into evaluation of the anti-viral and other biological activities of novel 5-methyl-1-(arylamino)-1*H*-1,2,3-triazole derivatives.[18]

Results and discussion

Molecular structures

The molecular structures of **1–3** are illustrated in Fig. S1 (see ESI)† and key geometric parameters are collected in Table 1; each structure comprises a single molecule in the asymmetric unit. As the molecular structures bear a close similarity, the focus of the description will be upon **1**. The molecule comprises a five-membered 1,2,3-triazole ring connected to a phenyl ring *via* a secondary amine group. The phenyl ring is almost orthogonal to the 1,2,3-triazole ring, forming a dihedral angle of 87.69(7)° (the equivalent angles for **2** and **3** are 89.01(10) and 87.72(13)°, respectively). Also connected to the five-membered ring are methyl and hydroxymethyl substituents. Fig. 1 shows an overlay diagram for the three molecules whereby the five-membered rings are coincident. It is clear that the differences relate to the torsion angles connecting the phenyl and hydroxymethyl substituents to the central ring. From Table 1, the latter O1–C1–C2–N1 torsion angles vary by about the 13°. Similarly, the N2–N3–N4–C5 angles vary by nearly 15°. The relative homogeneity in the molecular structures indicates that successive substitution of H in **1**, for F in **2** and Cl in **3**, does not significantly influence the molecular conformation. However, a systematic influence upon the geometric parameters is evident.

Referring to the canonical form shown in Scheme 1, the geometric parameters describing the five-membered ring for each of **1** and **2** are consistent with that shown. However, in **3** a systematic elongation of the endo- and exo-cyclic N–N bonds as well as the formally ethylenic bond, Table 1 is noted. This observation is related to the supramolecular aggregation patterns, specifically, the interaction of the 4-chloro substituent with the 1,2,3-triazole ring, as described below.



Scheme 1 Chemical structures and numbering scheme for the molecules investigated herein: (a) **1** (Y = H) (b) **2** (Y = F), and (c) **3** (Y = Cl).

Table 1 Selected geometric parameters (Å, °) for **1–3**

Parameter	(1)	(2)	(3)
C1–O1	1.4301(17)	1.423(2)	1.407(3)
N1–N2	1.3172(17)	1.313(2)	1.352(3)
N2–N3	1.3510(17)	1.348(2)	1.381(3)
N3–N4	1.3946(16)	1.3828(19)	1.438(3)
N1–C2	1.3668(19)	1.361(2)	1.367(3)
C3–N3	1.3565(17)	1.360(2)	1.359(3)
C2–C3	1.376(2)	1.373(2)	1.429(3)
N1–N2–N3	105.53(11)	105.45(14)	108.30(18)
N2–N3–N4	121.45(11)	122.03(14)	123.92(18)
N2–N1–C2	109.95(12)	110.10(14)	107.71(19)
N2–N3–C3	112.60(12)	112.67(14)	110.44(18)
N4–N3–C3	125.94(12)	125.29(14)	125.56(19)
N3–C3–C2	103.47(12)	103.07(15)	104.3(2)
N3–N4–C5	114.74(11)	116.46(13)	118.52(17)
O1–C1–C2–N1	68.12(17)	53.6(2)	44.9(3)
N2–N3–N4–C5	66.22(16)	80.3(2)	81.9(2)

Supramolecular assemblies based on hydrogen bonding

The common feature of the hydrogen bonding operating in the structures of **1–3** is the formation of O–H···N1(triazole) and amine–N4–H···O hydrogen bonds. However, the hydrogen bonding patterns are quite distinct, falling into two classes, *i.e.* one adopted by **1** and the other by isostructural **2** and **3**; geometric details describing the intermolecular forces operating in the crystal structures of **1–3** are listed in Table 2.

The hydrogen bonding in **1** leads to the formation of linear supramolecular chains along the *b*-axis, Fig. 2a, comprising alternating centrosymmetric ten-membered $\{\cdots HOC_2N\}_2$ and larger centrosymmetric 14-membered $\{\cdots HN_2C_3O\}_2$ synthons. A consequence of this arrangement is that the five-membered triazole rings are disposed to lie within the 14-membered rings and so are orientated to form π···π interactions which serve to stabilise the supramolecular chains. A distinctive supramolecular association is found in the structures of **2** and **3** which is related to the direct intervention of the F and Cl substituents as discussed below. In each of **2** and **3**, the centrosymmetric 14-membered $\{\cdots HN_2C_3O\}_2$ synthons observed in **1** persist bringing

