



Conversion of 3-amino-4-arylamino-1*H*-isochromen-1-ones to 1-arylisochromeno[3,4-*d*]-[1,2,3]triazol-5(1*H*)-ones: synthesis, spectroscopic characterization and the structures of four products and one ring-opened derivative

Daniel E. Vicentes,^a Andrea L. Romero,^a Ricuarte Rodríguez,^b Justo Cobo^c and Christopher Glidewell^{d*}

Received 12 March 2020

Accepted 13 March 2020

Edited by A. L. Spek, Utrecht University, The Netherlands

Keywords: synthesis; heterocyclic compounds; isocoumarins; triazoles; crystal structure; molecular conformation; hydrogen bonding; supramolecular assembly.

CCDC references: 1990381; 1990380; 1990379; 1990378; 1990377

Supporting information: this article has supporting information at journals.iucr.org/c

^aFacultad de Ciencias, Universidad de Ciencias Aplicadas y Ambientales, Calle 222, No. 55-37, Bogotá, Colombia,

^bDepartamento de Química, Universidad Nacional de Colombia, Ciudad Universitaria, Carrera 30, No. 45-03, Edificio 451, Bogotá, Colombia, ^cDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and

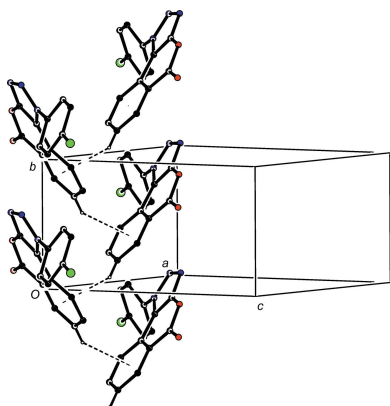
^dSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland. *Correspondence e-mail: cg@st-andrews.ac.uk

An efficient synthesis of 1-arylisochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-ones, involving the diazotization of 3-amino-4-arylamino-1*H*-isochromen-1-ones in weakly acidic solution, has been developed and the spectroscopic characterization and crystal structures of four examples are reported. The molecules of 1-phenylisochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, C₁₅H₉N₃O₂, (I), are linked into sheets by a combination of C—H···N and C—H···O hydrogen bonds, while the structures of 1-(2-methylphenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, C₁₆H₁₁N₃O₂, (II), and 1-(3-chlorophenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, C₁₅H₈ClN₃O₂, (III), each contain just one hydrogen bond which links the molecules into simple chains, which are further linked into sheets by π -stacking interactions in (II) but not in (III). In the structure of 1-(4-chlorophenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, (IV), isomeric with (III), a combination of C—H···O and C—H··· π (arene) hydrogen bonds links the molecules into sheets. When compound (II) was exposed to a strong acid in methanol, quantitative conversion occurred to give the ring-opened transesterification product methyl 2-[4-hydroxy-1-(2-methylphenyl)-1*H*-1,2,3-triazol-5-yl]benzoate, C₁₇H₁₅N₃O₃, (V), where the molecules are linked by paired O—H···O hydrogen bonds to form centrosymmetric dimers.

1. Introduction

Isocoumarins are an important building block in synthetic medicinal chemistry because they have shown interesting bioactivities, for example, as anticoagulants (Oweida *et al.*, 1990), as herbicides (Zhang *et al.*, 2016) and as insecticides (Qadeer *et al.*, 2007). In order to gain access to compounds of this type in a straightforward way, a synthetic route has been developed using reactions between 2-formylbenzoic acid, hydrogen cyanide and anilines to yield *N*-aryldiaminoisocoumarins (Opatz & Ferenc, 2005). We have reported the structures of several compounds of this type (Vicentes *et al.*, 2013) and, more recently using such compounds as precursors, we have developed the synthesis of a new heterocyclic system, namely fused imidazoloisocoumarins, as part of an exploration of possible synergies between the imidazole and isocoumarin pharmacophores (Rodríguez *et al.*, 2017).

The bioactivity of hybrid systems containing the 1,2,3-triazole unit has been reviewed recently (Xu *et al.*, 2019) and, with this in mind, we have now developed an efficient synthesis of 1-arylisochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-ones starting



from the same *N*-aryldiaminoisocoumarins as were used in the synthesis of imidazoloisocoumarins (Rodríguez *et al.*, 2017). Thus, we now report the synthesis and spectroscopic characterization, and the molecular and supramolecular structures of four representative examples, namely, 1-phenylisochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, (I), 1-(2-methylphenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, (II), 1-(3-chlorophenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, (III), and 1-(4-chlorophenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one, (IV), carrying substituents at different positions in the pendent aryl group, along with those of a transesterification product, namely, methyl 2-[4-hydroxy-1-(2-methylphenyl)-1*H*-1,2,3-triazol-5-yl]benzoate, (V). Compounds (I)–(IV) were prepared by reaction of sodium nitrite in acetic acid with the corresponding 3-amino-4-arylamino-1*H*-isochromen-1-ones (**A**) (see Scheme 1); the precursors of type (**A**) having aryl = phenyl, 2-methylphenyl or 4-chlorophenyl were prepared (Scheme 1) as reported previously (Rodríguez *et al.*, 2017), and the new analogue having aryl = 3-chlorophenyl was prepared in the same way. The conversion of the precursors of type (**A**) to the products (I)–(IV) proceeds *via* the diazonium intermediate (**B**) (Scheme 1), which itself undergoes an intramolecular cyclization to form the triazolo ring. It is important to stress here the necessity of using a weak acid, here acetic acid, in the diazotization of (**A**) to form (**B**), as isocoumarins often readily undergo ring opening in the presence of strong acids. To confirm this, a sample of compound (II) was stirred in methanol in the presence of aqueous hydrochloric acid, resulting in a quantitative conversion of (II) to ester (V).

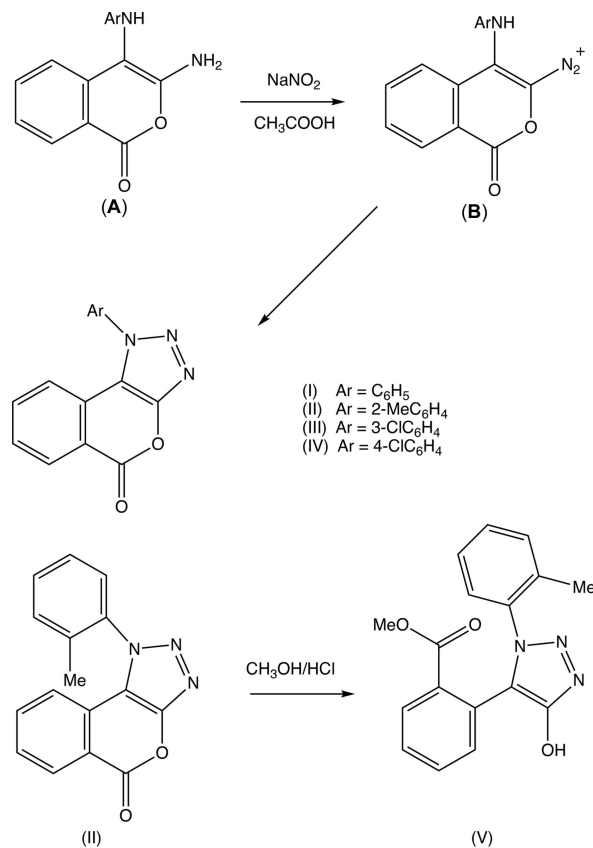
2. Experimental

2.1. Synthesis and crystallization

The known precursors of type (**A**) (see Scheme 1) having Ar = C₆H₅, 2-CH₃C₆H₄ and 4-ClC₆H₄ were prepared as described previously (Rodríguez *et al.*, 2017); the new analogue having Ar = 3-ClC₆H₄ was prepared following the same procedure. Analytical data for 3-amino-4-(3-chloroanilino)-1*H*-isochromen-1-one: yellow solid, yield 71%, m.p. 451–452 K; IR (ATR, cm⁻¹): 3456, 3319, 2922, 1701, 1592, 1474, 1306, 1089, 767, 679; NMR [CDCl₃, the numbering of the chlorophenyl ring follows that for compound (III)]: δ(¹H) 8.15 (*dd*, *J* = 8.0, 0.7 Hz, 1H, H8), 7.53 (*t*, *J* = 7.6 Hz, 1H, H6), 7.20 (*t*, *J* = 7.6 Hz, 1H, H7), 7.16 (*d*, *J* = 8.1 Hz, 1H, H5), 7.10 (*t*, *J* = 8.0 Hz, 1H, H15), 6.76 (*dd*, *J* = 7.9, 1.1 Hz, 1H, H14), 6.65 (*t*, *J* = 2.0 Hz, 1H, H12), 6.56 (*dd*, *J* = 8.2, 1.6 Hz, 1H, H16), 4.85 (*s*, 1H, NH), 4.57 (*s*, 2H, NH₂); δ(¹³C) 160.64 (CO), 154.78 (C3), 147.59 (C11), 140.40 (C4A), 135.65 (C13), 135.52 (C6), 130.86 (C15), 130.56 (C8), 124.23 (C7), 119.74 (C5), 119.29 (C14), 116.15 (C8A), 113.24 (C12), 111.59 (C16), 92.19 (C4); MS (EI, 70 eV): *m/z* (%) 285.9 (12) [M]⁺, 259.94 (31), 257.93 (100), 177.97 (16), 148.92 (20), 129.93 (21), 110.89 (17), 103.92 (17); HRMS (ESI-QTOF) found 287.0582, C₁₅H₁₁³⁵ClN₂O₂ requires for [M + H]⁺ 287.0578.

For the synthesis of compounds (I)–(IV), sodium nitrite (153 mg, 2.22 mmol) was added to a suspension of the

appropriate precursor (**A**) [1.09 mmol; 275 mg for (I), 290 mg for (II) and 313 mg for each of (III) and (IV)] in acetic acid (1.0 ml) and the resulting mixture was then stirred at ambient temperature for 5 min. The resulting solid precipitate was collected by filtration and washed with an aqueous solution of sodium hydrogen carbonate (10% *w/v*) and then with water. The crude solid products were purified by column chromatography on silica gel 60 (0.040–0.063 mm) using dichloromethane as eluent.



Scheme 1

Analytical data for compound (I), colourless solid, yield 77%, m.p. 433–434 K; IR (ATR, cm⁻¹): 3065, 1736, 1622, 1493, 1208, 1019, 763, 715; NMR (CDCl₃): δ(¹H) 8.46 (*dd*, *J* = 7.5, 1.6 Hz, 1H, H6), 7.72–7.55 (*m*, 7H, H7, H8, H12, H13, H14, H15, H16), 7.29 (*dd*, *J* = 7.8, 1.0 Hz, 1H, H9); δ(¹³C) 160.18 (CO), 154.65 (C3A), 136.89 (C11), 135.41 (C8), 132.84 (C6), 131.24 (C14), 130.23 (C13, C15), 129.79 (C7), 126.27 (C9A), 126.11 (C12, C16), 121.25 (C9), 120.57 (C9B), 115.26 (C5A); MS (EI, 70 eV): *m/z* (%) 262.98 (2) [M]⁺, 223.99 (35), 178.98 (100), 178.00 (29), 148.93 (36), 104.94 (23), 76.95 (35); HRMS (ESI-QTOF) found 264.0768, C₁₅H₉N₃O₃ requires for [M + H]⁺ 264.0768.

Analytical data for compound (II), colourless solid, yield 74%, m.p. 439–440 K; IR (ATR, cm⁻¹): 1745, 1622, 1012, 987, 764, 680; NMR (CDCl₃): δ(¹H) 8.45 (*dd*, *J* = 7.1, 2.2 Hz, 1H, H8), 7.66–7.57 (*m*, 3H, H6, H7, H13), 7.55–7.48 (*m*, 2H, H14, H15), 7.46 (*dd*, *J* = 7.8, 1.6 Hz, 1H, H16), 6.92 (*dd*, *J* = 7.0, 2.1 Hz, 1H, H5), 2.10 (*s*, 3H, CH₃); δ(¹³C) 160.22 (CO), 154.34 (C3A), 135.85 (C11), 135.69 (C8), 132.67 (C6), 131.89 (C14), 131.66 (C13), 129.78 (C7), 127.73 (C16), 127.38 (C15), 126.19

Table 1

Experimental details.

For all structures: $Z = 4$. Experiments were carried out at 100 K with Mo $K\alpha$ radiation using a Bruker D8 Venture diffractometer. Absorption was corrected for by multi-scan methods (SADABS; Bruker, 2016).

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_{15}H_9N_3O_2$	$C_{16}H_{11}N_3O_2$	$C_{15}H_8ClN_3O_2$
M_r	263.25	277.28	297.69
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
a, b, c (Å)	11.6814 (5), 6.4310 (3), 16.0589 (8)	7.5676 (5), 20.2663 (14), 9.2503 (7)	11.0993 (8), 12.8996 (9), 9.2234 (6)
β (°)	100.687 (2)	112.957 (3)	106.675 (2)
V (Å ³)	1185.47 (10)	1306.33 (16)	1265.04 (15)
μ (mm ⁻¹)	0.10	0.10	0.31
Crystal size (mm)	0.20 × 0.12 × 0.06	0.28 × 0.17 × 0.16	0.20 × 0.12 × 0.05
Data collection			
T_{min}, T_{max}	0.936, 0.994	0.941, 0.985	0.895, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26237, 2747, 2400	36209, 3242, 2915	28194, 2905, 2495
R_{int}	0.037	0.034	0.044
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.652	0.668	0.650
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.103, 1.04	0.036, 0.098, 1.05	0.032, 0.089, 1.08
No. of reflections	2747	3242	2905
No. of parameters	181	191	190
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.31, -0.21	0.31, -0.25	0.32, -0.36
	(IV)	(V)	
Crystal data			
Chemical formula	$C_{15}H_8ClN_3O_2$	$C_{17}H_{15}N_3O_3$	
M_r	297.69	309.32	
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	
a, b, c (Å)	16.7331 (12), 5.9676 (4), 13.681 (1)	11.1518 (5), 9.3143 (4), 14.2417 (6)	
β (°)	112.820 (3)	98.655 (2)	
V (Å ³)	1259.21 (16)	1462.46 (11)	
μ (mm ⁻¹)	0.31	0.10	
Crystal size (mm)	0.25 × 0.14 × 0.11	0.19 × 0.11 × 0.07	
Data collection			
T_{min}, T_{max}	0.880, 0.967	0.960, 0.993	
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34775, 2891, 2413	33834, 3360, 3084	
R_{int}	0.056	0.036	
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.650	0.650	
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.087, 1.12	0.042, 0.098, 1.07	
No. of reflections	2891	3360	
No. of parameters	190	213	
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.37, -0.26	0.34, -0.22	

Computer programs: APEX3 (Bruker, 2018), SAINT (Bruker, 2018), SHELXT2014 (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b) and PLATON (Spek, 2020).

