

(*E*)-2,4-Diamino-5-{7-[(4-chlorophenyl)diazenyl]-3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl}-6-oxo-1,6-dihydropyridine-3-carbonitrile dimethylformamide monosolvate

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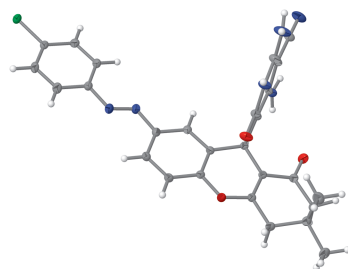
CCDC reference: 2497635

Structural data: full structural data are available from iucrdata.iucr.org

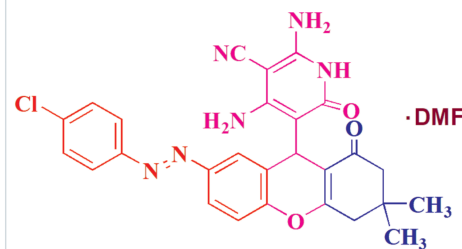
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In the title compound, $C_{27}H_{23}ClN_6O_3 \cdot C_3H_7NO$, much of the molecule is approximately planar, excluding the pyridinic ring, which is almost perpendicular to this plane, and the sp^3 atoms of the modified xanthen system. The diazene group is *E*-configured. In the extended structure, two hydrogen bonds of the type $N-H \cdots O$ and one $N-H \cdots Cl$ combine to form a layer structure parallel to (111). The solvent is severely disordered and this necessitated the use of SQUEEZE for a reliable refinement.

3D view



Chemical scheme



Structure description

In a variety of chemical processes, activated nitriles, which involve active methylene groups, are used for the synthesis of heterocyclic, pharmaceutically significant compounds (Wang *et al.*, 2016; Fleming & Wang, 2003; Zhang *et al.*, 2023; Abu-Zaied *et al.*, 2024*a,b*; Zhang *et al.*, 2019). Using such nitriles as starting materials, we have published a number of new approaches for the synthesis of heterocycles (Elgemeie *et al.*, 1998*a,b*, 2010). Using dimedone as the starting material, we and others have continued this work by synthesizing a number of condensed carbocyclic pyridines and carbocyclic pyrans (Hebishy *et al.*, 2022, 2023; Tu *et al.*, 2014). The current study describes a one-pot synthesis of a tetrahydroxanthen derivative by the reaction of dimedone with enamino nitriles and *o*-hydroxy aromatic aldehydes.

It was found (Fig. 1) that dimedone reacted with (4-chlorophenyl)diazanyl-2-hydroxybenzaldehyde (**1**) and 2-aminoprop-1-ene-1,1,3-tricarbonitrile (**2**) in refluxing acetonitrile containing catalytic amounts of trimethylamine to give the condensation