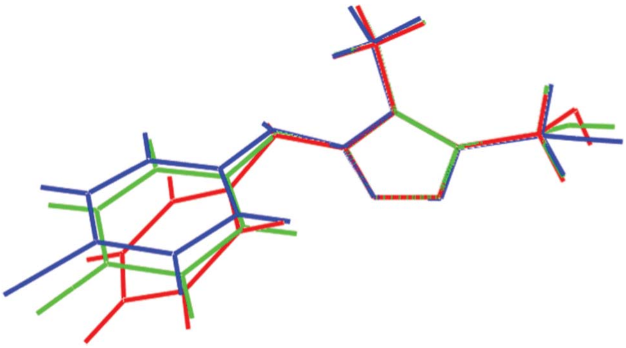


Fig. 1 Overlay diagram for molecules **1** (red), **2** (green) and **3** (blue) drawn so that the five-membered rings are superimposed.

Table 2 Summary of intermolecular interactions (A–H···B; Å, °) operating in the crystal structures of **1–3**[a]

A	H	B	A–H	H···B	A···B	A–H···B	Symmetry operation
(**1**)							
O1	H1o	N1	0.85(2)	1.93(2)	2.7751(18)	173(2)	$1 - x, 1-y, 1- z$
N4	H4n	O1	0.89(1)	1.99(1)	2.8753(18)	171(1)	$1 - x, -y, 1 - z$
C6	H6	Cg(C5–C10)	0.95	2.92	3.7390(19)	145	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
C9	H9	Cg(C5–C10)	0.95	2.77	3.6074(18)	148	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$
Cg(N1–N3,C2,C3)	—	Cg(N1–N3,C2,C3)	—	—	3.6329(13)	0	$1 - x, -y, 1 - z$
(**2**)							
O1	H1o	N1	0.84(2)	1.93(2)	2.757(2)	170(2)	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$
N4	H4n	O1	0.89(2)	1.93(2)	2.814(2)	173(2)	$2 - x, 1 - y, 1 - z$
Cg(N1–N3,C2,C3)	—	Cg(N1–N3,C2,C3)	—	—	3.4435(11)	0	$2 - x, 1 - y, 1 - z$
C8	F1	Cg(N1–N3,C2,C3)	1.367(2)	3.4497(18)	4.521(3)	134.98(14)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
(**3**)							
O1	H1o	N1	0.84(2)	2.00(2)	2.835(3)	169(3)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
N4	H4n	O1	0.88(2)	1.87(3)	2.738(3)	172(2)	$1 - x, 1 - y, 1 - z$
C1	H1B	Cl1	0.99	2.80	3.401(3)	120	$2 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$
Cg(N1–N3,C2,C3)	—	Cg(N1–N3,C2,C3)	—	—	3.2843(15)	0	$1 - x, 1 - y, 1 - z$
C8	Cl1	Cg(N1–N3,C2,C3)	1.691(2)	3.4413(13)	4.787(3)	134.90(9)	$2 - x, -\frac{1}{2} + y, 1\frac{1}{2} - z$

[a] Cg corresponds to the ring centroid of the specified atoms, and the "A–H···B" refers to the angle between the rings.

two five-membered triazole rings close together enabling the formation of π···π interactions, see Table 2 for geometric details. However, in these structures the O–H···N1 hydrogen bonds occur between dimeric aggregates related by glide symmetry along the *c*-axis to generate 24-membered synthons incorporating six hydrogen bonds, $\{\cdots HO\cdots NC_2OH\cdots N_4H\}_2$. The result is the formation of supramolecular layers in the *bc*-plane, Fig. 2b.

Three-dimensional architectures

The chains in **1** pack into layers in the *ab*-plane. The pendent phenyl rings inter-digitate along the *c*-direction allowing for the formation of edge-to-face C–H···π(arene) interactions, whereby each phenyl ring effectively bridges two other molecules thereby stabilising a three-dimensional architecture, Fig. 3a. There are no intermolecular connections between the phenyl groups and the five-membered rings. In **2** (and **3**), supramolecular layers stack to enable inter-digitation of the phenyl rings where offset-face-to-face π···π interactions are evident between centrosymmetrically related rings. While the inter-centroid distance is 4.0504 (14) Å, pairs of C8 and C9 atoms interact with the $C8\cdots C9^i$ separation being 3.455(3) Å; symmetry operation *i*: $1 - x, 1 - y, 1 - z$. The comparable separation in **3** is 3.555(4) Å. As opposed to the situation in **1**, the halide substituents in **2** and **3** project out of the phenyl-rich region to interact with the five-membered rings *via* C–X···π interactions, Fig. 3b.