(C9A), 120.63 (C9), 120.46 (C9B), 115.62 (C5A), 17.32 (CH₃); MS (EI, 70 eV): m/z (%) 276.97 (2) [M]⁺, 220.99 (16), 194.02 (15), 193.00 (100), 192.02 (21), 164.97 (22), 88.94 (22); HRMS (ESI-QTOF) found 278.0923, $C_{16}H_{11}N_3O_2$ requires for [$M + H$]⁺ 278.0924.

Analytical data for compound (III), yellow solid, yield 75%, m.p. 448–449 K; IR (ATR, cm⁻¹): 3072, 2919, 2850, 1748, 1617, 1587, 1010, 885, 867, 783; NMR (CDCl₃): δ (¹H) 8.46 (*dd*, $J = 7.9, 1.4$ Hz, 1H, H6), 7.75–7.60 (*m*, 5H, H7, H8, H12, H14, H15), 7.56 (*ddd*, $J = 7.7, 1.9, 1.4$ Hz, 1H, H16), 7.34 (*dd*, $J = 7.9, 0.6$ Hz, 1H, H9); δ (¹³C) 159.94 (CO), 154.65 (C3A), 137.75

(C11), 136.03 (C13), 135.57 (C8), 132.95 (C6), 131.47 (C15), 131.22 (C14), 130.04 (C7), 126.46 (C12), 125.92 (C9A), 124.23 (C16), 121.20 (C9), 120.57 (C9B), 115.22 (C5A); MS (EI, 70 eV): m/z (%) 296.95 (2) [M]⁺, 214.96 (29), 213.98 (15), 212.01 (100), 177.98 (47), 150.97 (15), 74.94 (27); HRMS (ESI-QTOF) found 298.0380, $C_{15}H_8^{35}ClN_3O_2$ requires for [$M + H$]⁺ 298.0378.

Analytical data for compound (IV), pink solid, yield 62%, m.p. 490–492 K; IR (ATR, cm⁻¹): 3087, 3066, 1740, 1620, 1457, 1217, 1013, 832, 764; NMR (CDCl₃) δ (¹H) 8.46 (*ddd*, $J = 7.8, 1.5, 0.6$ Hz, 1H, H6), 7.72–7.58 (*m*, 6H, H7, H8, H12, H13, H15,

H16), 7.32 (*ddd*, $J = 7.9, 1.3, 0.5$ Hz, 1H, H9); $\delta(^{13}\text{C})$ 159.98 (CO), 154.69 (C3A), 137.45 (C11), 135.51 (C8), 135.30 (C14), 132.96 (C6), 130.53 (C13, C15), 130.00 (C7), 127.39 (C12, C16), 126.02 (C9A), 121.14 (C9), 120.59 (C9B), 115.25 (C5A); MS (EI, 70 eV): m/z (%) 296.93 (1.4) $[M]^+$, 214.95 (31), 213.96 (15), 212.90 (100), 177.97 (39), 150.96 (14), 110.91 (13), 74.93 (25); HRMS (ESI-QTOF) found 298.0379, $\text{C}_{15}\text{H}_8^{35}\text{ClN}_3\text{O}_2$ requires for $[M + \text{H}]^+$ 298.0378.

For the conversion of compound (II) into compound (V), a sample of (II) (2.00 g, 7.22 mmol) and aqueous hydrochloric acid (1 mol dm^{-3} , 1 ml) were added to methanol (9 ml) and the resulting mixture was then stirred for 24 h at ambient temperature. The solvent was removed under reduced pressure and the resulting solid product was washed with an aqueous solution of sodium hydrogen carbonate (10% *w/v*) and then with water and finally dried in air to provide (V) as a colourless solid in quantitative yield (m.p. 463–464 K). Analytical data: IR (ATR, cm^{-1}): 2982, 2948, 1722, 1623, 1512, 1259, 764, 713; NMR (CDCl_3): $\delta(^1\text{H})$ 10.48 (*s*, 1H, OH), 7.76 (*d*, $J = 7.7$ Hz, 1H, H3), 7.51 (*td*, $J = 7.5, 1.2$ Hz, 1H, H5), 7.44 (*t*, $J = 7.2$ Hz, 1H, H4), 7.40–7.29 (*m*, 2H, H213, H214), 7.26 (*td*, $J = 7.7, 1.1$ Hz, 1H, H215), 7.23–7.16 (*m*, 2H, H6, H216), 3.67 (*s*, 3H, OCH_3), 2.02 (*s*, 3H, CH_3); $\delta(^{13}\text{C})$ 166.53 (CO), 155.36 (C24), 135.61 (C211), 134.49 (C214), 131.80 (C5), 131.38 (C6), 131.09 (C213), 130.85 (C25), 129.94 (C3), 129.70 (C214), 128.85 (C4), 127.39 (C216), 126.52 (C215), 126.40 (C1), 119.03 (C2), 52.12 (OCH_3), 17.07 (CH_3); MS (EI, 70 eV): m/z (%) 309.00 (2) $[M]^+$, 239.01 (16), 237.98 (100), 219.99 (21), 193.00 (70), 164.97 (23), 90.96 (30); HRMS (ESI-QTOF) found 310.1186, $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_2$ requires for $[M + \text{H}]^+$ 310.1186.

Crystals of compounds (I)–(V) suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in the presence of air, of solutions in chloroform.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps. H atoms bonded to C atoms were subsequently treated as riding atoms in geometrically idealized positions, with $\text{C}–\text{H} = 0.95$ (alkenyl and aromatic) or 0.98 Å (CH_3) and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.5$ for the methyl groups, which were allowed to rotate but not to tilt, and 1.2 for all other H atoms bonded to C atoms. For the H atom bonded to an O atom in compound (V), the atomic coordinates were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, giving an $\text{O}–\text{H}$ distance of 0.90 (2) Å. Several low-angle reflections which had been attenuated by the beam stop were omitted, *i.e.* $\bar{1}01$ for (II) and $\bar{1}02$ for (IV); in addition, one bad outlier reflection, *i.e.* $\bar{6}06$, was omitted from the data set for (II) before the final refinements. For several of the refinements, the final analyses of variance showed unexpected values of $K = [\text{mean}(F_o^2)/\text{mean}(F_c^2)]$ for the groups of the very weakest reflections. Thus, for (III) and (IV), respectively, -0.035 and -0.125 for 312 and 289 reflections in the $F_o/F_c(\text{max})$ ranges 0.000–0.008 and 0.000–0.010, and for (V), 3.550 for 339

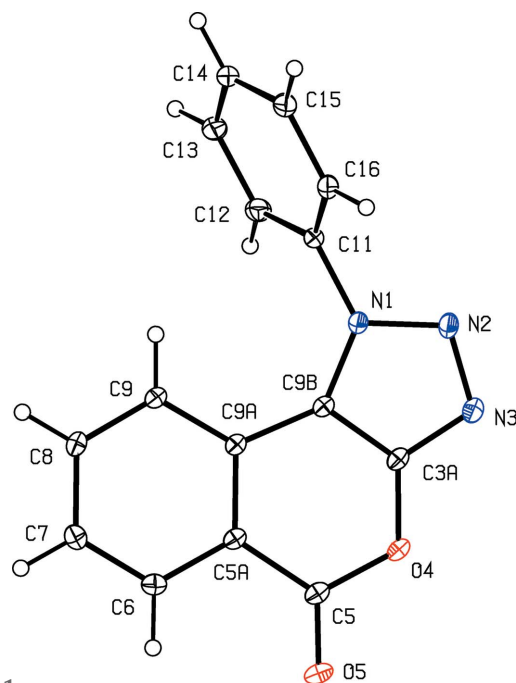


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

reflections in the $F_o/F_c(\text{max})$ range 0.000–0.009; these values are probably statistical artefacts.

3. Results and discussion

The constitutions of compounds (I)–(V) were all fully established by a combination of high-resolution mass spectrometry (HRMS), IR spectroscopy and ^1H and ^{13}C NMR spectroscopy, further confirmed by the structure analyses reported here (Figs. 1–5). The HRMS data for (I)–(IV) demonstrate the incorporation of an additional H atom, the IR data show the absence of an NH_2 absorption around 3400 cm^{-1} and the ^1H NMR spectra show the absence of signals around δ 4.5–5.0 arising from an amino group; these observations taken together confirm the conversion of the diamino precursors of type (A) (Scheme 1) into the triazolo products (I)–(IV), whose constitutions were fully confirmed by the detailed assignments of the ^1H and ^{13}C NMR spectra (see §2.1). Hence, the constitutions of (I)–(IV) show clearly that the anticipated triazolo ring formation has occurred, with the additional N atom arising from the diazotization process; similarly, the constitution of (V) confirms the occurrence of a ring-opening transesterification process.

Aside from the orientation of the 2-methyl and 3-chloro substituents in compounds (II) and (III), respectively, the conformations of compounds (I)–(IV) are fairly similar; the dihedral angles between the triazolo ring and the pendent ring (C11–C16) are 65.32 (5), 64.59 (4), 45.48 (8) and 52.32 (9)° in (I)–(IV), respectively. The molecules thus exhibit no internal symmetry and so are conformationally chiral in the crystalline state; the centrosymmetric space groups (Table 1) confirm that (I)–(IV) have all crystallized as conformational racemates. For

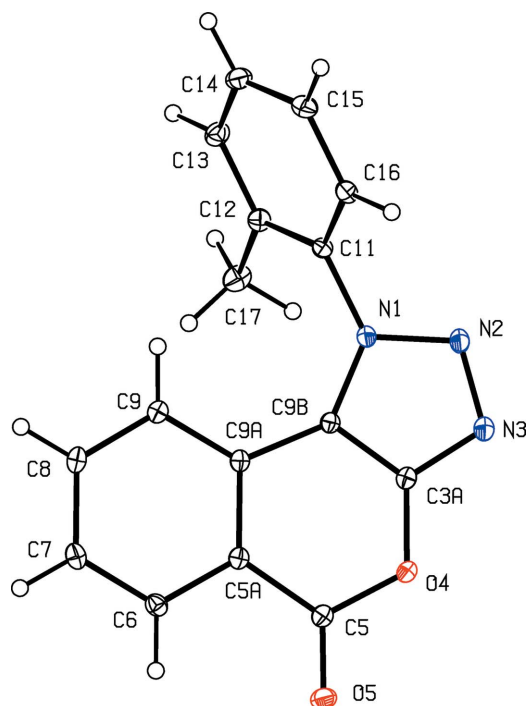


Figure 2
The molecular structure of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

all of (I)–(IV), the reference molecules were selected to have the same sign for the torsion angle $N2-N1-C11-C12$, or $N2-N1-C11-C16$ in the case of (III). A comparison of the conformation of ester (V) with that of its precursor (II) (Figs. 2 and 5) indicates that, in the crystalline state, there appear to

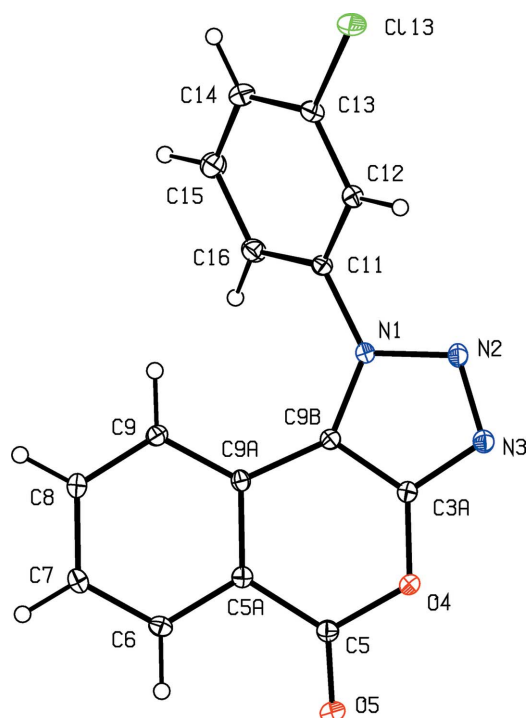


Figure 3
The molecular structure of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

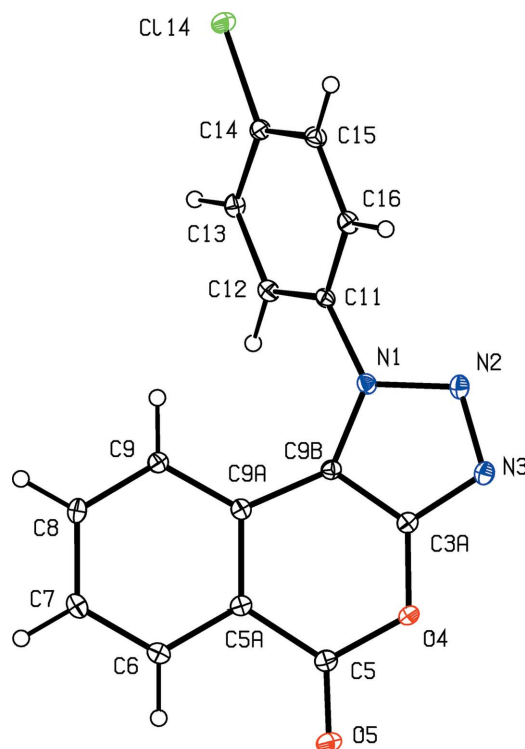


Figure 4
The molecular structure of compound (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

have been rotations about both the bonds exocyclic to the triazolo ring in (V), along with a rotation about the bond linking the ester unit to the adjacent aryl ring. The significance of these differences is unclear. The bond lengths in (I)–(V) show no unusual features.