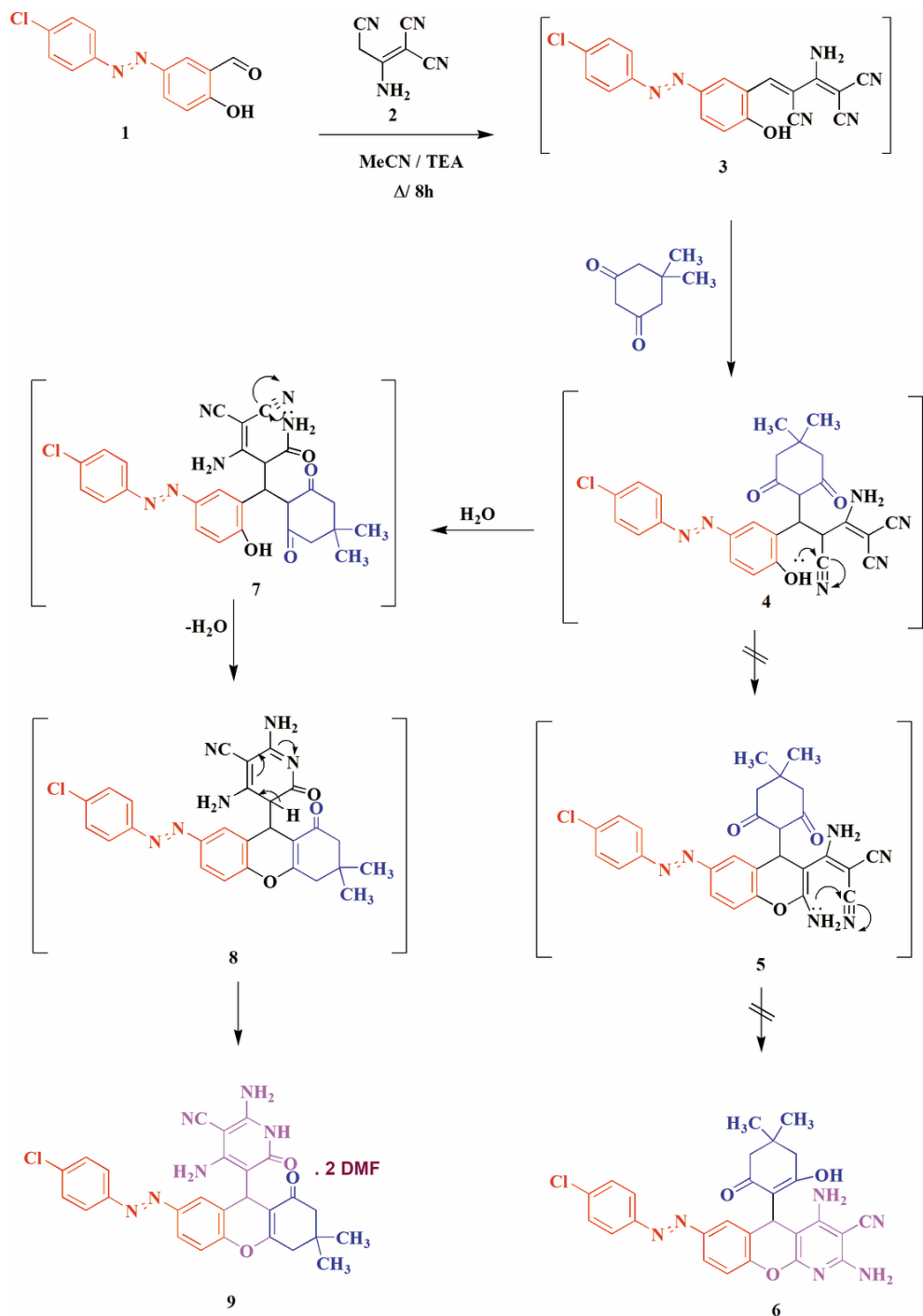


Figure 1
The reaction scheme and proposed mechanism for the formation of **9**.

product (*E*)-5-[7-[(4-chlorophenyl)diazenyl]-2,3,4,9-tetrahydro-3,3-dimethyl-1-oxo-1*H*-xanthen-9-yl]-2,4-diamino-1,6-dihydro-6-oxopyridine-3-carbonitrile (**9**). The structure of **9** was suggested by elemental analysis and spectroscopic studies (¹H NMR, IR and MS). As a mechanism we propose a condensation reaction that consists of an initial Michael addition of the methylene group of the dimedone to the double bond of intermediate **3** to give a further intermediate **4**, which then cyclizes to give the tetrahydroxanthene structure **8** rather than the alternative cyclization leading to the

chromeno[2,3-*b*]pyridine structure **6**. The same reaction has been carried out, under the same reaction conditions, by other researchers, who however stated that they obtained structure **6** as the sole product, but no X-ray single-crystal studies were performed (Vereshchagin *et al.*, 2017; Ryzhkova *et al.*, 2022). In order to establish the structure of the compound unambiguously, the crystal structure of **9** was determined and is presented here.

The structure of compound **9** (excluding solvent, see *Refinement details*) is shown in Figs. 2 and 3. Molecular

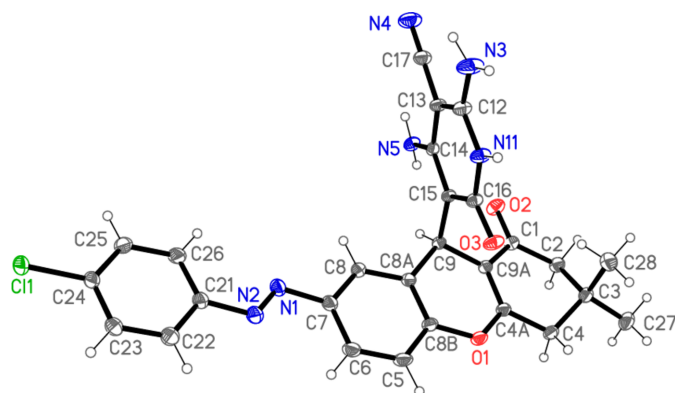


Figure 2
The molecule of compound **9** in the crystal (excluding the severely disordered solvent). Ellipsoids are drawn at the 50% probability level.

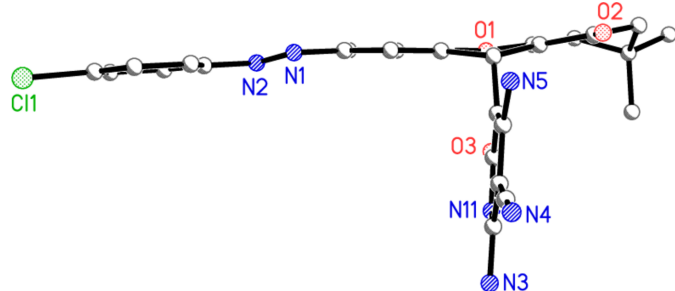


Figure 3
Side view of the molecule of **9** (excluding hydrogen atoms); radii are arbitrary.

dimensions, a brief selection of which are given in Table 1, may be regarded as normal. Despite the presence of sp^3 carbon atoms and the possibility of rotation about the C–N bonds to the *E*-configured diazene group, much of the molecule is

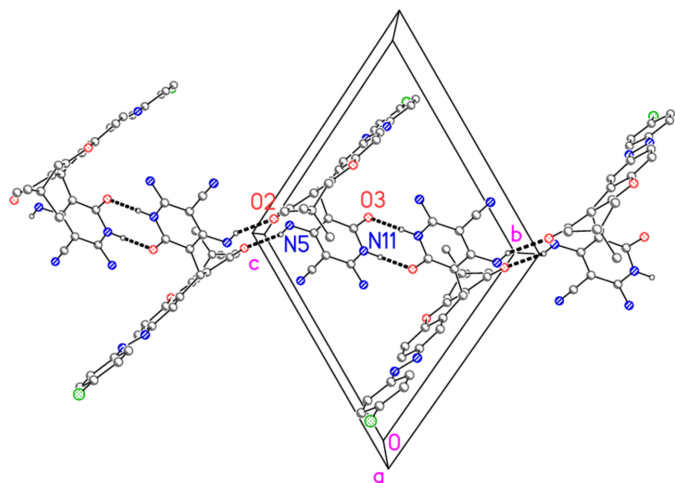


Figure 4
Packing of compound **9** viewed parallel to the *a* axis (thick dashed lines indicate hydrogen bonds; atoms of the asymmetric unit are numbered). Hydrogen atoms not involved in the hydrogen bonds N11–H011...O3' and N5–H052...O2' are omitted. Labels indicate atoms of the asymmetric unit.