While the role of organic fluorine in supramolecular chemistry attracts significant debate and remains controversial,[19] a definitive contribution of F to the stabilisation of the crystal packing is evident in **2**. As detailed in Fig. 4, the F atom is proximate to a methylene-H atom and the five-membered 1,2,3-triazole ring. The H···F separation of 2.68 Å is just beyond the established distance criterion for an H···F interaction of 2.67 Å,[20] and probably contributes little to the stability of the crystal packing. However, it is acknowledged that distance/significance correlations can be arbitrary and that naturally interactions can and do persist, for example, beyond sums of van der Waals radii.[10d,22] The F···ring centroid(N1–N3,C2,C3) distance is 3.4497(18) Å but the F···ring atom distances span a range of values, *i.e.* short 3.096(3) Å [C2] and 3.258(3) [C3] to a long 4.022(2) Å [N2]. It has been reported in the literature that C–X atoms can approach an aromatic ring at various angles,[11,17] nevertheless, can be directional.[15] Terminology[17b,20] describing the different geometries of interaction seem to be uniformly adopted,[17] *i.e.* delocalised, semi-localised and localised when X is perpendicular to the ring centroid, a specific bond and a particular atom within the ring, respectively. On this basis, the F(lone pair)···π interaction in **2** might be best described as semi-localised or even as a F(lone pair)···π(ethylene) interaction.

As anticipated from their isostructural relationship, the Cl atom in **3** forms similar interactions. The H···Cl separation of 2.80 Å is within the established distance criterion for an H···Cl interaction of 2.95 Å,[21] and indicates a weak contact. What is remarkable is that the Cl···ring centroid(N1–N3,C2,C3) distance of 3.4413(13) Å is shorter that the analogous distance in **2** despite the considerable increase in size of Cl over F, *i.e.* 0.28 Å. As for **2**, the ring centroid distances span a range, short 3.154(3) [C2] and 3.401(3) [C3] to a long 4.004(2) Å [N2], again consistent with a Cl(lone pair)···π(ethylene) interaction operating in isolation of supportive supramolecular synthons.

The tighter interactions in **3** are reflected in the Kitaigorodsky's packing index (as calculated in PLATON[21]) of 68.5 which is greater than 67.8 for **2**. Further, the magnitude of this interaction can be gauged from the influence upon the C2–C3 bond distance which elongates to 1.429(3) Å in **3** compared to 1.373(2) Å in **2**. This observation coupled with the fact that the π···π interaction between the five-membered triazole rings in **3** is significantly stronger than those in each of **2** and **1**, as indicated by the shorter ring centroid distance, Table 3, suggests considerable sharing of electron density between the molecules in **3** which concomitantly diminishes the electron density within the five-membered five-membered triazole ring, Table 1.

Summary and conclusion

A compact supramolecular chain comprising alternating ten-membered $\{\cdots HOC_2N\}_2$ and 14-membered $\{\cdots HN_2C_3O\}_2$ synthons is observed in the crystal structure of **1**. The chains pack