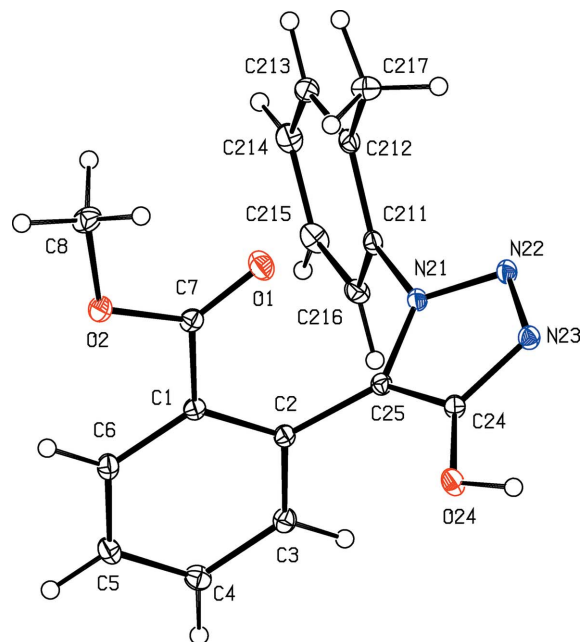
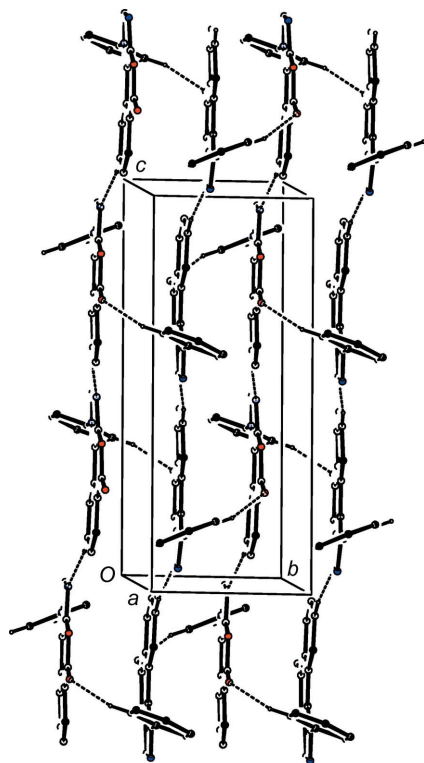


Figure 5
The molecular structure of compound (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.


Figure 6

Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded sheet of $R_2^2(28)$ rings parallel to $(10\bar{1})$. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

The supramolecular assembly in compounds (I)–(IV) is dominated by contacts of C–H···N, C–H···O and C–H··· π (arene) types (Table 2) and it is therefore worthwhile to specify the criteria under which such interactions are regarded here as structurally significant, or otherwise. Firstly, we discount all C–H···N and C–H···O contacts in which the D –H··· A angle is less than 140° , as the interaction energies associated with such contacts are likely to be extremely small (Wood *et al.*, 2009). Secondly, we discount all contacts involving methyl C–H bonds; these are not only of low acidity, but methyl groups CH_3 – E are generally undergoing very fast rotation about the C– E bonds, even in the solid state (Riddell & Rogerson, 1996, 1997). In particular, for methyl groups bonded to aryl rings, as found in (II) and (V), the rotation of the methyl group relative to the ring is subject to a sixfold rotation barrier, known to be in general extremely low, typically just a few J mol^{-1} rather than the more typical magnitude of a few kJ mol^{-1} (Tannenbaum *et al.*, 1956; Naylor & Wilson, 1957). Hence, there is just one significant intermolecular C–H··· X interaction in each of (II), (III) and (V), involving atoms C13, C16 and O24, respectively, as the donors, and two each in (I) and (IV), involving as the donors C8 and C12 in (I), and C7 and C8 in (IV).

The supramolecular assembly in compound (I) is mediated by two hydrogen bonds, one each of the C–H···N and C–H···O types (Table 2). Molecules which are related by an n -glide plane are linked by the C–H···N hydrogen bond to form a $C(7)$ (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*,

Table 2

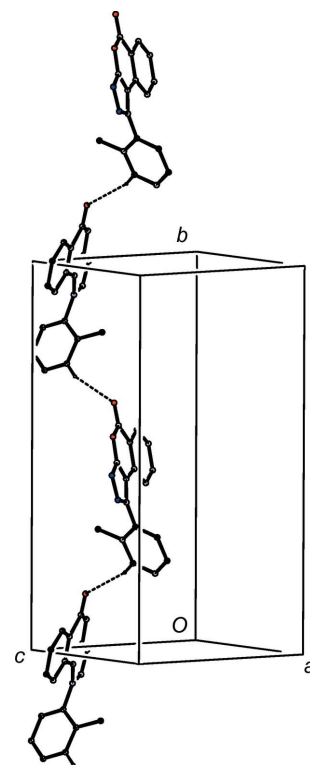
Hydrogen bonds and short intermolecular contacts (\AA , $^\circ$) for compounds (I)–(V).

$Cg1$ and $Cg2$ represent the centroids of the C5A/C6–C9/C9A and C1–C6 rings, respectively.

Compound	D –H··· A	D –H	H··· A	D ··· A	D –H··· A
(I)	C8–H8···N3 ⁱ	0.95	2.52	3.4641 (16)	173
	C12–H12···O5 ⁱⁱ	0.95	2.50	3.4136 (16)	161
(II)	C7–H7···N3 ⁱⁱⁱ	0.95	2.55	3.2770 (15)	133
	C13–H13···O5 ^{iv}	0.95	2.54	3.4083 (16)	151
(III)	C15–H15···O5 ^v	0.95	2.48	3.2482 (16)	138
	C8–H8···N3 ^{vi}	0.95	2.58	3.2465 (19)	127
(IV)	C16–H16···N2 ^{vii}	0.95	2.56	3.500 (2)	169
	C6–H6···O5 ^{viii}	0.95	2.53	3.287 (3)	137
	C8–H8···O5 ^{ix}	0.95	2.57	3.578 (2)	161
	C15–H15···N3 ^x	0.95	2.52	3.271 (2)	136
	C7–H7···Cg1 ^{xi}	0.95	2.69	3.517 (2)	146
(V)	O24–H24···N23 ^{xii}	0.90 (2)	1.77 (2)	2.6721 (15)	177.5 (19)
	C8–H8A···Cg2 ^{xiii}	0.98	2.90	3.6605 (16)	135
	C8–H8B···Cg2 ^{xiii}	0.98	2.90	3.5007 (16)	120
	C8–H8C···O24 ^{xiii}	0.98	2.59	3.4004 (19)	140
	C215–H215···O24 ^{xiv}	0.95	2.57	3.2972 (19)	134

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - 1, y, z - 1$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $x, y, z + 1$; (vii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $-x, -y + 1, -z + 1$; (ix) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (x) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (xi) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (xii) $-x + 1, -y + 1, -z + 1$; (xiii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (xiv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

1995) chain running parallel to the $[101]$ direction, while molecules which are related by a 2_1 screw axis are linked by a C–H···O hydrogen bond to form a $C(9)$ chain running parallel to the $[010]$ direction. The combination of these two


Figure 7

Part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded $C(10)$ chain parallel to $[010]$. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

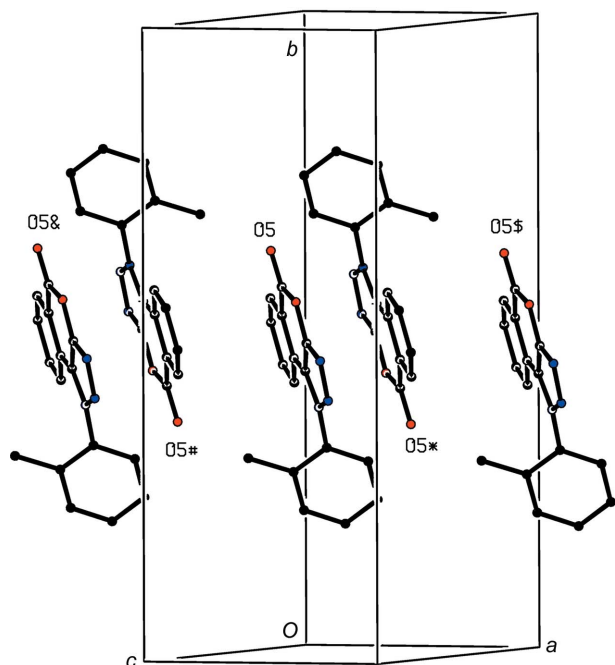


Figure 8
Part of the crystal structure of compound (II), showing the formation of a π -stacked chain parallel to $[100]$. For the sake of clarity, H atoms have all been omitted. O atoms marked with an asterisk (*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(-x + 1, -y + 1, -z + 1)$, $(-x, -y + 1, -z + 1)$, $(x + 1, y, z)$ and $(x - 1, y, z)$, respectively.

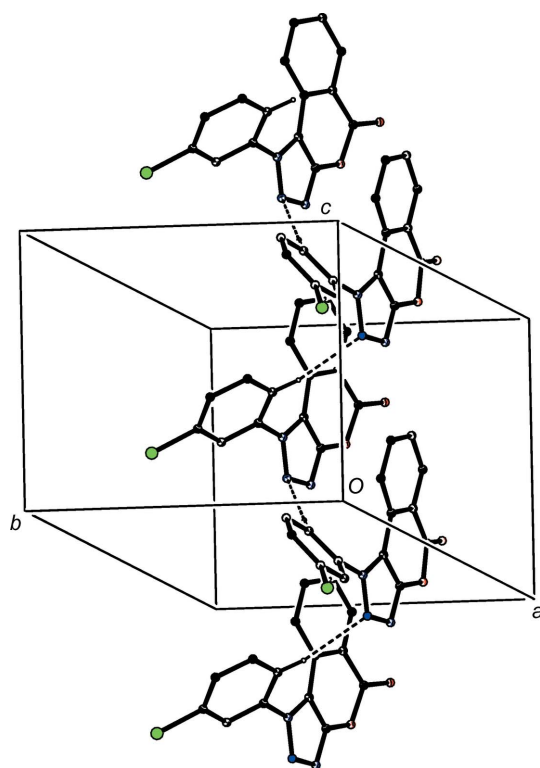


Figure 9
Part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded $C(5)$ chain parallel to $[001]$. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

chain motifs generates a sheet lying parallel to $(10\bar{1})$ and built of $R_4^+(28)$ rings (Fig. 6).

For compound (II), a single $C-H \cdots O$ hydrogen bond links molecules which are related by a 2_1 screw axis to form a $C(10)$ chain running parallel to the $[010]$ direction (Fig. 7), and chains of this type are linked by two π - π stacking interactions, both involving the fused carbocyclic ring, which together generate a π -stacked chain running parallel to $[100]$ (Fig. 8). The combination of these two motifs generates a sheet lying parallel to (001) . There is again just one hydrogen bond in the structure of compound (III), this time of the $C-H \cdots N$ type, linking molecules which are related by a c -glide plane to form a $C(5)$ chain running parallel to the $[001]$ direction (Fig. 9), but here there are no direction-specific interactions between adjacent chains.

The assembly in compound (IV) is built from a combination of $C-H \cdots O$ and $C-H \cdots \pi(\text{arene})$ hydrogen bonds (Table 2). The $C-H \cdots O$ hydrogen bond links molecules which are related by a c -glide plane to form a $C(7)$ chain running parallel to the $[001]$ direction (Fig. 10). By contrast, molecules which are related by a 2_1 screw axis are linked by the $C-H \cdots \pi(\text{arene})$ hydrogen bond to form a chain running parallel to the $[010]$ direction (Fig. 11), and the combination of these two chain motifs generates a sheet lying parallel to (100) .

Paired $O-H \cdots O$ hydrogen bonds link inversion-related pairs of molecules of (V) to form a cyclic centrosymmetric $R_2^2(8)$ dimer (Fig. 12), but there are no direction-specific interactions between adjacent dimer units.

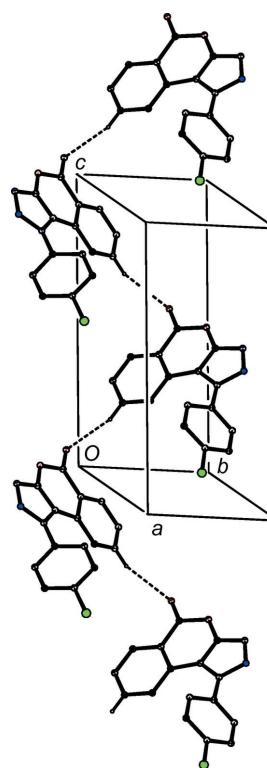


Figure 10
Part of the crystal structure of compound (IV), showing the formation of a hydrogen-bonded $C(7)$ chain parallel to $[001]$. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

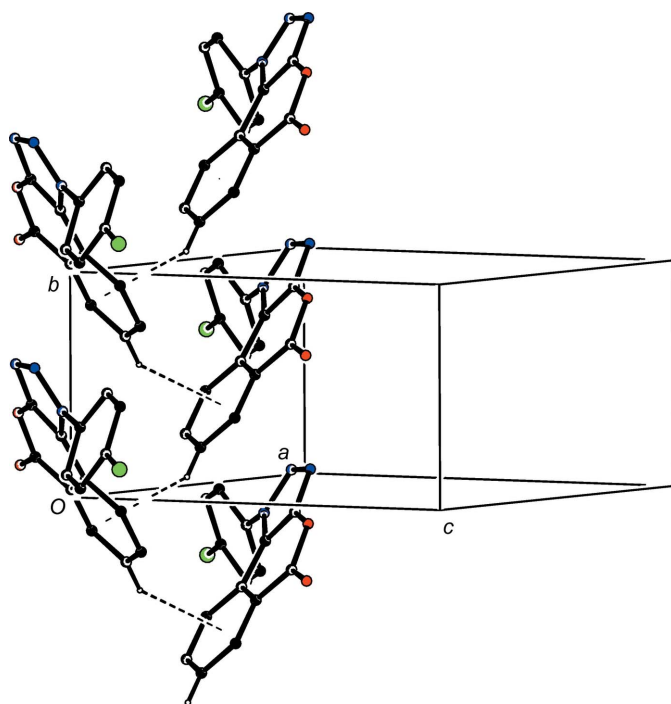


Figure 11
Part of the crystal structure of compound (IV), showing the formation of a hydrogen-bonded chain parallel to [010]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

Thus, minor variations in the substituent on the pendent aryl ring in compounds (I)–(IV) are associated with significant changes in the pattern of supramolecular assembly. Whereas for the unsubstituted parent compound (I), the molecules are linked into hydrogen-bonded sheets by a combination of C–

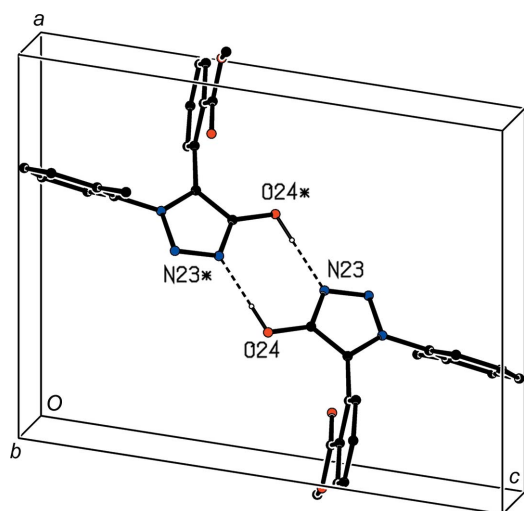


Figure 12
Part of the crystal structure of compound (V), showing the formation of a centrosymmetric $R_2^2(8)$ dimer. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms bonded to C atoms have all been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x + 1, -y + 1, -z + 1)$.