Table 1
Selected geometric parameters (Å, °).

N1–N2	1.2572 (13)	N11–C16	1.3875 (12)
N1–C7	1.4217 (13)	C12–N3	1.3517 (14)
N2–C21	1.4224 (14)	C14–N5	1.3489 (12)
N11–C12	1.3483 (13)		
N2–N1–C7	112.74 (9)	C12–N11–C16	124.32 (8)
N1–N2–C21	114.76 (9)		
C7–N1–N2–C21	−179.90 (8)	C9A–C9–C15–C16	−64.70 (11)
C9A–C9–C15–C14	118.20 (10)	C8A–C9–C15–C16	57.63 (11)
C8A–C9–C15–C14	−119.47 (10)		

Table 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>
N11–H011...O3 ⁱ	0.898 (17)	1.758 (17)	2.6558 (11)	178.7 (18)
N5–H051...O2	0.83 (1)	2.62 (2)	3.1939 (12)	128 (1)
N5–H051...Cl1 ⁱⁱ	0.83 (1)	2.69 (1)	3.3709 (9)	141 (1)
N5–H052...O2 ⁱⁱⁱ	0.85 (1)	2.08 (1)	2.8266 (11)	147 (2)
C4–H4A...N1 ^{iv}	0.99	2.66	3.5236 (14)	146
C5–H05...Cl1 ^v	0.95	2.82	3.6093 (10)	141

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

approximately planar (Fig. 3); excluding the pyridinic ring and the atoms C3, C27 and C28, the r.m.s. deviation from the best plane is 0.10 Å. The pyridinic ring (including substituents) has an r.m.s. deviation of 0.03 Å and subtends an interplanar angle of 88.66 (2)° with the main plane. The intramolecular hydrogen bond H051...O2, not drawn explicitly in Fig. 2 for reasons of clarity, is part of a three-centre system (Table 2).

The molecular packing may be analysed in terms of hydrogen bonds (Table 3). The hydrogen bonds N11–H011...O3' and N5–H052...O2' combine to form a one-dimensional array propagating in the $[01\bar{1}]$ direction (Fig. 4), whereas N11–H011...O3' and N5–H051...Cl1' form a one-dimensional array parallel to $[10\bar{1}]$ (Fig. 5). The zone law then suggests that the layer structure formed by all three hydrogen bonds should be parallel to (111), which is indeed the case (Fig. 6). We note that the potential hydrogen bond donors at N3 do not appear to form hydrogen bonds; in

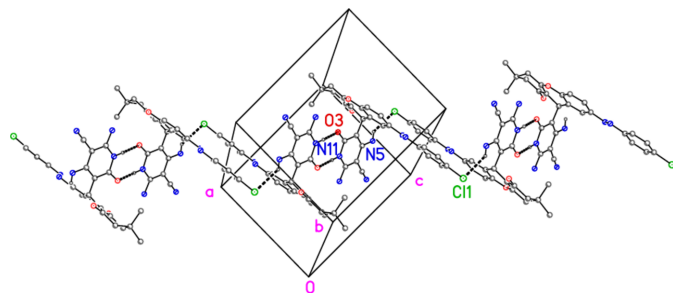


Figure 5
Packing of compound **9** viewed perpendicular to the *ac* plane (thick dashed lines indicate hydrogen bonds; atoms of the asymmetric unit are numbered). Hydrogen atoms not involved in the hydrogen bonds N11–H011...O3' and N5–H051...Cl1' are omitted. Labels indicate atoms of the asymmetric unit.

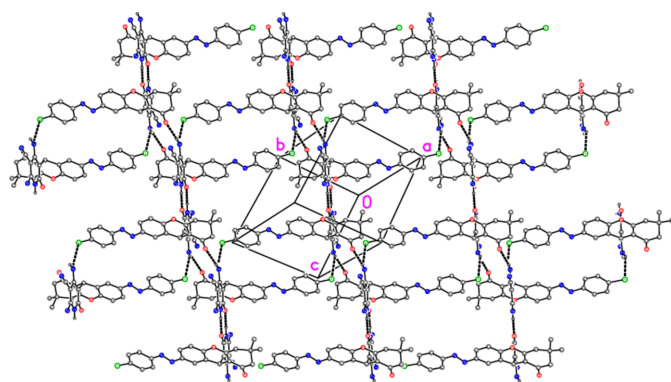


Figure 6
The layer structure of compound **9** viewed perpendicular to (111) (thick dashed lines indicate hydrogen bonds). Hydrogen atoms not involved in hydrogen bonds are omitted.

fact there are short contacts between these hydrogen atoms and the difference peaks arising from the severely disordered solvent.

A search of the Cambridge Database (Version 2025.1.1; Groom *et al.*, 2016) using the routine CONQUEST (Bruno *et al.*, 2002) found no other examples of a similarly modified xanthene derivative either with a nitrogen substituent at C7 or a nitrogen heterocycle at C9.

Synthesis and crystallization

A mixture of 4-(chlorophenyldiazenyl)-2-hydroxybenzaldehyde **1** (2.6 g, 0.01 mmol), 2-aminoprop-1-ene-1,1,3-tricarbonitrile **2** (1.32 g, 0.01 mmol), 5,5-dimethylcyclohexane-1,3-dione ('dimedone', 1.4 g, 0.01 mmol) and few drops of trimethylamine in acetonitrile (30 ml) was refluxed for 8 h. After cooling, the precipitate of compound **9** was collected by filtration and recrystallized from dimethylformamide (DMF) as large orange blocks. Yield 4.00 g (78%). For X-ray measurements, an irregular single crystalline fragment of suitable dimensions was cut from a larger block.