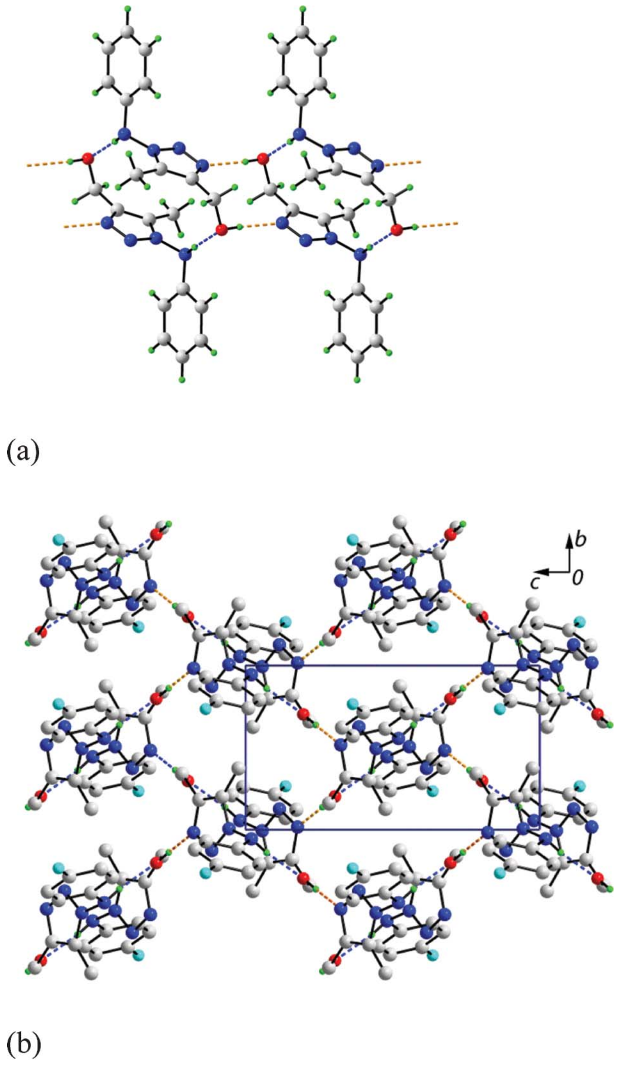


Fig. 2 Supramolecular assemblies in **1** and **2** (and isostructural **3**) mediated by O–H···N (orange dashed lines) and N–H···O (blue dashed lines) hydrogen bonding: (a) Linear supramolecular chain in **1**, and (b) Supramolecular layer parallel to the *bc*-plane in **2**; hydrogen atoms not involved in hydrogen bonding have been omitted for reasons of clarity.

into layers that sandwich the phenyl rings. The latter stabilise the three-dimensional structure by self-associating *via* edge-to-face C–H···π(arene) interactions. For **2** and **3**, to allow for the participation of the halide atoms in C–X···π interactions, two key changes in crystal structure occur. Firstly, the chains in **1** are disrupted in that the compact 10-membered $\{\cdots HOC_2N\}_2$ synthons are substituted by more open 24-membered $\{\cdots HO\cdots NC_2OH\cdots N_4H\}_2$ synthons so that layers are formed. Secondly, the original pseudo layers in **1** (repeat distance = *c*/2 = 10.51 Å) are brought closer together in **2** and **3** (repeat distances = *b* = 6.64 and 6.63 Å, respectively).

From the foregoing, it is likely that the C–X···π interactions are capable of moderating strong hydrogen bonding patterns in the crystal structures of molecular compounds as has been noted previously by others during crystal engineering studies of C–H···X interactions.[11,15–17]

Experimental

Synthesis

Compounds **1–3** were obtained by reduction of the ethyl ester precursor molecules.[18a] A solution of the desired ethyl ester precursor[18a] (1.00 mmol) in anhydrous THF (5 mL) was added drop-wise under a nitrogen atmosphere, to a $LiAlH_4$ (2 mmol) suspension in anhydrous THF (10 mL). The reaction mixture was stirred at room temperature for 2 h after which water (10 mL) and HCl (1 M) were added until pH = 1. The solution was stirred for a few minutes and then extracted into dichloromethane (3x). The organic extracts were combined, concentrated under reduced pressure. The resulting residue was collected, washed with hexane/dichloromethane (3:1) and dried under vacuum. The samples used in the crystallographic study were grown from ethanol solutions.