H \cdots N and C–H \cdots O hydrogen bonds, the sheet formation in 4-chloro derivative (IV) is based on a combination of C–H \cdots O and C–H \cdots π (arene) hydrogen bonds. In each of the methyl compound (II) and the 3-chloro compound (III), a single hydrogen bond, of the C–H \cdots O and C–H \cdots N types, respectively, links the molecules into simple chains; these chains form π -stacked sheets in (II), but not in (III).

In summary, therefore, we have developed a simple and efficient route to new 1-arylisochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-ones, with full spectroscopic and structural characterization of four examples, which show that small changes in substituents are associated with substantial changes in the patterns of supramolecular aggregation, and we have demonstrated the necessity of using only a weak acid in the synthesis, along with the spectroscopic and structural characterization of a ring-opened derivative.

Acknowledgements

The authors thank ‘Centro de Instrumentación Científico-Técnica of Universidad de Jaén’ for data collection. The authors thank Universidad de Ciencias Aplicadas y Ambientales (UDCA), Universidad Nacional de Colombia, the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support.

References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2016). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2018). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Naylor, R. E. & Wilson, E. B. (1957). *J. Chem. Phys.* **26**, 1057–1060.
- Opatz, T. & Ferenc, D. (2005). *Eur. J. Org. Chem.* **2005**, 817–821.
- Oweida, S. W., Ku, D. N., Lumsden, A. B., Kam, C. M. & Powers, J. C. (1990). *Thromb. Res.* **58**, 191–197.
- Qadeer, G., Rama, N. H., Fan, Z. J., Liu, B. & Liu, X. F. (2007). *J. Braz. Chem. Soc.* **18**, 1176–1182.
- Riddell, F. G. & Rogerson, M. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 493–504.
- Riddell, F. G. & Rogerson, M. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 249–256.
- Rodríguez, R., Vicentes, D. E., Cobo, J. & Nogueras, M. (2017). *Tetrahedron Lett.* **58**, 1487–1489.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Tannenbaum, E., Myers, R. J. & Gwinn, W. D. (1956). *J. Chem. Phys.* **25**, 42–47.
- Vicentes, D. E., Rodríguez, R., Cobo, J. & Glidewell, C. (2013). *Acta Cryst.* **C69**, 770–773.
- Wood, P. A., Allen, F. H. & Pidcock, E. (2009). *CrystEngComm*, **11**, 1563–1571.
- Xu, Z., Zhao, S. J. & Liu, Y. (2019). *Eur. J. Med. Chem.* **183**, 111700.
- Zhang, Z., Huo, J. Q., Dong, H. J., Shi, J. M. & Zhang, J. L. (2016). *Asian J. Chem.* **28**, 666–668.

supporting information

Acta Cryst. (2020). C76, 446-453 [https://doi.org/10.1107/S2053229620003757]

Conversion of 3-amino-4-arylamino-1*H*-isochromen-1-ones to 1-aryl-isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-ones: synthesis, spectroscopic characterization and the structures of four products and one ring-opened derivative

Daniel E. Vicentes, Andrea L. Romero, Ricuarte Rodríguez, Justo Cobo and Christopher Glidewell

Computing details

For all structures, data collection: *APEX3* (Bruker, 2018); cell refinement: *APEX3* (Bruker, 2018); data reduction: *APEX3* (Bruker, 2018); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *PLATON* (Spek, 2020).

1-Phenylisochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one (I)

Crystal data

$C_{15}H_9N_3O_2$	$F(000) = 544$
$M_r = 263.25$	$D_x = 1.475 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 11.6814 (5) \text{ \AA}$	Cell parameters from 2747 reflections
$b = 6.4310 (3) \text{ \AA}$	$\theta = 2.6\text{--}27.6^\circ$
$c = 16.0589 (8) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 100.687 (2)^\circ$	$T = 100 \text{ K}$
$V = 1185.47 (10) \text{ \AA}^3$	Plate, colourless
$Z = 4$	$0.20 \times 0.12 \times 0.06 \text{ mm}$

Data collection

Bruker D8 Venture diffractometer	26237 measured reflections
Radiation source: INCOATEC high brilliance microfocus sealed tube	2747 independent reflections
Multilayer mirror monochromator	2400 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.037$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{\text{max}} = 27.6^\circ$, $\theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.936$, $T_{\text{max}} = 0.994$	$h = -15 \rightarrow 15$
	$k = -8 \rightarrow 8$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.103$
 $S = 1.04$
 2747 reflections
 181 parameters
 0 restraints

Primary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.6009P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.42457 (8)	0.29285 (15)	0.11368 (6)	0.0179 (2)
N2	0.35944 (9)	0.28467 (17)	0.03458 (6)	0.0220 (2)
N3	0.24822 (9)	0.28866 (16)	0.04153 (7)	0.0215 (2)
C3A	0.24551 (10)	0.29942 (17)	0.12447 (8)	0.0173 (2)
O4	0.14429 (7)	0.30258 (13)	0.15478 (5)	0.0192 (2)
C5	0.15189 (10)	0.30615 (17)	0.24186 (8)	0.0181 (2)
O5	0.06155 (7)	0.31098 (14)	0.26774 (6)	0.0235 (2)
C5A	0.26924 (10)	0.30227 (17)	0.29667 (7)	0.0164 (2)
C6	0.27436 (10)	0.29619 (18)	0.38439 (8)	0.0195 (2)
H6	0.2046	0.2987	0.4068	0.023*
C7	0.38124 (11)	0.28646 (19)	0.43835 (8)	0.0216 (3)
H7	0.3847	0.2809	0.4979	0.026*
C8	0.48402 (10)	0.28471 (19)	0.40587 (7)	0.0205 (3)
H8	0.5570	0.2775	0.4435	0.025*
C9	0.48066 (10)	0.29343 (17)	0.31931 (7)	0.0178 (2)
H9	0.5511	0.2939	0.2977	0.021*
C9A	0.37320 (10)	0.30147 (16)	0.26375 (7)	0.0153 (2)
C9B	0.35513 (9)	0.30231 (17)	0.17263 (7)	0.0159 (2)
C11	0.54952 (10)	0.28664 (19)	0.12449 (7)	0.0189 (2)
C12	0.61353 (11)	0.4585 (2)	0.15790 (8)	0.0247 (3)
H12	0.5758	0.5803	0.1726	0.030*
C13	0.73450 (11)	0.4484 (2)	0.16938 (8)	0.0282 (3)
H13	0.7801	0.5636	0.1931	0.034*
C14	0.78884 (11)	0.2714 (2)	0.14647 (8)	0.0284 (3)
H14	0.8714	0.2658	0.1544	0.034*
C15	0.72280 (11)	0.1026 (2)	0.11200 (8)	0.0275 (3)
H15	0.7604	-0.0176	0.0956	0.033*
C16	0.60190 (10)	0.1080 (2)	0.10133 (7)	0.0224 (3)
H16	0.5563	-0.0082	0.0787	0.027*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0164 (5)	0.0208 (5)	0.0157 (5)	0.0001 (4)	0.0010 (4)	-0.0015 (4)
N2	0.0204 (5)	0.0266 (5)	0.0173 (5)	-0.0001 (4)	-0.0013 (4)	-0.0024 (4)
N3	0.0191 (5)	0.0229 (5)	0.0206 (5)	0.0002 (4)	-0.0010 (4)	-0.0012 (4)
C3A	0.0147 (5)	0.0141 (5)	0.0220 (6)	0.0002 (4)	0.0002 (4)	-0.0006 (4)
O4	0.0124 (4)	0.0196 (4)	0.0243 (4)	-0.0004 (3)	-0.0002 (3)	-0.0002 (3)
C5	0.0154 (5)	0.0121 (5)	0.0262 (6)	-0.0008 (4)	0.0026 (4)	-0.0001 (4)
O5	0.0146 (4)	0.0224 (4)	0.0341 (5)	-0.0003 (3)	0.0064 (3)	0.0015 (4)
C5A	0.0147 (5)	0.0124 (5)	0.0219 (6)	-0.0005 (4)	0.0025 (4)	-0.0004 (4)
C6	0.0193 (5)	0.0164 (5)	0.0239 (6)	-0.0006 (4)	0.0070 (4)	-0.0006 (4)
C7	0.0255 (6)	0.0212 (6)	0.0181 (5)	-0.0013 (5)	0.0044 (5)	-0.0007 (4)
C8	0.0180 (5)	0.0218 (6)	0.0198 (6)	-0.0008 (4)	-0.0014 (4)	-0.0014 (4)
C9	0.0142 (5)	0.0181 (5)	0.0205 (6)	0.0000 (4)	0.0019 (4)	-0.0006 (4)
C9A	0.0148 (5)	0.0118 (5)	0.0186 (5)	0.0000 (4)	0.0016 (4)	-0.0009 (4)
C9B	0.0141 (5)	0.0135 (5)	0.0195 (6)	0.0002 (4)	0.0017 (4)	-0.0006 (4)
C11	0.0155 (5)	0.0265 (6)	0.0148 (5)	-0.0001 (4)	0.0030 (4)	0.0008 (4)
C12	0.0228 (6)	0.0272 (6)	0.0254 (6)	-0.0039 (5)	0.0077 (5)	-0.0034 (5)
C13	0.0227 (6)	0.0389 (7)	0.0241 (6)	-0.0102 (5)	0.0066 (5)	-0.0043 (5)
C14	0.0168 (6)	0.0504 (8)	0.0182 (6)	-0.0018 (5)	0.0042 (4)	-0.0009 (5)
C15	0.0215 (6)	0.0400 (8)	0.0208 (6)	0.0069 (5)	0.0035 (5)	-0.0037 (5)
C16	0.0202 (6)	0.0285 (6)	0.0177 (5)	0.0017 (5)	0.0013 (4)	-0.0028 (5)

Geometric parameters (\AA , $^\circ$)

N1—N2	1.3552 (14)	C8—C9	1.3845 (16)
N1—C9B	1.3574 (15)	C8—H8	0.9500
N1—C11	1.4381 (14)	C9—C9A	1.3997 (15)
N2—N3	1.3247 (15)	C9—H9	0.9500
N3—C3A	1.3398 (15)	C9A—C9B	1.4392 (15)
C3A—O4	1.3598 (14)	C11—C16	1.3844 (17)
C3A—C9B	1.3678 (15)	C11—C12	1.3855 (17)
O4—C5	1.3848 (15)	C12—C13	1.3923 (17)
C5—O5	1.2042 (14)	C12—H12	0.9500
C5—C5A	1.4856 (15)	C13—C14	1.386 (2)
C5A—C6	1.3993 (16)	C13—H13	0.9500
C5A—C9A	1.4116 (15)	C14—C15	1.387 (2)
C6—C7	1.3829 (17)	C14—H14	0.9500
C6—H6	0.9500	C15—C16	1.3912 (16)
C7—C8	1.3949 (17)	C15—H15	0.9500
C7—H7	0.9500	C16—H16	0.9500
N2—N1—C9B	110.56 (9)	C9A—C9—H9	120.1
N2—N1—C11	119.53 (10)	C9—C9A—C5A	119.57 (11)
C9B—N1—C11	129.89 (10)	C9—C9A—C9B	126.40 (10)
N3—N2—N1	108.01 (9)	C5A—C9A—C9B	114.00 (10)
N2—N3—C3A	106.80 (10)	N1—C9B—C3A	102.88 (10)