M.p.: above 573 K. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): $\delta\text{H} = 0.98$ (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 2.07 (d, 1H, $J = 16.4$ Hz, CH_2), 2.33 (d, 1H, $J = 16.14$ Hz, CH_2), 2.40–2.59 (m, 2H, CH_2), 4.94 (s, 1H, pyran-H), 6.35 (s, 2H, NH_2), 6.47 (s, 2H, NH_2), 7.14 (d, 1H, $J = 8.64$ Hz, Ar-H), 7.55 (s, 1H, Ar-H), 7.60 (d, 2H, $J = 8.6$ Hz, Ar-H), 7.67–7.69 (m, 1H, Ar-H), 7.85 (d, 2H, $J = 8.6$ Hz, Ar-H), 9.67 (s, 1H, NH) p.p.m.. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): $\delta\text{C} = 26.82, 27.60, 29.48, 31.24, 32.21, 50.82, 62.50, 99.39, 110.75, 116.73, 117.43, 121.98, 124.17, 124.55, 127.23, 129.95, 135.99, 148.50, 151.02, 153.27, 153.38, 155.05, 160.20, 162.77, 165.10, 196.91$. Analysis calculated for $\text{C}_{27}\text{H}_{23}\text{ClN}_6\text{O}_3$ (514.96): C 62.97, H 4.50, Cl 6.88, N 16.32. Found: C 62.80, H 4.69, N 16.08%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Table 3
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{27}\text{H}_{23}\text{ClN}_6\text{O}_3 \cdot \text{C}_3\text{H}_7\text{NO}$
M_r	588.06
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	11.0172 (3), 12.3285 (3), 12.6748 (4)
α, β, γ (°)	64.450 (3), 89.344 (3), 78.658 (2)
V (Å ³)	1517.63 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.18
Crystal size (mm)	0.16 × 0.16 × 0.12
Data collection	
Diffractometer	XtaLAB Synergy
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2025)
T_{\min}, T_{\max}	0.872, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	100274, 11619, 9160
R_{int}	0.056
θ values (°)	$\theta_{\text{max}} = 33.2, \theta_{\text{min}} = 2.4$
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.770
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.050, 0.126, 1.07
No. of reflections	11619
No. of parameters	356
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.56, -0.29

Computer programs: *CrysAlis PRO* (Rigaku OD, 2025), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/3* (Sheldrick, 2015b), *XP* (Bruker, 1998) and *publCIF* (Westrip, 2010).

Hydrogen atoms bonded to nitrogen were refined with an N–H distance restraint (SADI) for the NH_2 groups. Methyl groups were refined as idealized rigid groups allowed to rotate but not tip ('AFIX 137'), with C–H = 0.98, H–C–H = 109.5°. Other hydrogen atoms were included using a riding model starting from calculated positions (C–H_{methylene} = 1.00, C–H_{methylene} = 0.99 Å). The $U_{\text{iso}}(\text{H})$ values were fixed for methyl groups at $1.5 \times U_{\text{eq}}$, and for other H atoms at $1.2 \times U_{\text{eq}}$ of the parent carbon atoms. Three badly-fitting reflections (deviations $> 7.5\sigma$) were omitted from the refinement. The weighting parameters a and b (Sheldrick, 2015b) oscillated over a small range.

A region of residual electron density around the inversion centre at (0, 0, 1/2) was tentatively interpreted as several overlapping (and thus partially occupied) DMF sites (DMF was used for the recrystallization). One clear DMF position could be refined (with occupation 0.58) but the remaining difference peaks could not be interpreted satisfactorily; no suitable model of disordered DMF was found. It is possible that some other solvent, perhaps remaining from the synthesis, may be involved. The routine SQUEEZE (as implemented in the program system *PLATON*; Spek, 2020) was used to remove mathematically the effects of the disordered solvent. The electron content of the void was estimated as 98, corresponding to two DMF molecules per void (and thus per cell) and one DMF per asymmetric unit. This content was used to

calculate the formula weight and other related quantities, but should be interpreted with caution. The number of parameters in the refinement was adjusted upwards by 55 (recommended by the SQUEEZE routine; command 'L.S. 6 0 55') to allow for the solvent parameters when calculating su's. The use of SQUEEZE causes a long series of 'G ALERTS' when the CIF file is analysed by checkCIF.

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full crystallographic data

IUCrData (2025). **10**, x250939 [<https://doi.org/10.1107/S2414314625009393>]

(E)-2,4-Diamino-5-{7-[(4-chlorophenyl)diazenyl]-3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl}-6-oxo-1,6-dihydropyridine-3-carbonitrile dimethylformamide monosolvate

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Crystal data

$C_{27}H_{23}ClN_6O_3 \cdot C_3H_7NO$

$M_r = 588.06$

Triclinic, $P\bar{1}$

$a = 11.0172$ (3) Å

$b = 12.3285$ (3) Å

$c = 12.6748$ (4) Å

$\alpha = 64.450$ (3)°

$\beta = 89.344$ (3)°

$\gamma = 78.658$ (2)°

$V = 1517.63$ (8) Å³

$Z = 2$

$F(000) = 696$

$D_x = 1.447$ Mg m⁻³

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

Cell parameters from 38596 reflections

$\theta = 2.4$ – 33.2 °

$\mu = 0.18$ mm⁻¹

$T = 100$ K

Irregular, orange

$0.16 \times 0.16 \times 0.12$ mm

Data collection

XtaLAB Synergy
diffractometer

Radiation source: micro-focus sealed X-ray tube

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2025)

$T_{\min} = 0.872$, $T_{\max} = 1.000$

100274 measured reflections

11619 independent reflections

9160 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\max} = 33.2$ °, $\theta_{\min} = 2.4$ °