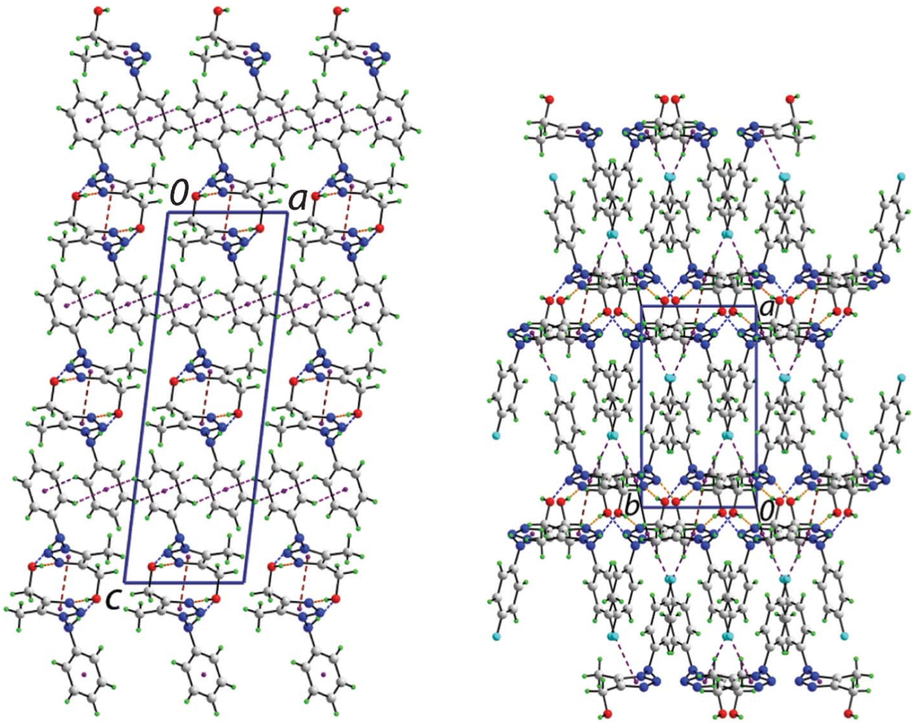
(5-Methyl-1-(phenylamino)-1*H*-1,2,3-triazol-4-yl)methanol (1). Obtained in 50% yield as a brown solid, m.p.: 197–198 °C. Recrystallisation from EtOH produced colourless crystals. IR (KBr) ν_{max} (cm^{-1}) 3199 (N–H); 3128 (O–H). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (*s*, 3H, CH_3), 4.52 (*d*, 2H, *J* = 5.6 Hz, CH_2OH), 5.13 (*t*, 1H, *J* = 5.6 Hz, CH_2OH), 6.40 (*dd*, 2H, *J* = 1.0, 8.7 Hz, arom.), 6.89 (*tt*, 1H, *J* = 1.0, 7.4 Hz, arom.), 7.21–7.25 (*m*, 2H, arom.), 10.00 (bs, 1H, N–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 6.9 (CH_3), 54.8 (CH_2OH), 112.6 (C-2′ and C-6′), 121.0 (C-4′), 129.3 (C-3′ and C-5′), 131.8 (C-4 or C-5), 143.4 (C-4 or C-5), 146.7 (C-1′) ppm. Anal. Calcd. for $C_{10}H_{12}N_4O$: C, 58.81; H, 5.92; N, 27.43. Found: C, 58.25; H, 6.02; N, 27.48.

(5-Methyl-1-(4-fluorophenylamino)-1*H*-1,2,3-triazol-4-yl)methanol (2). Obtained in 44% yield as a brown solid, m.p.: 178–182 °C. Recrystallisation from EtOH produced colourless crystals. IR (KBr) ν_{max} (cm^{-1}) 3207 (N–H); 3144 (O–H). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18 (*s*, 3H, CH_3), 4.52 (*d*, 2H, *J* = 4.7 Hz, CH_2OH), 5.08 (*t*, 1H, *J* = 4.7 Hz, CH_2OH), 6.44 (*ddd*, 2H, *J* = 2.0, 4.5, 8.9 Hz, H-2′ and H-6′), 7.04–7.11 (*m*, 2H, H-3′ and H-5′), 9.96 (bs, 1H, N–H) ppm. Anal. Calcd. for $C_{10}H_{11}FN_4O$: C, 54.05; H, 4.99; N, 25.21. Found: C, 53.98; H, 4.93; N, 25.27.

(5-Methyl-1-(4-chlorophenylamino)-1*H*-1,2,3-triazol-4-yl)methanol (3). Obtained in 39% yield as a brown solid, m.p.: 189–190 °C. Recrystallisation from EtOH produced colourless crystals. IR (KBr) ν_{max} (cm^{-1}) 3228 (N–H); 3118 (O–H). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (*s*, 3H, CH_3), 4.53 (*d*, 2H, *J* = 5.4 Hz, CH_2OH), 5.10 (*t*, 1H, *J* = 5.4 Hz, CH_2OH), 6.42 (*d*, 2H, *J* = 8.7 Hz, H-2′ and H-6′), 7.28 (*d*, 2H, *J* = 8.7 Hz, H-3′ and H-5′), 10.10 (bs, 1H, N–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 6.9 (CH_3), 54.8 (CH_2OH), 114.3 (C-2′ and C-6′), 124.6 (C-4′), 129.2 (C-3′ and C-5′), 131.8 (C-4 or C-5), 143.5 (C-4 or C-5), 145.6 (C-1′) ppm. Anal. Calcd. for $C_{10}H_{11}ClN_4O$: C, 50.32; H, 4.65; N, 23.47. Found: C, 49.89; H, 4.80; N, 23.06.