N3—C3A—O4	122.62 (10)	N1—C9B—C9A	135.65 (10)
N3—C3A—C9B	111.75 (10)	C3A—C9B—C9A	121.35 (10)
O4—C3A—C9B	125.62 (11)	C16—C11—C12	122.15 (11)
C3A—O4—C5	117.69 (9)	C16—C11—N1	118.68 (11)
O5—C5—O4	116.93 (10)	C12—C11—N1	119.17 (11)
O5—C5—C5A	124.56 (11)	C11—C12—C13	118.40 (12)
O4—C5—C5A	118.51 (10)	C11—C12—H12	120.8
C6—C5A—C9A	119.85 (10)	C13—C12—H12	120.8
C6—C5A—C5	117.35 (10)	C14—C13—C12	120.46 (12)
C9A—C5A—C5	122.79 (11)	C14—C13—H13	119.8
C7—C6—C5A	119.81 (11)	C12—C13—H13	119.8
C7—C6—H6	120.1	C13—C14—C15	120.06 (12)
C5A—C6—H6	120.1	C13—C14—H14	120.0
C6—C7—C8	120.38 (11)	C15—C14—H14	120.0
C6—C7—H7	119.8	C14—C15—C16	120.42 (12)
C8—C7—H7	119.8	C14—C15—H15	119.8
C9—C8—C7	120.60 (11)	C16—C15—H15	119.8
C9—C8—H8	119.7	C11—C16—C15	118.50 (12)
C7—C8—H8	119.7	C11—C16—H16	120.8
C8—C9—C9A	119.78 (11)	C15—C16—H16	120.8
C8—C9—H9	120.1		
C9B—N1—N2—N3	-0.02 (13)	N2—N1—C9B—C3A	-0.02 (12)
C11—N1—N2—N3	178.80 (10)	C11—N1—C9B—C3A	-178.69 (11)
N1—N2—N3—C3A	0.06 (13)	N2—N1—C9B—C9A	175.65 (12)
N2—N3—C3A—O4	-178.86 (10)	C11—N1—C9B—C9A	-3.0 (2)
N2—N3—C3A—C9B	-0.08 (13)	N3—C3A—C9B—N1	0.06 (13)
N3—C3A—O4—C5	177.66 (10)	O4—C3A—C9B—N1	178.80 (10)
C9B—C3A—O4—C5	-0.95 (16)	N3—C3A—C9B—C9A	-176.40 (10)
C3A—O4—C5—O5	179.30 (10)	O4—C3A—C9B—C9A	2.34 (17)
C3A—O4—C5—C5A	-1.14 (14)	C9—C9A—C9B—N1	1.4 (2)
O5—C5—C5A—C6	2.43 (17)	C5A—C9A—C9B—N1	-176.43 (12)
O4—C5—C5A—C6	-177.09 (10)	C9—C9A—C9B—C3A	176.48 (11)
O5—C5—C5A—C9A	-178.50 (11)	C5A—C9A—C9B—C3A	-1.36 (15)
O4—C5—C5A—C9A	1.98 (15)	N2—N1—C11—C16	-65.11 (15)
C9A—C5A—C6—C7	-0.91 (16)	C9B—N1—C11—C16	113.45 (13)
C5—C5A—C6—C7	178.19 (10)	N2—N1—C11—C12	115.11 (13)
C5A—C6—C7—C8	0.62 (17)	C9B—N1—C11—C12	-66.33 (16)
C6—C7—C8—C9	0.24 (18)	C16—C11—C12—C13	-0.94 (18)
C7—C8—C9—C9A	-0.80 (17)	N1—C11—C12—C13	178.83 (11)
C8—C9—C9A—C5A	0.50 (16)	C11—C12—C13—C14	1.08 (19)
C8—C9—C9A—C9B	-177.24 (11)	C12—C13—C14—C15	-0.2 (2)
C6—C5A—C9A—C9	0.35 (16)	C13—C14—C15—C16	-1.0 (2)
C5—C5A—C9A—C9	-178.69 (10)	C12—C11—C16—C15	-0.15 (18)
C6—C5A—C9A—C9B	178.36 (10)	N1—C11—C16—C15	-179.92 (11)
C5—C5A—C9A—C9B	-0.69 (15)	C14—C15—C16—C11	1.11 (19)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C8—H8 \cdots N3 ⁱ	0.95	2.52	3.4641 (16)	173
C12—H12 \cdots O5 ⁱⁱ	0.95	2.50	3.4136 (16)	161

Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $-x+1/2, y+1/2, -z+1/2$.

1-(2-Methylphenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one (II)

Crystal data

$C_{16}H_{11}N_3O_2$	$F(000) = 576$
$M_r = 277.28$	$D_x = 1.410 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 7.5676 (5) \text{ \AA}$	Cell parameters from 3244 reflections
$b = 20.2663 (14) \text{ \AA}$	$\theta = 2.6\text{--}28.3^\circ$
$c = 9.2503 (7) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 112.957 (3)^\circ$	$T = 100 \text{ K}$
$V = 1306.33 (16) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.28 \times 0.17 \times 0.16 \text{ mm}$

Data collection

Bruker D8 Venture diffractometer	36209 measured reflections
Radiation source: INCOATEC high brilliance microfocus sealed tube	3242 independent reflections
Multilayer mirror monochromator	2915 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.034$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{\text{max}} = 28.3^\circ, \theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.941, T_{\text{max}} = 0.985$	$h = -9 \rightarrow 10$
	$k = -26 \rightarrow 27$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.6412P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
3242 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
191 parameters	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.64617 (13)	0.39965 (4)	0.84757 (10)	0.01530 (19)

N2	0.78444 (13)	0.41415 (5)	0.99005 (11)	0.0188 (2)
N3	0.77052 (14)	0.47755 (5)	1.01796 (11)	0.0193 (2)
C3A	0.62518 (15)	0.50189 (5)	0.89301 (12)	0.0159 (2)
O4	0.57303 (11)	0.56642 (4)	0.88252 (9)	0.01773 (17)
C5	0.41921 (15)	0.58629 (5)	0.74851 (12)	0.0162 (2)
O5	0.37021 (12)	0.64284 (4)	0.74350 (10)	0.02200 (19)
C5A	0.33179 (15)	0.53730 (5)	0.62166 (12)	0.0149 (2)
C6	0.18714 (15)	0.56044 (5)	0.48412 (13)	0.0175 (2)
H6	0.1472	0.6052	0.4769	0.021*
C7	0.10215 (16)	0.51836 (6)	0.35852 (13)	0.0190 (2)
H7	0.0044	0.5342	0.2648	0.023*
C8	0.15996 (15)	0.45252 (6)	0.36942 (12)	0.0183 (2)
H8	0.1004	0.4238	0.2828	0.022*
C9	0.30339 (15)	0.42840 (5)	0.50514 (12)	0.0165 (2)
H9	0.3422	0.3836	0.5110	0.020*
C9A	0.39036 (14)	0.47069 (5)	0.63331 (12)	0.0141 (2)
C9B	0.54239 (14)	0.45455 (5)	0.78150 (12)	0.0141 (2)
C11	0.63623 (15)	0.33424 (5)	0.78533 (12)	0.0157 (2)
C12	0.47496 (16)	0.29469 (5)	0.75875 (13)	0.0181 (2)
C13	0.47388 (17)	0.23249 (6)	0.69298 (14)	0.0215 (2)
H13	0.3660	0.2044	0.6714	0.026*
C14	0.62740 (18)	0.21092 (6)	0.65863 (14)	0.0227 (2)
H14	0.6219	0.1688	0.6119	0.027*
C15	0.78913 (17)	0.25035 (6)	0.69194 (14)	0.0215 (2)
H15	0.8954	0.2349	0.6713	0.026*
C16	0.79318 (15)	0.31249 (5)	0.75567 (13)	0.0181 (2)
H16	0.9024	0.3400	0.7789	0.022*
C17	0.30969 (17)	0.31669 (6)	0.79939 (15)	0.0243 (2)
H17A	0.2431	0.2779	0.8167	0.036*
H17B	0.2201	0.3429	0.7128	0.036*
H17C	0.3584	0.3435	0.8951	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0137 (4)	0.0163 (4)	0.0143 (4)	-0.0003 (3)	0.0038 (3)	-0.0002 (3)
N2	0.0166 (4)	0.0208 (5)	0.0156 (4)	-0.0009 (3)	0.0025 (3)	-0.0004 (3)
N3	0.0184 (4)	0.0203 (5)	0.0162 (4)	-0.0009 (3)	0.0035 (4)	-0.0010 (3)
C3A	0.0154 (5)	0.0170 (5)	0.0151 (5)	-0.0016 (4)	0.0059 (4)	-0.0013 (4)
O4	0.0192 (4)	0.0152 (4)	0.0164 (4)	-0.0013 (3)	0.0042 (3)	-0.0028 (3)
C5	0.0160 (5)	0.0168 (5)	0.0169 (5)	-0.0017 (4)	0.0076 (4)	-0.0005 (4)
O5	0.0246 (4)	0.0157 (4)	0.0257 (4)	0.0003 (3)	0.0099 (3)	-0.0012 (3)
C5A	0.0140 (5)	0.0165 (5)	0.0149 (5)	-0.0019 (4)	0.0066 (4)	-0.0002 (4)
C6	0.0167 (5)	0.0179 (5)	0.0177 (5)	0.0002 (4)	0.0064 (4)	0.0031 (4)
C7	0.0157 (5)	0.0241 (5)	0.0155 (5)	-0.0011 (4)	0.0043 (4)	0.0032 (4)
C8	0.0171 (5)	0.0228 (5)	0.0143 (5)	-0.0046 (4)	0.0053 (4)	-0.0025 (4)
C9	0.0164 (5)	0.0172 (5)	0.0160 (5)	-0.0017 (4)	0.0064 (4)	-0.0016 (4)
C9A	0.0125 (4)	0.0166 (5)	0.0138 (5)	-0.0017 (4)	0.0059 (4)	-0.0001 (4)

C9B	0.0134 (5)	0.0149 (4)	0.0143 (5)	-0.0009 (4)	0.0056 (4)	-0.0003 (4)
C11	0.0172 (5)	0.0140 (5)	0.0144 (5)	0.0005 (4)	0.0045 (4)	0.0012 (4)
C12	0.0185 (5)	0.0179 (5)	0.0182 (5)	-0.0010 (4)	0.0075 (4)	0.0007 (4)
C13	0.0231 (5)	0.0179 (5)	0.0232 (5)	-0.0043 (4)	0.0087 (4)	-0.0011 (4)
C14	0.0290 (6)	0.0157 (5)	0.0229 (5)	0.0013 (4)	0.0098 (5)	-0.0007 (4)
C15	0.0216 (5)	0.0205 (5)	0.0234 (5)	0.0045 (4)	0.0099 (4)	0.0016 (4)
C16	0.0160 (5)	0.0185 (5)	0.0186 (5)	0.0009 (4)	0.0055 (4)	0.0025 (4)
C17	0.0224 (6)	0.0235 (6)	0.0318 (6)	-0.0046 (4)	0.0157 (5)	-0.0039 (5)

Geometric parameters (Å, °)

N1—N2	1.3574 (12)	C9—C9A	1.4016 (14)
N1—C9B	1.3616 (13)	C9—H9	0.9500
N1—C11	1.4353 (13)	C9A—C9B	1.4421 (14)
N2—N3	1.3229 (13)	C11—C16	1.3909 (15)
N3—C3A	1.3406 (14)	C11—C12	1.3994 (15)
C3A—O4	1.3586 (13)	C12—C13	1.3982 (15)
C3A—C9B	1.3686 (14)	C12—C17	1.5071 (16)
O4—C5	1.3886 (13)	C13—C14	1.3892 (17)
C5—O5	1.2000 (13)	C13—H13	0.9500
C5—C5A	1.4815 (14)	C14—C15	1.3919 (17)
C5A—C6	1.3966 (14)	C14—H14	0.9500
C5A—C9A	1.4118 (14)	C15—C16	1.3857 (16)
C6—C7	1.3813 (15)	C15—H15	0.9500
C6—H6	0.9500	C16—H16	0.9500
C7—C8	1.3955 (16)	C17—H17A	0.9800
C7—H7	0.9500	C17—H17B	0.9800
C8—C9	1.3894 (15)	C17—H17C	0.9800
C8—H8	0.9500		
N2—N1—C9B	110.50 (9)	C5A—C9A—C9B	113.56 (9)
N2—N1—C11	119.30 (9)	N1—C9B—C3A	102.72 (9)
C9B—N1—C11	130.07 (9)	N1—C9B—C9A	135.95 (10)
N3—N2—N1	108.05 (9)	C3A—C9B—C9A	121.23 (10)
N2—N3—C3A	106.87 (9)	C16—C11—C12	122.48 (10)
N3—C3A—O4	122.25 (9)	C16—C11—N1	117.17 (9)
N3—C3A—C9B	111.86 (10)	C12—C11—N1	120.34 (9)
O4—C3A—C9B	125.89 (10)	C13—C12—C11	116.72 (10)
C3A—O4—C5	117.51 (8)	C13—C12—C17	120.71 (10)
O5—C5—O4	116.76 (10)	C11—C12—C17	122.57 (10)
O5—C5—C5A	125.01 (10)	C14—C13—C12	121.31 (11)
O4—C5—C5A	118.20 (9)	C14—C13—H13	119.3
C6—C5A—C9A	120.12 (10)	C12—C13—H13	119.3
C6—C5A—C5	116.46 (9)	C13—C14—C15	120.69 (11)
C9A—C5A—C5	123.40 (9)	C13—C14—H14	119.7
C7—C6—C5A	120.08 (10)	C15—C14—H14	119.7
C7—C6—H6	120.0	C16—C15—C14	119.18 (10)
C5A—C6—H6	120.0	C16—C15—H15	120.4