$h = -16 \rightarrow 16$

$k = -18 \rightarrow 18$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.126$

$S = 1.07$

11619 reflections

356 parameters

6 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.2643P]$

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

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

$\Delta\rho_{\max} = 0.56$ e Å⁻³

$\Delta\rho_{\min} = -0.29$ e Å⁻³

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	0.14828 (8)	0.65466 (8)	0.84932 (8)	0.02025 (17)
N2	0.10393 (9)	0.76856 (9)	0.80198 (9)	0.02349 (18)
O1	0.65579 (7)	0.52573 (6)	0.81948 (7)	0.01912 (14)
C1	0.72160 (9)	0.18661 (9)	0.93834 (8)	0.01572 (16)
O2	0.66692 (7)	0.10096 (7)	0.97332 (7)	0.02217 (15)
C2	0.86182 (9)	0.16316 (9)	0.94458 (9)	0.01906 (18)
H2A	0.893707	0.087344	0.934964	0.023*
H2B	0.893364	0.148495	1.023451	0.023*
C3	0.91361 (9)	0.26893 (10)	0.85173 (9)	0.01951 (18)
C4	0.85135 (9)	0.38947 (9)	0.85687 (9)	0.01856 (18)
H4A	0.885379	0.390258	0.928422	0.022*
H4B	0.871513	0.459764	0.788082	0.022*
C4A	0.71351 (9)	0.40505 (9)	0.85790 (8)	0.01557 (16)
C5	0.47856 (10)	0.67623 (10)	0.80104 (11)	0.0235 (2)
H05	0.530245	0.734582	0.776609	0.028*
C6	0.35346 (10)	0.71337 (10)	0.80853 (10)	0.0231 (2)
H06	0.318453	0.796859	0.790331	0.028*
C7	0.27887 (9)	0.62564 (9)	0.84350 (9)	0.01862 (18)
C8	0.33099 (9)	0.50313 (9)	0.87186 (8)	0.01639 (17)
H08	0.279648	0.444474	0.897171	0.020*
C8A	0.45709 (9)	0.46475 (8)	0.86387 (8)	0.01459 (16)
C8B	0.52913 (9)	0.55330 (9)	0.82927 (9)	0.01740 (17)
C9	0.51168 (8)	0.33465 (8)	0.88298 (8)	0.01328 (15)
H9	0.485321	0.276919	0.958844	0.016*
C9A	0.65145 (8)	0.31294 (8)	0.89250 (8)	0.01400 (15)
N11	0.42705 (9)	0.37815 (8)	0.57725 (7)	0.01944 (17)
H011	0.4374 (16)	0.4289 (16)	0.5031 (15)	0.036 (4)*
C12	0.35524 (10)	0.29688 (10)	0.59099 (9)	0.01940 (18)
C13	0.33734 (9)	0.21558 (9)	0.70441 (8)	0.01629 (17)
C14	0.39335 (8)	0.22110 (8)	0.80298 (8)	0.01318 (15)
C15	0.46177 (8)	0.31130 (8)	0.78490 (8)	0.01323 (15)
C16	0.48166 (9)	0.38942 (9)	0.66910 (8)	0.01586 (16)
N3	0.30702 (12)	0.29933 (11)	0.49221 (9)	0.0312 (2)
H031	0.3275 (16)	0.3486 (15)	0.4255 (12)	0.040 (5)*
H032	0.2477 (16)	0.2626 (18)	0.4947 (17)	0.058 (6)*
N4	0.21380 (11)	0.04876 (11)	0.73639 (10)	0.0322 (2)
N5	0.37648 (8)	0.14009 (8)	0.91206 (7)	0.01654 (15)
H051	0.4246 (14)	0.1289 (15)	0.9669 (12)	0.030 (4)*
H052	0.3407 (15)	0.0814 (14)	0.9237 (14)	0.037 (4)*
O3	0.54610 (7)	0.47042 (7)	0.64269 (6)	0.02039 (15)
C17	0.26884 (10)	0.12390 (10)	0.72123 (9)	0.02006 (19)
C21	-0.02659 (9)	0.80208 (10)	0.80584 (10)	0.02030 (19)
C22	-0.07321 (10)	0.92779 (10)	0.76723 (11)	0.0243 (2)
H22	-0.018664	0.983383	0.740749	0.029*
C23	-0.19902 (10)	0.97174 (10)	0.76743 (10)	0.0232 (2)