X-ray crystallography

Intensity data for **1** were measured at 150 K on a Rigaku AFC12κ/SATURN724 diffractometer fitted with MoKα radiation. Data processing and absorption corrections were accomplished with CrystalClear[23a] and ABSCOR,[23b] respectively. Intensity data for **2** and **3** were measured at 120 K on an



(a) (b)

Fig. 3 Crystal packing in **1** and **2** (and isostructural **3**): (a) View in projection down the *b*-axis of the unit cell contents of **1**, and (b) View in projection down the *c*-axis of the unit cell contents of **2**. The O–H···N, N–H···O and π···π interactions are indicated by orange, blue and brown dashed lines, respectively, and the edge-to-face C–H···π (Fig. 3a) and C–F···π (Fig. 3b) interactions are shown as purple dashed lines.

Enraf-Nonius KappaCCD area detector diffractometer (fitted with MoKα radiation) of the EPSRC National crystallographic service at the University of Southampton, UK.[23c] Data collection was carried out under the control of the program COLLECT[23d] and data reduction and unit cell refinement was achieved with the COLLECT and DENZO[23e] software combination. Correction for absorption effects was by comparison of the intensities of equivalent reflections as applied by the program SADABS.[23f] Details of cell data, X-ray data collection, and structure refinement are given in Table 3. The structures were solved by direct-methods.[23g] Full-matrix least-squares refinement on F^2 with anisotropic displacement parameters for all non-hydrogen atoms was performed.[23g] The C-bound H atoms were placed on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.2 times (1.5 times for

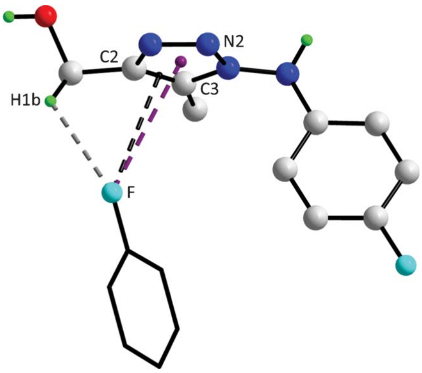


Fig. 4 Detail of the intermolecular interactions formed by the F atom in **2**. The putative C–H..F, C–F···π(ring) and C–F···π(ethylene) interactions are shown as grey, purple and black dashed lines, respectively. Non-acidic hydrogen atoms not participating in these interactions are omitted for reasons of clarity.

Table 3 Crystallographic data and refinement details for **1–3**

Compound	(**1**)	(**2**)	(**3**)
Formula	$C_{10}H_{12}N_4O$	$C_{10}H_{11}FN_4O$	$C_{10}H_{11}ClN_4O$
Formula weight	204.24	222.22	238.68
Temperature/K	150	120	120
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	6.7842(19)	13.4975(6)	13.4984(8)
b/Å	7.258(2)	6.6420(2)	6.6361(4)
c/Å	21.155(6)	13.8024(6)	14.0835(5)
β/°	96.751(8)	120.480(3)	118.380(3)
V/Å^3	1034.5(5)	1066.39(7)	1109.93(10)
Z	4	4	4
D_c/g cm^{-3}	1.311	1.384	1.428
F(000)	432	464	496
μ(Mo$K\alpha$)/mm^{-1}	0.090	0.107	0.328
Measured data	25 445	9414	15 735
θ range/°	3.0–27.5	3.0–27.5	2.9–27.5
Unique data	2363	2434	2479
Observed data ($I \geqslant 2.0\sigma(I)$)	2320	2012	1694
R, obs. data; all data	0.053; 0.145	0.054; 0.111	0.048; 0.113
a; b in weighting scheme	0.074; 0.298	0.021; 1.046	0.062; 0.567
R_w, obs. data; all data	0.053; 0.145	0.067; 0.120	0.086; 0.133

methyl-H) the value of the equivalent isotropic displacement parameter of the respective carrier atom. The O– and N–bound H atoms were located in difference maps and refined with O–H = 0.84 ± 0.01 Å and N–H = 0.88 ± 0.01 Å, respectively, and with U_{iso} = 1.2 times (1.5 for O–H) U_{eq}(parent atom). A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced in each case. The programs WinGX,[23h] PLATON,[21] ORTEP-3[23i] and DIAMOND[23j] were also used in the study.

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