C6—C7—C8	119.97 (10)	C14—C15—H15	120.4
C6—C7—H7	120.0	C15—C16—C11	119.55 (10)
C8—C7—H7	120.0	C15—C16—H16	120.2
C9—C8—C7	120.94 (10)	C11—C16—H16	120.2
C9—C8—H8	119.5	C12—C17—H17A	109.5
C7—C8—H8	119.5	C12—C17—H17B	109.5
C8—C9—C9A	119.53 (10)	H17A—C17—H17B	109.5
C8—C9—H9	120.2	C12—C17—H17C	109.5
C9A—C9—H9	120.2	H17A—C17—H17C	109.5
C9—C9A—C5A	119.35 (10)	H17B—C17—H17C	109.5
C9—C9A—C9B	127.07 (10)		
C9B—N1—N2—N3	0.61 (12)	N2—N1—C9B—C9A	175.50 (11)
C11—N1—N2—N3	176.84 (9)	C11—N1—C9B—C9A	-0.2 (2)
N1—N2—N3—C3A	-0.29 (12)	N3—C3A—C9B—N1	0.46 (12)
N2—N3—C3A—O4	-179.29 (9)	O4—C3A—C9B—N1	179.60 (10)
N2—N3—C3A—C9B	-0.12 (13)	N3—C3A—C9B—C9A	-176.40 (9)
N3—C3A—O4—C5	-179.41 (9)	O4—C3A—C9B—C9A	2.74 (16)
C9B—C3A—O4—C5	1.54 (15)	C9—C9A—C9B—N1	-0.72 (19)
C3A—O4—C5—O5	177.28 (9)	C5A—C9A—C9B—N1	-179.19 (11)
C3A—O4—C5—C5A	-4.34 (13)	C9—C9A—C9B—C3A	174.88 (10)
O5—C5—C5A—C6	2.91 (16)	C5A—C9A—C9B—C3A	-3.59 (14)
O4—C5—C5A—C6	-175.32 (9)	N2—N1—C11—C16	-62.57 (13)
O5—C5—C5A—C9A	-178.43 (10)	C9B—N1—C11—C16	112.81 (12)
O4—C5—C5A—C9A	3.34 (15)	N2—N1—C11—C12	116.56 (11)
C9A—C5A—C6—C7	-0.59 (16)	C9B—N1—C11—C12	-68.06 (15)
C5—C5A—C6—C7	178.11 (9)	C16—C11—C12—C13	-3.01 (16)
C5A—C6—C7—C8	0.43 (16)	N1—C11—C12—C13	177.90 (10)
C6—C7—C8—C9	-0.35 (16)	C16—C11—C12—C17	176.43 (11)
C7—C8—C9—C9A	0.43 (16)	N1—C11—C12—C17	-2.66 (16)
C8—C9—C9A—C5A	-0.58 (15)	C11—C12—C13—C14	1.10 (17)
C8—C9—C9A—C9B	-178.97 (10)	C17—C12—C13—C14	-178.35 (11)
C6—C5A—C9A—C9	0.67 (15)	C12—C13—C14—C15	1.34 (18)
C5—C5A—C9A—C9	-177.95 (9)	C13—C14—C15—C16	-1.95 (17)
C6—C5A—C9A—C9B	179.27 (9)	C14—C15—C16—C11	0.10 (16)
C5—C5A—C9A—C9B	0.65 (14)	C12—C11—C16—C15	2.46 (16)
N2—N1—C9B—C3A	-0.64 (11)	N1—C11—C16—C15	-178.43 (9)
C11—N1—C9B—C3A	-176.34 (10)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7 \cdots N3 ⁱ	0.95	2.55	3.2770 (15)	133
C13—H13 \cdots O5 ⁱⁱ	0.95	2.54	3.4083 (16)	151
C15—H15 \cdots O5 ⁱⁱⁱ	0.95	2.48	3.2482 (16)	138

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x+1/2, y-1/2, -z+3/2$; (iii) $-x+3/2, y-1/2, -z+3/2$.

1-(3-Chlorophenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one (III)*Crystal data*C₁₅H₈ClN₃O₂ $M_r = 297.69$ Monoclinic, $P2_1/c$ $a = 11.0993$ (8) Å $b = 12.8996$ (9) Å $c = 9.2234$ (6) Å $\beta = 106.675$ (2)° $V = 1265.04$ (15) Å³ $Z = 4$ $F(000) = 608$ $D_x = 1.563$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2905 reflections

 $\theta = 2.5$ – 27.5° $\mu = 0.31$ mm⁻¹ $T = 100$ K

Plate, yellow

 $0.20 \times 0.12 \times 0.05$ mm*Data collection*Bruker D8 Venture
diffractometerRadiation source: INCOATEC high brilliance
microfocus sealed tube

Multilayer mirror monochromator

 φ and ω scansAbsorption correction: multi-scan
(SADABS; Bruker, 2016) $T_{\min} = 0.895$, $T_{\max} = 0.985$

28194 measured reflections

2905 independent reflections

2495 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.044$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.5^\circ$ $h = -14 \rightarrow 14$ $k = -16 \rightarrow 16$ $l = -11 \rightarrow 11$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.089$ $S = 1.08$

2905 reflections

190 parameters

0 restraints

Primary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.8531P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.32$ e Å⁻³ $\Delta\rho_{\min} = -0.36$ e Å⁻³*Special details*

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.31229 (11)	0.37182 (9)	0.35005 (13)	0.0154 (2)
N2	0.33212 (12)	0.37226 (9)	0.21107 (13)	0.0178 (3)
N3	0.45443 (12)	0.37148 (9)	0.23045 (13)	0.0178 (3)
C3A	0.50995 (13)	0.37008 (10)	0.38001 (15)	0.0150 (3)
O4	0.63690 (9)	0.36761 (8)	0.43901 (11)	0.0173 (2)
C5	0.68473 (13)	0.35314 (11)	0.59491 (16)	0.0169 (3)
O5	0.79506 (10)	0.33562 (9)	0.64252 (12)	0.0235 (2)
C5A	0.59649 (13)	0.36403 (10)	0.68762 (15)	0.0152 (3)

C6	0.64946 (14)	0.36544 (11)	0.84469 (16)	0.0172 (3)
H6	0.7377	0.3578	0.8868	0.021*
C7	0.57345 (14)	0.37794 (11)	0.93857 (16)	0.0184 (3)
H7	0.6092	0.3784	1.0453	0.022*
C8	0.44389 (14)	0.38985 (11)	0.87597 (16)	0.0178 (3)
H8	0.3922	0.3991	0.9411	0.021*
C9	0.38931 (13)	0.38851 (11)	0.72091 (16)	0.0168 (3)
H9	0.3010	0.3971	0.6802	0.020*
C9A	0.46493 (13)	0.37448 (10)	0.62463 (15)	0.0145 (3)
C9B	0.42430 (13)	0.37109 (10)	0.46111 (15)	0.0146 (3)
C11	0.18482 (13)	0.37130 (11)	0.35641 (15)	0.0165 (3)
C12	0.10125 (13)	0.43927 (11)	0.26168 (16)	0.0183 (3)
H12	0.1280	0.4848	0.1961	0.022*
C13	-0.02249 (14)	0.43847 (12)	0.26588 (17)	0.0217 (3)
Cl13	-0.12819 (4)	0.52194 (3)	0.14523 (5)	0.03006 (12)
C14	-0.06264 (15)	0.37398 (14)	0.36282 (18)	0.0266 (3)
H14	-0.1474	0.3758	0.3659	0.032*
C15	0.02333 (15)	0.30666 (14)	0.45542 (19)	0.0278 (4)
H15	-0.0031	0.2623	0.5226	0.033*
C16	0.14708 (14)	0.30312 (12)	0.45149 (17)	0.0217 (3)
H16	0.2048	0.2552	0.5124	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0152 (6)	0.0181 (6)	0.0128 (5)	0.0003 (4)	0.0039 (4)	0.0002 (4)
N2	0.0201 (6)	0.0196 (6)	0.0146 (6)	0.0005 (5)	0.0062 (5)	-0.0001 (4)
N3	0.0191 (6)	0.0184 (6)	0.0163 (6)	0.0005 (5)	0.0055 (5)	-0.0004 (4)
C3A	0.0161 (7)	0.0142 (6)	0.0151 (6)	0.0002 (5)	0.0052 (5)	0.0001 (5)
O4	0.0145 (5)	0.0217 (5)	0.0165 (5)	-0.0004 (4)	0.0057 (4)	0.0001 (4)
C5	0.0172 (7)	0.0161 (6)	0.0173 (7)	-0.0017 (5)	0.0047 (5)	-0.0009 (5)
O5	0.0152 (5)	0.0317 (6)	0.0236 (5)	0.0013 (4)	0.0058 (4)	0.0006 (4)
C5A	0.0163 (7)	0.0134 (6)	0.0161 (7)	-0.0009 (5)	0.0049 (5)	0.0002 (5)
C6	0.0155 (7)	0.0161 (6)	0.0183 (7)	-0.0011 (5)	0.0020 (5)	0.0004 (5)
C7	0.0221 (7)	0.0182 (7)	0.0138 (6)	-0.0010 (5)	0.0036 (5)	0.0005 (5)
C8	0.0218 (7)	0.0171 (7)	0.0159 (6)	0.0001 (5)	0.0078 (5)	0.0001 (5)
C9	0.0153 (7)	0.0177 (7)	0.0179 (7)	0.0005 (5)	0.0056 (5)	0.0002 (5)
C9A	0.0168 (7)	0.0133 (6)	0.0134 (6)	-0.0006 (5)	0.0044 (5)	-0.0003 (5)
C9B	0.0152 (6)	0.0136 (6)	0.0150 (6)	0.0008 (5)	0.0042 (5)	-0.0002 (5)
C11	0.0141 (7)	0.0197 (7)	0.0150 (6)	-0.0016 (5)	0.0032 (5)	-0.0029 (5)
C12	0.0181 (7)	0.0203 (7)	0.0162 (6)	-0.0007 (5)	0.0046 (5)	-0.0015 (5)
C13	0.0174 (7)	0.0274 (8)	0.0182 (7)	0.0024 (6)	0.0018 (5)	-0.0002 (6)
Cl13	0.0192 (2)	0.0406 (2)	0.0283 (2)	0.00990 (16)	0.00339 (15)	0.00611 (16)
C14	0.0167 (7)	0.0377 (9)	0.0255 (8)	-0.0022 (6)	0.0065 (6)	0.0008 (7)
C15	0.0230 (8)	0.0359 (9)	0.0250 (8)	-0.0059 (7)	0.0077 (6)	0.0058 (7)
C16	0.0201 (7)	0.0238 (7)	0.0196 (7)	-0.0024 (6)	0.0033 (6)	0.0031 (6)

Geometric parameters (Å, °)

N1—N2	1.3614 (16)	C8—C9	1.3841 (19)
N1—C9B	1.3654 (18)	C8—H8	0.9500
N1—C11	1.4328 (18)	C9—C9A	1.3977 (19)
N2—N3	1.3175 (17)	C9—H9	0.9500
N3—C3A	1.3399 (18)	C9A—C9B	1.4455 (18)
C3A—O4	1.3574 (17)	C11—C12	1.388 (2)
C3A—C9B	1.3680 (19)	C11—C16	1.389 (2)
O4—C5	1.3950 (17)	C12—C13	1.385 (2)
C5—O5	1.1979 (18)	C12—H12	0.9500
C5—C5A	1.4801 (19)	C13—C14	1.385 (2)
C5A—C6	1.3986 (19)	C13—C113	1.7392 (15)
C5A—C9A	1.4146 (19)	C14—C15	1.388 (2)
C6—C7	1.381 (2)	C14—H14	0.9500
C6—H6	0.9500	C15—C16	1.385 (2)
C7—C8	1.396 (2)	C15—H15	0.9500
C7—H7	0.9500	C16—H16	0.9500
N2—N1—C9B	110.37 (11)	C9A—C9—H9	120.2
N2—N1—C11	117.83 (11)	C9—C9A—C5A	119.26 (13)
C9B—N1—C11	131.80 (12)	C9—C9A—C9B	127.04 (13)
N3—N2—N1	108.11 (11)	C5A—C9A—C9B	113.69 (12)
N2—N3—C3A	106.94 (12)	N1—C9B—C3A	102.46 (12)
N3—C3A—O4	122.07 (12)	N1—C9B—C9A	136.62 (13)
N3—C3A—C9B	112.11 (13)	C3A—C9B—C9A	120.87 (13)
O4—C3A—C9B	125.82 (12)	C12—C11—C16	121.95 (14)
C3A—O4—C5	117.43 (11)	C12—C11—N1	117.43 (12)
O5—C5—O4	116.73 (12)	C16—C11—N1	120.60 (13)
O5—C5—C5A	125.62 (13)	C13—C12—C11	117.81 (14)
O4—C5—C5A	117.62 (12)	C13—C12—H12	121.1
C6—C5A—C9A	120.11 (13)	C11—C12—H12	121.1
C6—C5A—C5	116.65 (12)	C12—C13—C14	121.86 (14)
C9A—C5A—C5	123.23 (12)	C12—C13—C113	118.02 (12)
C7—C6—C5A	120.01 (13)	C14—C13—C113	120.12 (12)
C7—C6—H6	120.0	C13—C14—C15	118.77 (15)
C5A—C6—H6	120.0	C13—C14—H14	120.6
C6—C7—C8	119.72 (13)	C15—C14—H14	120.6
C6—C7—H7	120.1	C16—C15—C14	121.09 (15)
C8—C7—H7	120.1	C16—C15—H15	119.5
C9—C8—C7	121.31 (13)	C14—C15—H15	119.5
C9—C8—H8	119.3	C15—C16—C11	118.47 (14)
C7—C8—H8	119.3	C15—C16—H16	120.8
C8—C9—C9A	119.57 (13)	C11—C16—H16	120.8
C8—C9—H9	120.2		
C9B—N1—N2—N3	0.20 (15)	C11—N1—C9B—C3A	178.81 (14)
C11—N1—N2—N3	-179.28 (11)	N2—N1—C9B—C9A	176.95 (15)

N1—N2—N3—C3A	0.28 (14)	C11—N1—C9B—C9A	-3.7 (3)
N2—N3—C3A—O4	179.12 (12)	N3—C3A—C9B—N1	0.77 (15)
N2—N3—C3A—C9B	-0.68 (16)	O4—C3A—C9B—N1	-179.02 (13)
N3—C3A—O4—C5	-172.11 (12)	N3—C3A—C9B—C9A	-177.25 (12)
C9B—C3A—O4—C5	7.7 (2)	O4—C3A—C9B—C9A	3.0 (2)
C3A—O4—C5—O5	169.17 (13)	C9—C9A—C9B—N1	-5.6 (3)
C3A—O4—C5—C5A	-12.78 (17)	C5A—C9A—C9B—N1	175.67 (15)
O5—C5—C5A—C6	7.6 (2)	C9—C9A—C9B—C3A	171.59 (14)
O4—C5—C5A—C6	-170.28 (12)	C5A—C9A—C9B—C3A	-7.14 (19)
O5—C5—C5A—C9A	-173.50 (14)	N2—N1—C11—C12	-45.43 (17)
O4—C5—C5A—C9A	8.6 (2)	C9B—N1—C11—C12	135.22 (15)
C9A—C5A—C6—C7	-0.6 (2)	N2—N1—C11—C16	132.99 (14)
C5—C5A—C6—C7	178.40 (13)	C9B—N1—C11—C16	-46.4 (2)
C5A—C6—C7—C8	-0.4 (2)	C16—C11—C12—C13	0.9 (2)
C6—C7—C8—C9	0.6 (2)	N1—C11—C12—C13	179.30 (13)
C7—C8—C9—C9A	0.3 (2)	C11—C12—C13—C14	1.3 (2)
C8—C9—C9A—C5A	-1.3 (2)	C11—C12—C13—C13	-178.97 (11)
C8—C9—C9A—C9B	-179.96 (13)	C12—C13—C14—C15	-1.6 (2)
C6—C5A—C9A—C9	1.4 (2)	C13—C13—C14—C15	178.64 (13)
C5—C5A—C9A—C9	-177.46 (13)	C13—C14—C15—C16	-0.2 (3)
C6—C5A—C9A—C9B	-179.74 (12)	C14—C15—C16—C11	2.3 (2)
C5—C5A—C9A—C9B	1.38 (19)	C12—C11—C16—C15	-2.6 (2)
N2—N1—C9B—C3A	-0.58 (15)	N1—C11—C16—C15	179.00 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8—H8...N3 ⁱ	0.95	2.58	3.2465 (19)	127
C16—H16...N2 ⁱⁱ	0.95	2.56	3.500 (2)	169