H23	-0.231313	1.057128	0.742361	0.028*
C24	-0.27692 (9)	0.88893 (9)	0.80484 (9)	0.01874 (18)
C11	-0.43554 (2)	0.94466 (2)	0.79962 (2)	0.02262 (6)
C25	-0.23163 (10)	0.76299 (10)	0.84473 (10)	0.0232 (2)
H25	-0.286433	0.707667	0.871535	0.028*
C26	-0.10597 (10)	0.71939 (10)	0.84486 (11)	0.0238 (2)
H26	-0.073774	0.633779	0.871307	0.029*
C27	1.05426 (10)	0.24386 (11)	0.87808 (12)	0.0273 (2)
H27A	1.072060	0.240009	0.955343	0.041*
H27B	1.087824	0.310192	0.818031	0.041*
H27C	1.092951	0.165326	0.877734	0.041*
C28	0.88616 (11)	0.27880 (11)	0.72925 (10)	0.0264 (2)
H28A	0.924472	0.201162	0.726918	0.040*
H28B	0.920329	0.345764	0.670810	0.040*
H28C	0.796121	0.295779	0.711728	0.040*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0175 (4)	0.0204 (4)	0.0240 (4)	0.0002 (3)	-0.0005 (3)	-0.0125 (3)
N2	0.0173 (4)	0.0198 (4)	0.0350 (5)	0.0001 (3)	-0.0013 (3)	-0.0151 (4)
O1	0.0146 (3)	0.0128 (3)	0.0298 (4)	-0.0040 (2)	0.0003 (3)	-0.0087 (3)
C1	0.0161 (4)	0.0144 (4)	0.0149 (4)	-0.0032 (3)	-0.0003 (3)	-0.0047 (3)
O2	0.0199 (3)	0.0128 (3)	0.0274 (4)	-0.0048 (3)	-0.0011 (3)	-0.0023 (3)
C2	0.0153 (4)	0.0164 (4)	0.0236 (5)	-0.0018 (3)	-0.0010 (3)	-0.0076 (4)
C3	0.0152 (4)	0.0191 (4)	0.0255 (5)	-0.0044 (3)	0.0029 (3)	-0.0106 (4)
C4	0.0144 (4)	0.0173 (4)	0.0253 (5)	-0.0056 (3)	0.0018 (3)	-0.0096 (4)
C4A	0.0149 (4)	0.0134 (4)	0.0187 (4)	-0.0036 (3)	0.0008 (3)	-0.0070 (3)
C5	0.0186 (4)	0.0145 (4)	0.0394 (6)	-0.0037 (3)	-0.0034 (4)	-0.0135 (4)
C6	0.0192 (4)	0.0170 (4)	0.0358 (6)	-0.0011 (4)	-0.0041 (4)	-0.0151 (4)
C7	0.0164 (4)	0.0186 (4)	0.0224 (5)	-0.0010 (3)	-0.0012 (3)	-0.0116 (4)
C8	0.0153 (4)	0.0165 (4)	0.0181 (4)	-0.0033 (3)	0.0008 (3)	-0.0083 (3)
C8A	0.0149 (4)	0.0137 (4)	0.0157 (4)	-0.0031 (3)	0.0000 (3)	-0.0069 (3)
C8B	0.0147 (4)	0.0152 (4)	0.0234 (5)	-0.0032 (3)	-0.0012 (3)	-0.0094 (3)
C9	0.0138 (4)	0.0120 (4)	0.0136 (4)	-0.0040 (3)	0.0009 (3)	-0.0047 (3)
C9A	0.0140 (4)	0.0128 (4)	0.0145 (4)	-0.0037 (3)	0.0005 (3)	-0.0049 (3)
N11	0.0263 (4)	0.0199 (4)	0.0129 (4)	-0.0135 (3)	0.0018 (3)	-0.0043 (3)
C12	0.0239 (5)	0.0202 (4)	0.0168 (4)	-0.0107 (4)	0.0018 (3)	-0.0081 (3)
C13	0.0187 (4)	0.0149 (4)	0.0173 (4)	-0.0079 (3)	0.0019 (3)	-0.0071 (3)
C14	0.0126 (4)	0.0103 (3)	0.0158 (4)	-0.0028 (3)	0.0022 (3)	-0.0048 (3)
C15	0.0143 (4)	0.0115 (4)	0.0136 (4)	-0.0048 (3)	0.0015 (3)	-0.0044 (3)
C16	0.0181 (4)	0.0150 (4)	0.0144 (4)	-0.0064 (3)	0.0010 (3)	-0.0052 (3)
N3	0.0444 (6)	0.0377 (6)	0.0177 (4)	-0.0260 (5)	0.0010 (4)	-0.0107 (4)
N4	0.0406 (6)	0.0320 (5)	0.0342 (5)	-0.0231 (5)	0.0075 (4)	-0.0174 (4)
N5	0.0189 (4)	0.0137 (3)	0.0152 (4)	-0.0076 (3)	0.0016 (3)	-0.0029 (3)
O3	0.0268 (4)	0.0201 (3)	0.0152 (3)	-0.0151 (3)	0.0024 (3)	-0.0044 (3)
C17	0.0236 (5)	0.0199 (4)	0.0201 (4)	-0.0095 (4)	0.0030 (4)	-0.0099 (4)
C21	0.0165 (4)	0.0191 (4)	0.0271 (5)	-0.0003 (3)	-0.0016 (4)	-0.0131 (4)

C22	0.0210 (5)	0.0165 (4)	0.0341 (6)	-0.0032 (4)	0.0020 (4)	-0.0102 (4)
C23	0.0211 (5)	0.0139 (4)	0.0329 (5)	-0.0002 (3)	0.0001 (4)	-0.0101 (4)
C24	0.0155 (4)	0.0190 (4)	0.0224 (4)	0.0002 (3)	-0.0027 (3)	-0.0112 (4)
C11	0.01652 (11)	0.02239 (12)	0.02925 (13)	0.00158 (8)	-0.00234 (8)	-0.01387 (10)
C25	0.0180 (4)	0.0177 (4)	0.0338 (6)	-0.0025 (4)	-0.0037 (4)	-0.0116 (4)
C26	0.0189 (5)	0.0163 (4)	0.0369 (6)	0.0001 (4)	-0.0048 (4)	-0.0138 (4)
C27	0.0155 (4)	0.0281 (5)	0.0401 (6)	-0.0049 (4)	0.0051 (4)	-0.0166 (5)
C28	0.0288 (6)	0.0290 (5)	0.0258 (5)	-0.0089 (4)	0.0075 (4)	-0.0151 (4)

Geometric parameters (Å, °)