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*, -*y*+1/2, *z*+1/2.1-(4-Chlorophenyl)isochromeno[3,4-*d*][1,2,3]triazol-5(1*H*)-one (IV)

Crystal data

C₁₅H₈ClN₃O₂*M_r* = 297.69Monoclinic, *P*2₁/*c**a* = 16.7331 (12) Å*b* = 5.9676 (4) Å*c* = 13.681 (1) Å

β = 112.820 (3)°

V = 1259.21 (16) Å³*Z* = 4*F*(000) = 608*D_x* = 1.570 Mg m⁻³Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 2892 reflections

θ = 2.6–27.5°

μ = 0.31 mm⁻¹*T* = 100 K

Block, pink

0.25 × 0.14 × 0.11 mm

Data collection

Bruker D8 Venture
diffractometerRadiation source: INCOATEC high brilliance
microfocus sealed tube

Multilayer mirror monochromator

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)*T_{min}* = 0.880, *T_{max}* = 0.967

34775 measured reflections

2891 independent reflections
 2413 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.6^\circ$

$h = -21 \rightarrow 21$
 $k = -7 \rightarrow 7$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.087$
 $S = 1.12$
 2891 reflections
 190 parameters
 0 restraints

Primary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 1.2186P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.28243 (8)	0.9201 (2)	0.34381 (11)	0.0144 (3)
N2	0.31078 (9)	1.1119 (2)	0.40077 (11)	0.0171 (3)
N3	0.27667 (9)	1.1220 (2)	0.47311 (11)	0.0167 (3)
C3A	0.22867 (10)	0.9365 (3)	0.46143 (12)	0.0148 (3)
O4	0.18490 (7)	0.89279 (19)	0.52497 (9)	0.0165 (2)
C5	0.13882 (10)	0.6934 (3)	0.50868 (13)	0.0164 (3)
O5	0.10574 (8)	0.6503 (2)	0.57022 (10)	0.0229 (3)
C5A	0.13207 (10)	0.5537 (3)	0.41602 (12)	0.0144 (3)
C6	0.07782 (10)	0.3663 (3)	0.39504 (13)	0.0167 (3)
H6	0.0483	0.3316	0.4401	0.020*
C7	0.06720 (11)	0.2317 (3)	0.30858 (13)	0.0179 (3)
H7	0.0309	0.1033	0.2948	0.021*
C8	0.10969 (10)	0.2841 (3)	0.24148 (13)	0.0165 (3)
H8	0.1013	0.1921	0.1816	0.020*
C9	0.16389 (10)	0.4687 (3)	0.26127 (13)	0.0149 (3)
H9	0.1926	0.5028	0.2152	0.018*
C9A	0.17630 (10)	0.6048 (3)	0.34916 (12)	0.0136 (3)
C9B	0.22950 (10)	0.8037 (3)	0.38052 (12)	0.0138 (3)
C11	0.32143 (10)	0.8577 (3)	0.27144 (13)	0.0140 (3)
C12	0.36182 (10)	0.6505 (3)	0.28242 (13)	0.0162 (3)
H12	0.3594	0.5457	0.3335	0.019*
C13	0.40594 (10)	0.5987 (3)	0.21758 (13)	0.0162 (3)
H13	0.4329	0.4566	0.2227	0.019*
C14	0.41012 (10)	0.7567 (3)	0.14533 (13)	0.0158 (3)
Cl14	0.47074 (3)	0.69834 (7)	0.07027 (3)	0.02089 (12)

C15	0.36852 (11)	0.9621 (3)	0.13295 (13)	0.0170 (3)
H15	0.3709	1.0667	0.0818	0.020*
C16	0.32319 (10)	1.0128 (3)	0.19655 (13)	0.0160 (3)
H16	0.2938	1.1520	0.1889	0.019*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0145 (6)	0.0119 (6)	0.0174 (7)	-0.0002 (5)	0.0067 (5)	-0.0001 (5)
N2	0.0175 (7)	0.0139 (7)	0.0189 (7)	-0.0001 (5)	0.0059 (6)	-0.0025 (5)
N3	0.0168 (7)	0.0155 (7)	0.0167 (7)	0.0012 (5)	0.0054 (5)	-0.0016 (5)
C3A	0.0142 (7)	0.0152 (7)	0.0147 (7)	0.0019 (6)	0.0051 (6)	0.0007 (6)
O4	0.0200 (6)	0.0170 (6)	0.0151 (5)	-0.0010 (5)	0.0097 (5)	-0.0023 (4)
C5	0.0146 (8)	0.0176 (8)	0.0169 (8)	0.0023 (6)	0.0059 (6)	0.0010 (6)
O5	0.0248 (7)	0.0287 (7)	0.0201 (6)	-0.0039 (5)	0.0141 (5)	-0.0030 (5)
C5A	0.0134 (7)	0.0155 (8)	0.0139 (7)	0.0023 (6)	0.0049 (6)	0.0015 (6)
C6	0.0149 (8)	0.0170 (8)	0.0182 (8)	0.0006 (6)	0.0065 (6)	0.0028 (6)
C7	0.0157 (8)	0.0150 (8)	0.0203 (8)	-0.0011 (6)	0.0040 (7)	0.0018 (6)
C8	0.0162 (8)	0.0142 (7)	0.0159 (8)	0.0017 (6)	0.0029 (6)	-0.0021 (6)
C9	0.0153 (8)	0.0141 (7)	0.0150 (7)	0.0012 (6)	0.0057 (6)	0.0008 (6)
C9A	0.0128 (7)	0.0125 (7)	0.0142 (7)	0.0023 (6)	0.0039 (6)	0.0020 (6)
C9B	0.0135 (7)	0.0139 (7)	0.0146 (7)	0.0013 (6)	0.0060 (6)	0.0004 (6)
C11	0.0108 (7)	0.0153 (7)	0.0163 (7)	-0.0024 (6)	0.0056 (6)	-0.0015 (6)
C12	0.0151 (8)	0.0160 (8)	0.0165 (8)	-0.0008 (6)	0.0050 (6)	0.0016 (6)
C13	0.0142 (7)	0.0139 (7)	0.0191 (8)	0.0021 (6)	0.0051 (6)	-0.0004 (6)
C14	0.0126 (7)	0.0199 (8)	0.0150 (8)	-0.0027 (6)	0.0053 (6)	-0.0031 (6)
C114	0.0205 (2)	0.0249 (2)	0.0211 (2)	-0.00127 (16)	0.01233 (16)	-0.00372 (16)
C15	0.0183 (8)	0.0170 (8)	0.0153 (8)	-0.0017 (6)	0.0062 (6)	0.0019 (6)
C16	0.0155 (8)	0.0132 (7)	0.0185 (8)	0.0016 (6)	0.0056 (6)	0.0018 (6)

Geometric parameters (Å, °)

N1—N2	1.3625 (19)	C8—C9	1.386 (2)
N1—C9B	1.365 (2)	C8—H8	0.9500
N1—C11	1.430 (2)	C9—C9A	1.398 (2)
N2—N3	1.3217 (19)	C9—H9	0.9500
N3—C3A	1.341 (2)	C9A—C9B	1.445 (2)
C3A—O4	1.3615 (19)	C11—C12	1.389 (2)
C3A—C9B	1.366 (2)	C11—C16	1.390 (2)
O4—C5	1.388 (2)	C12—C13	1.391 (2)
C5—O5	1.201 (2)	C12—H12	0.9500
C5—C5A	1.485 (2)	C13—C14	1.387 (2)
C5A—C6	1.398 (2)	C13—H13	0.9500
C5A—C9A	1.415 (2)	C14—C15	1.387 (2)
C6—C7	1.383 (2)	C14—C114	1.7358 (16)
C6—H6	0.9500	C15—C16	1.391 (2)
C7—C8	1.397 (2)	C15—H15	0.9500
C7—H7	0.9500	C16—H16	0.9500

N2—N1—C9B	110.42 (13)	C9A—C9—H9	120.1
N2—N1—C11	117.62 (13)	C9—C9A—C5A	119.34 (14)
C9B—N1—C11	131.09 (13)	C9—C9A—C9B	126.95 (14)
N3—N2—N1	108.11 (13)	C5A—C9A—C9B	113.69 (14)
N2—N3—C3A	106.61 (13)	N1—C9B—C3A	102.40 (14)
N3—C3A—O4	121.86 (14)	N1—C9B—C9A	136.18 (14)
N3—C3A—C9B	112.45 (14)	C3A—C9B—C9A	121.21 (14)
O4—C3A—C9B	125.69 (15)	C12—C11—C16	121.61 (15)
C3A—O4—C5	117.68 (12)	C12—C11—N1	119.38 (14)
O5—C5—O4	116.70 (15)	C16—C11—N1	118.85 (14)
O5—C5—C5A	125.10 (15)	C11—C12—C13	119.03 (15)
O4—C5—C5A	118.18 (13)	C11—C12—H12	120.5
C6—C5A—C9A	120.04 (15)	C13—C12—H12	120.5
C6—C5A—C5	116.93 (14)	C14—C13—C12	119.27 (15)
C9A—C5A—C5	123.02 (14)	C14—C13—H13	120.4
C7—C6—C5A	119.86 (15)	C12—C13—H13	120.4
C7—C6—H6	120.1	C15—C14—C13	121.75 (15)
C5A—C6—H6	120.1	C15—C14—C14	119.07 (13)
C6—C7—C8	120.19 (15)	C13—C14—C14	119.17 (13)
C6—C7—H7	119.9	C14—C15—C16	119.03 (15)
C8—C7—H7	119.9	C14—C15—H15	120.5
C9—C8—C7	120.71 (15)	C16—C15—H15	120.5
C9—C8—H8	119.6	C11—C16—C15	119.26 (15)
C7—C8—H8	119.6	C11—C16—H16	120.4
C8—C9—C9A	119.85 (15)	C15—C16—H16	120.4
C8—C9—H9	120.1		
C9B—N1—N2—N3	-0.38 (17)	C11—N1—C9B—C3A	168.64 (15)
C11—N1—N2—N3	-170.86 (13)	N2—N1—C9B—C9A	174.36 (17)
N1—N2—N3—C3A	0.74 (17)	C11—N1—C9B—C9A	-16.8 (3)
N2—N3—C3A—O4	179.27 (13)	N3—C3A—C9B—N1	0.63 (18)
N2—N3—C3A—C9B	-0.88 (18)	O4—C3A—C9B—N1	-179.53 (14)
N3—C3A—O4—C5	-178.29 (14)	N3—C3A—C9B—C9A	-174.93 (14)
C9B—C3A—O4—C5	1.9 (2)	O4—C3A—C9B—C9A	4.9 (2)
C3A—O4—C5—O5	174.88 (14)	C9—C9A—C9B—N1	-1.2 (3)
C3A—O4—C5—C5A	-6.7 (2)	C5A—C9A—C9B—N1	-179.60 (17)
O5—C5—C5A—C6	4.8 (2)	C9—C9A—C9B—C3A	172.55 (16)
O4—C5—C5A—C6	-173.41 (14)	C5A—C9A—C9B—C3A	-5.9 (2)
O5—C5—C5A—C9A	-176.28 (16)	N2—N1—C11—C12	122.23 (16)
O4—C5—C5A—C9A	5.5 (2)	C9B—N1—C11—C12	-45.9 (2)
C9A—C5A—C6—C7	-0.3 (2)	N2—N1—C11—C16	-53.3 (2)
C5—C5A—C6—C7	178.64 (15)	C9B—N1—C11—C16	138.61 (17)
C5A—C6—C7—C8	-0.8 (2)	C16—C11—C12—C13	0.8 (2)
C6—C7—C8—C9	1.0 (2)	N1—C11—C12—C13	-174.59 (14)
C7—C8—C9—C9A	-0.1 (2)	C11—C12—C13—C14	1.4 (2)
C8—C9—C9A—C5A	-1.0 (2)	C12—C13—C14—C15	-2.6 (2)
C8—C9—C9A—C9B	-179.30 (15)	C12—C13—C14—C14	176.09 (12)

C6—C5A—C9A—C9	1.1 (2)	C13—C14—C15—C16	1.6 (2)
C5—C5A—C9A—C9	-177.70 (14)	C14—C14—C15—C16	-177.12 (12)
C6—C5A—C9A—C9B	179.70 (14)	C12—C11—C16—C15	-1.8 (2)
C5—C5A—C9A—C9B	0.9 (2)	N1—C11—C16—C15	173.59 (14)
N2—N1—C9B—C3A	-0.14 (17)	C14—C15—C16—C11	0.6 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C6—H6...O5 ⁱ	0.95	2.53	3.287 (2)	137
C8—H8...O5 ⁱⁱ	0.95	2.57	3.478 (2)	161
C15—H15...N3 ⁱⁱⁱ	0.95	2.52	3.271 (2)	136
C7—H7...Cg1 ^{iv}	0.95	2.69	3.517 (2)	146

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, -y+1/2, z-1/2$; (iii) $x, -y+5/2, z-1/2$; (iv) $-x, y-1/2, -z+1/2$.