N1—N2	1.2572 (13)	N11—C16	1.3875 (12)
N1—C7	1.4217 (13)	N11—H011	0.898 (17)
N2—C21	1.4224 (14)	C12—N3	1.3517 (14)
O1—C4A	1.3657 (12)	C12—C13	1.3923 (14)
O1—C8B	1.3871 (12)	C13—C17	1.4200 (13)
C1—O2	1.2306 (12)	C13—C14	1.4331 (13)
C1—C9A	1.4549 (13)	C14—N5	1.3489 (12)
C1—C2	1.5112 (14)	C14—C15	1.4011 (12)
C2—C3	1.5377 (14)	C15—C16	1.4094 (12)
C2—H2A	0.9900	C16—O3	1.2642 (11)
C2—H2B	0.9900	N3—H031	0.861 (13)
C3—C27	1.5306 (15)	N3—H032	0.858 (14)
C3—C28	1.5328 (16)	N4—C17	1.1522 (14)
C3—C4	1.5378 (14)	N5—H051	0.825 (12)
C4—C4A	1.4933 (13)	N5—H052	0.848 (13)
C4—H4A	0.9900	C21—C22	1.3941 (15)
C4—H4B	0.9900	C21—C26	1.3980 (15)
C4A—C9A	1.3485 (13)	C22—C23	1.3859 (15)
C5—C6	1.3800 (15)	C22—H22	0.9500
C5—C8B	1.3928 (14)	C23—C24	1.3861 (15)
C5—H05	0.9500	C23—H23	0.9500
C6—C7	1.4033 (15)	C24—C25	1.3926 (14)
C6—H06	0.9500	C24—C11	1.7383 (10)
C7—C8	1.3911 (14)	C25—C26	1.3828 (15)
C8—C8A	1.3942 (13)	C25—H25	0.9500
C8—H08	0.9500	C26—H26	0.9500
C8A—C8B	1.3907 (13)	C27—H27A	0.9800
C8A—C9	1.5107 (13)	C27—H27B	0.9800
C9—C9A	1.5072 (13)	C27—H27C	0.9800
C9—C15	1.5223 (13)	C28—H28A	0.9800
C9—H9	1.0000	C28—H28B	0.9800
N11—C12	1.3483 (13)	C28—H28C	0.9800
N2—N1—C7	112.74 (9)	C12—N11—H011	116.4 (11)
N1—N2—C21	114.76 (9)	C16—N11—H011	119.3 (11)
C4A—O1—C8B	118.26 (7)	N11—C12—N3	116.93 (9)
O2—C1—C9A	120.10 (9)	N11—C12—C13	118.49 (9)

O2—C1—C2	121.11 (9)	N3—C12—C13	124.56 (9)
C9A—C1—C2	118.77 (8)	C12—C13—C17	119.55 (9)
C1—C2—C3	114.03 (8)	C12—C13—C14	119.79 (8)
C1—C2—H2A	108.7	C17—C13—C14	120.59 (8)
C3—C2—H2A	108.7	N5—C14—C15	121.31 (8)
C1—C2—H2B	108.7	N5—C14—C13	118.77 (8)
C3—C2—H2B	108.7	C15—C14—C13	119.90 (8)
H2A—C2—H2B	107.6	C14—C15—C16	118.79 (8)
C27—C3—C28	109.25 (9)	C14—C15—C9	123.90 (8)
C27—C3—C2	109.27 (9)	C16—C15—C9	117.25 (8)
C28—C3—C2	110.06 (9)	O3—C16—N11	117.22 (8)
C27—C3—C4	109.92 (9)	O3—C16—C15	124.23 (9)
C28—C3—C4	109.77 (9)	N11—C16—C15	118.55 (8)
C2—C3—C4	108.56 (8)	C12—N3—H031	118.6 (12)
C4A—C4—C3	112.29 (8)	C12—N3—H032	120.6 (13)
C4A—C4—H4A	109.1	H031—N3—H032	119.9 (17)
C3—C4—H4A	109.1	C14—N5—H051	118.2 (11)
C4A—C4—H4B	109.1	C14—N5—H052	121.7 (11)
C3—C4—H4B	109.1	H051—N5—H052	115.4 (16)
H4A—C4—H4B	107.9	N4—C17—C13	179.12 (12)
C9A—C4A—O1	123.10 (9)	C22—C21—C26	120.48 (10)
C9A—C4A—C4	125.22 (9)	C22—C21—N2	114.69 (9)
O1—C4A—C4	111.67 (8)	C26—C21—N2	124.83 (9)
C6—C5—C8B	120.08 (10)	C23—C22—C21	120.08 (10)
C6—C5—H05	120.0	C23—C22—H22	120.0
C8B—C5—H05	120.0	C21—C22—H22	120.0
C5—C6—C7	118.84 (10)	C22—C23—C24	118.84 (10)
C5—C6—H06	120.6	C22—C23—H23	120.6
C7—C6—H06	120.6	C24—C23—H23	120.6
C8—C7—C6	120.34 (9)	C23—C24—C25	121.77 (10)
C8—C7—N1	116.11 (9)	C23—C24—C11	118.85 (8)
C6—C7—N1	123.54 (9)	C25—C24—C11	119.37 (8)
C7—C8—C8A	121.30 (9)	C26—C25—C24	119.23 (10)
C7—C8—H08	119.4	C26—C25—H25	120.4
C8A—C8—H08	119.4	C24—C25—H25	120.4
C8B—C8A—C8	117.29 (9)	C25—C26—C21	119.59 (10)
C8B—C8A—C9	121.08 (8)	C25—C26—H26	120.2
C8—C8A—C9	121.47 (8)	C21—C26—H26	120.2
O1—C8B—C8A	122.45 (9)	C3—C27—H27A	109.5
O1—C8B—C5	115.40 (8)	C3—C27—H27B	109.5
C8A—C8B—C5	122.14 (9)	H27A—C27—H27B	109.5
C9A—C9—C8A	109.52 (7)	C3—C27—H27C	109.5
C9A—C9—C15	112.34 (7)	H27A—C27—H27C	109.5
C8A—C9—C15	110.07 (7)	H27B—C27—H27C	109.5
C9A—C9—H9	108.3	C3—C28—H28A	109.5
C8A—C9—H9	108.3	C3—C28—H28B	109.5
C15—C9—H9	108.3	H28A—C28—H28B	109.5
C4A—C9A—C1	119.03 (8)	C3—C28—H28C	109.5

C4A—C9A—C9	123.00 (8)	H28A—C28—H28C	109.5
C1—C9A—C9	117.95 (8)	H28B—C28—H28C	109.5
C12—N11—C16	124.32 (8)		
C7—N1—N2—C21	-179.90 (8)	C2—C1—C9A—C9	177.87 (8)
O2—C1—C2—C3	153.20 (10)	C8A—C9—C9A—C4A	-16.02 (12)
C9A—C1—C2—C3	-28.24 (13)	C15—C9—C9A—C4A	106.62 (10)
C1—C2—C3—C27	171.41 (9)	C8A—C9—C9A—C1	165.67 (8)
C1—C2—C3—C28	-68.62 (11)	C15—C9—C9A—C1	-71.68 (10)
C1—C2—C3—C4	51.54 (11)	C16—N11—C12—N3	178.74 (11)
C27—C3—C4—C4A	-167.54 (9)	C16—N11—C12—C13	-2.26 (17)
C28—C3—C4—C4A	72.27 (11)	N11—C12—C13—C17	-175.92 (10)
C2—C3—C4—C4A	-48.07 (11)	N3—C12—C13—C17	2.99 (18)
C8B—O1—C4A—C9A	7.66 (14)	N11—C12—C13—C14	0.93 (15)
C8B—O1—C4A—C4	-172.08 (8)	N3—C12—C13—C14	179.84 (11)
C3—C4—C4A—C9A	22.81 (14)	C12—C13—C14—N5	-178.89 (9)
C3—C4—C4A—O1	-157.45 (8)	C17—C13—C14—N5	-2.08 (14)
C8B—C5—C6—C7	-0.76 (17)	C12—C13—C14—C15	2.50 (14)
C5—C6—C7—C8	1.04 (16)	C17—C13—C14—C15	179.31 (9)
C5—C6—C7—N1	-177.21 (10)	N5—C14—C15—C16	176.81 (9)
N2—N1—C7—C8	-167.33 (9)	C13—C14—C15—C16	-4.62 (14)
N2—N1—C7—C6	10.98 (15)	N5—C14—C15—C9	-6.13 (14)
C6—C7—C8—C8A	-1.49 (15)	C13—C14—C15—C9	172.43 (8)
N1—C7—C8—C8A	176.89 (9)	C9A—C9—C15—C14	118.20 (10)
C7—C8—C8A—C8B	1.58 (14)	C8A—C9—C15—C14	-119.47 (10)
C7—C8—C8A—C9	-173.89 (9)	C9A—C9—C15—C16	-64.70 (11)
C4A—O1—C8B—C8A	-7.51 (14)	C8A—C9—C15—C16	57.63 (11)
C4A—O1—C8B—C5	173.03 (9)	C12—N11—C16—O3	-179.59 (10)
C8—C8A—C8B—O1	179.27 (9)	C12—N11—C16—C15	0.09 (16)
C9—C8A—C8B—O1	-5.24 (14)	C14—C15—C16—O3	-176.96 (9)
C8—C8A—C8B—C5	-1.31 (15)	C9—C15—C16—O3	5.79 (15)
C9—C8A—C8B—C5	174.18 (9)	C14—C15—C16—N11	3.38 (14)
C6—C5—C8B—O1	-179.61 (10)	C9—C15—C16—N11	-173.87 (9)
C6—C5—C8B—C8A	0.93 (17)	N1—N2—C21—C22	172.06 (10)
C8B—C8A—C9—C9A	15.75 (12)	N1—N2—C21—C26	-7.68 (16)
C8—C8A—C9—C9A	-168.95 (8)	C26—C21—C22—C23	0.09 (17)
C8B—C8A—C9—C15	-108.23 (10)	N2—C21—C22—C23	-179.66 (10)
C8—C8A—C9—C15	67.07 (11)	C21—C22—C23—C24	-0.95 (17)
O1—C4A—C9A—C1	-176.54 (9)	C22—C23—C24—C25	1.60 (17)
C4—C4A—C9A—C1	3.17 (15)	C22—C23—C24—C11	-177.48 (9)
O1—C4A—C9A—C9	5.17 (15)	C23—C24—C25—C26	-1.34 (17)
C4—C4A—C9A—C9	-175.12 (9)	C11—C24—C25—C26	177.73 (9)
O2—C1—C9A—C4A	178.07 (9)	C24—C25—C26—C21	0.43 (17)
C2—C1—C9A—C4A	-0.51 (13)	C22—C21—C26—C25	0.18 (17)
O2—C1—C9A—C9	-3.56 (13)	N2—C21—C26—C25	179.90 (11)

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>
N11—H011 \cdots O3 ⁱ	0.898 (17)	1.758 (17)	2.6558 (11)	178.7 (18)
N5—H051 \cdots O2	0.83 (1)	2.62 (2)	3.1939 (12)	128 (1)
N5—H051 \cdots Cl1 ⁱⁱ	0.83 (1)	2.69 (1)	3.3709 (9)	141 (1)
N5—H052 \cdots O2 ⁱⁱⁱ	0.85 (1)	2.08 (1)	2.8266 (11)	147 (2)
C4—H4 <i>A</i> \cdots N1 ^{iv}	0.99	2.66	3.5236 (14)	146
C5—H05 \cdots Cl1 ^v	0.95	2.82	3.6093 (10)	141

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