Methyl 2-[4-hydroxy-1-(2-methylphenyl)-1*H*-1,2,3-triazol-5-yl]benzoate (V)

Crystal data

$C_{17}H_{15}N_3O_3$

$M_r = 309.32$

Monoclinic, $P2_1/c$

$a = 11.1518$ (5) Å

$b = 9.3143$ (4) Å

$c = 14.2417$ (6) Å

$\beta = 98.655$ (2)°

$V = 1462.46$ (11) Å³

$Z = 4$

$F(000) = 648$

$D_x = 1.405$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3361 reflections

$\theta = 2.6$ – 27.5 °

$\mu = 0.10$ mm⁻¹

$T = 100$ K

Block, colourless

$0.19 \times 0.11 \times 0.07$ mm

Data collection

Bruker D8 Venture
diffractometer

Radiation source: INCOATEC high brilliance
microfocus sealed tube

Multilayer mirror monochromator
 φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)

$T_{\min} = 0.960$, $T_{\max} = 0.993$

33834 measured reflections

3360 independent reflections

3084 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.6$ °

$h = -14 \rightarrow 14$

$k = -12 \rightarrow 12$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.098$

$S = 1.07$

3360 reflections

213 parameters

0 restraints

Primary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 1.1492P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.34$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.09089 (12)	0.58783 (14)	0.64445 (9)	0.0143 (3)
C2	0.20897 (12)	0.64468 (14)	0.66637 (9)	0.0140 (3)
C3	0.22319 (12)	0.79047 (15)	0.68731 (9)	0.0171 (3)
H3	0.3024	0.8295	0.7027	0.021*
C4	0.12250 (13)	0.87957 (15)	0.68594 (10)	0.0194 (3)
H4	0.1333	0.9789	0.6998	0.023*
C5	0.00649 (13)	0.82309 (16)	0.66441 (10)	0.0194 (3)
H5	-0.0622	0.8837	0.6633	0.023*
C6	-0.00894 (12)	0.67859 (15)	0.64454 (9)	0.0176 (3)
H6	-0.0886	0.6403	0.6307	0.021*
C7	0.07137 (12)	0.43259 (15)	0.61927 (9)	0.0158 (3)
O1	0.15037 (9)	0.34535 (11)	0.61744 (8)	0.0255 (2)
O2	-0.04681 (9)	0.40148 (11)	0.59904 (7)	0.0205 (2)
C8	-0.07555 (14)	0.25126 (16)	0.58262 (11)	0.0227 (3)
H8A	-0.0554	0.1980	0.6423	0.034*
H8B	-0.0284	0.2131	0.5355	0.034*
H8C	-0.1623	0.2410	0.5590	0.034*
N21	0.38126 (10)	0.47254 (12)	0.72720 (8)	0.0142 (2)
N22	0.47490 (10)	0.40735 (12)	0.69580 (8)	0.0160 (2)
N23	0.47309 (10)	0.45003 (12)	0.60673 (8)	0.0157 (2)
C24	0.38003 (11)	0.54203 (14)	0.58314 (9)	0.0152 (3)
C25	0.31891 (11)	0.55871 (14)	0.65953 (9)	0.0140 (3)
C211	0.35990 (11)	0.44834 (15)	0.82315 (9)	0.0155 (3)
C212	0.33495 (12)	0.30970 (15)	0.85228 (9)	0.0171 (3)
C213	0.31541 (12)	0.29355 (16)	0.94627 (10)	0.0210 (3)
H213	0.2981	0.2009	0.9688	0.025*
C214	0.32075 (13)	0.40992 (18)	1.00731 (10)	0.0241 (3)
H214	0.3062	0.3962	1.0707	0.029*
C215	0.34696 (14)	0.54549 (17)	0.97710 (10)	0.0235 (3)
H215	0.3513	0.6246	1.0196	0.028*
C216	0.36705 (12)	0.56555 (15)	0.88384 (10)	0.0191 (3)
H216	0.3854	0.6582	0.8621	0.023*
C217	0.32682 (14)	0.18273 (15)	0.78655 (10)	0.0226 (3)
H27A	0.3030	0.0975	0.8196	0.034*
H27B	0.4060	0.1661	0.7665	0.034*
H27C	0.2662	0.2018	0.7306	0.034*
O24	0.35119 (9)	0.60183 (12)	0.49726 (7)	0.0208 (2)
H24	0.4112 (18)	0.587 (2)	0.4622 (14)	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0154 (6)	0.0175 (6)	0.0104 (6)	0.0008 (5)	0.0028 (4)	0.0018 (5)
C2	0.0145 (6)	0.0172 (6)	0.0109 (5)	0.0013 (5)	0.0035 (4)	0.0013 (5)
C3	0.0158 (6)	0.0192 (7)	0.0161 (6)	-0.0011 (5)	0.0016 (5)	-0.0004 (5)
C4	0.0225 (7)	0.0169 (6)	0.0188 (6)	0.0017 (5)	0.0036 (5)	-0.0024 (5)
C5	0.0178 (6)	0.0228 (7)	0.0179 (6)	0.0056 (5)	0.0034 (5)	0.0006 (5)
C6	0.0139 (6)	0.0229 (7)	0.0160 (6)	0.0010 (5)	0.0022 (5)	0.0012 (5)
C7	0.0162 (6)	0.0190 (6)	0.0119 (6)	-0.0011 (5)	0.0009 (5)	0.0021 (5)
O1	0.0179 (5)	0.0191 (5)	0.0386 (6)	0.0015 (4)	0.0014 (4)	-0.0051 (4)
O2	0.0152 (5)	0.0189 (5)	0.0268 (5)	-0.0028 (4)	0.0010 (4)	0.0002 (4)
C8	0.0231 (7)	0.0196 (7)	0.0248 (7)	-0.0066 (5)	0.0013 (6)	-0.0001 (6)
N21	0.0122 (5)	0.0158 (5)	0.0148 (5)	0.0015 (4)	0.0031 (4)	0.0013 (4)
N22	0.0139 (5)	0.0187 (5)	0.0164 (5)	0.0022 (4)	0.0049 (4)	0.0011 (4)
N23	0.0148 (5)	0.0186 (6)	0.0141 (5)	0.0011 (4)	0.0036 (4)	0.0010 (4)
C24	0.0134 (6)	0.0169 (6)	0.0155 (6)	0.0004 (5)	0.0027 (5)	0.0002 (5)
C25	0.0125 (6)	0.0149 (6)	0.0142 (6)	-0.0007 (5)	0.0011 (4)	0.0003 (5)
C211	0.0113 (6)	0.0216 (7)	0.0137 (6)	0.0027 (5)	0.0022 (4)	0.0029 (5)
C212	0.0121 (6)	0.0207 (7)	0.0179 (6)	0.0018 (5)	0.0004 (5)	0.0033 (5)
C213	0.0166 (6)	0.0250 (7)	0.0210 (7)	0.0014 (5)	0.0012 (5)	0.0085 (6)
C214	0.0234 (7)	0.0343 (8)	0.0151 (6)	0.0065 (6)	0.0046 (5)	0.0059 (6)
C215	0.0257 (7)	0.0279 (8)	0.0165 (7)	0.0072 (6)	0.0019 (5)	-0.0016 (6)
C216	0.0191 (6)	0.0194 (7)	0.0184 (6)	0.0037 (5)	0.0015 (5)	0.0020 (5)
C217	0.0264 (7)	0.0180 (7)	0.0231 (7)	-0.0005 (6)	0.0023 (6)	0.0024 (6)
O24	0.0199 (5)	0.0299 (6)	0.0138 (5)	0.0093 (4)	0.0068 (4)	0.0063 (4)

Geometric parameters (\AA , $^\circ$)

C1—C6	1.3981 (18)	N21—C211	1.4396 (16)
C1—C2	1.4100 (18)	N22—N23	1.3265 (15)
C1—C7	1.4977 (19)	N23—C24	1.3489 (17)
C2—C3	1.3941 (19)	C24—O24	1.3383 (16)
C2—C25	1.4798 (17)	C24—C25	1.3768 (17)
C3—C4	1.3941 (19)	C211—C216	1.3873 (19)
C3—H3	0.9500	C211—C212	1.3971 (19)
C4—C5	1.387 (2)	C212—C213	1.3963 (19)
C4—H4	0.9500	C212—C217	1.503 (2)
C5—C6	1.381 (2)	C213—C214	1.385 (2)
C5—H5	0.9500	C213—H213	0.9500
C6—H6	0.9500	C214—C215	1.379 (2)
C7—O1	1.2017 (17)	C214—H214	0.9500
C7—O2	1.3378 (16)	C215—C216	1.3924 (19)
O2—C8	1.4466 (17)	C215—H215	0.9500
C8—H8A	0.9800	C216—H216	0.9500
C8—H8B	0.9800	C217—H27A	0.9800
C8—H8C	0.9800	C217—H27B	0.9800
N21—N22	1.3415 (15)	C217—H27C	0.9800

N21—C25	1.3619 (16)	O24—H24	0.90 (2)
C6—C1—C2	119.34 (12)	N22—N23—C24	109.21 (10)
C6—C1—C7	119.80 (12)	O24—C24—N23	124.20 (12)
C2—C1—C7	120.85 (12)	O24—C24—C25	126.57 (12)
C3—C2—C1	119.05 (12)	N23—C24—C25	109.19 (11)
C3—C2—C25	118.19 (12)	N21—C25—C24	103.41 (11)
C1—C2—C25	122.52 (12)	N21—C25—C2	127.75 (11)
C4—C3—C2	120.76 (13)	C24—C25—C2	128.80 (12)
C4—C3—H3	119.6	C216—C211—C212	122.52 (12)
C2—C3—H3	119.6	C216—C211—N21	117.77 (12)
C5—C4—C3	119.98 (13)	C212—C211—N21	119.70 (12)
C5—C4—H4	120.0	C213—C212—C211	116.82 (13)
C3—C4—H4	120.0	C213—C212—C217	120.60 (13)
C6—C5—C4	119.88 (13)	C211—C212—C217	122.58 (12)
C6—C5—H5	120.1	C214—C213—C212	121.27 (14)
C4—C5—H5	120.1	C214—C213—H213	119.4
C5—C6—C1	120.99 (13)	C212—C213—H213	119.4
C5—C6—H6	119.5	C215—C214—C213	120.78 (13)
C1—C6—H6	119.5	C215—C214—H214	119.6
O1—C7—O2	123.40 (13)	C213—C214—H214	119.6
O1—C7—C1	125.27 (12)	C214—C215—C216	119.50 (14)
O2—C7—C1	111.32 (11)	C214—C215—H215	120.3
C7—O2—C8	115.56 (11)	C216—C215—H215	120.3
O2—C8—H8A	109.5	C211—C216—C215	119.10 (13)
O2—C8—H8B	109.5	C211—C216—H216	120.5
H8A—C8—H8B	109.5	C215—C216—H216	120.5
O2—C8—H8C	109.5	C212—C217—H27A	109.5
H8A—C8—H8C	109.5	C212—C217—H27B	109.5
H8B—C8—H8C	109.5	H27A—C217—H27B	109.5
N22—N21—C25	111.77 (10)	C212—C217—H27C	109.5
N22—N21—C211	119.60 (10)	H27A—C217—H27C	109.5
C25—N21—C211	128.62 (11)	H27B—C217—H27C	109.5
N23—N22—N21	106.42 (10)	C24—O24—H24	110.1 (12)
C6—C1—C2—C3	-0.23 (18)	C211—N21—C25—C2	-3.2 (2)
C7—C1—C2—C3	178.54 (12)	O24—C24—C25—N21	177.72 (13)
C6—C1—C2—C25	-174.48 (12)	N23—C24—C25—N21	0.04 (14)
C7—C1—C2—C25	4.29 (18)	O24—C24—C25—C2	-0.1 (2)
C1—C2—C3—C4	-0.53 (19)	N23—C24—C25—C2	-177.80 (13)
C25—C2—C3—C4	173.97 (12)	C3—C2—C25—N21	98.58 (16)
C2—C3—C4—C5	0.6 (2)	C1—C2—C25—N21	-87.12 (17)
C3—C4—C5—C6	0.1 (2)	C3—C2—C25—C24	-84.07 (18)
C4—C5—C6—C1	-0.9 (2)	C1—C2—C25—C24	90.23 (18)
C2—C1—C6—C5	0.94 (19)	N22—N21—C211—C216	117.83 (14)
C7—C1—C6—C5	-177.84 (12)	C25—N21—C211—C216	-60.69 (18)
C6—C1—C7—O1	-179.60 (13)	N22—N21—C211—C212	-61.17 (16)
C2—C1—C7—O1	1.6 (2)	C25—N21—C211—C212	120.30 (15)

C6—C1—C7—O2	0.11 (17)	C216—C211—C212—C213	0.88 (19)
C2—C1—C7—O2	-178.66 (11)	N21—C211—C212—C213	179.84 (11)
O1—C7—O2—C8	5.37 (19)	C216—C211—C212—C217	179.82 (13)
C1—C7—O2—C8	-174.35 (11)	N21—C211—C212—C217	-1.23 (19)
C25—N21—N22—N23	-0.60 (14)	C211—C212—C213—C214	0.0 (2)
C211—N21—N22—N23	-179.36 (11)	C217—C212—C213—C214	-179.00 (13)
N21—N22—N23—C24	0.61 (14)	C212—C213—C214—C215	-0.7 (2)
N22—N23—C24—O24	-178.16 (12)	C213—C214—C215—C216	0.7 (2)
N22—N23—C24—C25	-0.41 (15)	C212—C211—C216—C215	-1.0 (2)
N22—N21—C25—C24	0.34 (14)	N21—C211—C216—C215	-179.93 (12)
C211—N21—C25—C24	178.96 (12)	C214—C215—C216—C211	0.2 (2)
N22—N21—C25—C2	178.22 (12)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O24—H24...N23 ⁱ	0.90 (2)	1.77 (2)	2.6721 (15)	177.5 (19)
C8—H8 <i>A</i> ...C <i>g</i> 2 ⁱⁱ	0.98	2.90	3.6605 (16)	135
C8—H8 <i>B</i> ...C <i>g</i> 2 ⁱⁱⁱ	0.98	2.90	3.5007 (16)	120
C8—H8 <i>C</i> ...O24 ⁱⁱⁱ	0.98	2.59	3.4004 (19)	140
C215—H215...O24 ^{iv}	0.95	2.57	3.2972 (19)	134

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, y-1/2, -z+3/2$; (iii) $-x, -y+1, -z+1$; (iv) $x, -y+3/2, z+1/2$.