

Ethyl 5,5-dichloro-3-(4-chlorophenyl)-3a-methyl-4a-phenyl-3a,4,4a,5-tetrahydro-3H-aziridino[2,1-d][1,2,4]triazolo[4,3-a]-[1,5]benzodiazepine-1-carboxylate

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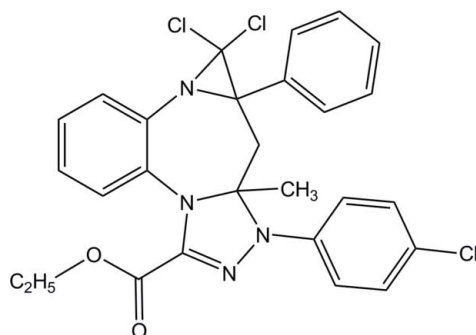
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Key indicators: single-crystal X-ray study; $T = 300\text{ K}$; mean $\sigma(\text{C}-\text{C}) = 0.002\text{ Å}$; R factor = 0.036; wR factor = 0.101; data-to-parameter ratio = 16.9.

In the title compound, $\text{C}_{27}\text{H}_{23}\text{Cl}_3\text{N}_4\text{O}_2$, the seven-membered diazepine ring adopts a boat conformation. The triazole ring makes dihedral angles of 17.24 (8) and 82.86 (8)° , respectively, with the chlorobenzene ring and the benzene ring of the benzodiazepine unit.

Related literature

For background to benzodiazepine derivatives, see: Barltrop *et al.* (1959); El Hazazi *et al.* (2003); Sharp & Hamilton (1946). For related structures, see: Chiaroni *et al.* (1995); El Hazazi *et al.* (2000).



Experimental

Crystal data

$\text{C}_{27}\text{H}_{23}\text{Cl}_3\text{N}_4\text{O}_2$
 $M_r = 541.84$
Triclinic, $P\bar{1}$
 $a = 9.679\text{ (3) Å}$
 $b = 11.256\text{ (3) Å}$
 $c = 12.661\text{ (2) Å}$
 $\alpha = 79.09\text{ (2)}^\circ$
 $\beta = 76.46\text{ (2)}^\circ$

$\gamma = 73.04\text{ (2)}^\circ$
 $V = 1271.8\text{ (6) Å}^3$
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.39\text{ mm}^{-1}$
 $T = 300\text{ K}$
 $0.3 \times 0.15 \times 0.1\text{ mm}$

Data collection

Enraf-Nonius CAD-4
diffractometer
6860 measured reflections
5536 independent reflections

4616 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.010$
2 standard reflections every 60 min
intensity decay: 1.0%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.101$
 $S = 1.05$
5536 reflections

327 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.24\text{ e Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33\text{ e Å}^{-3}$

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2697).

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supporting information

Acta Cryst. (2011). E67, o1211 [https://doi.org/10.1107/S1600536811014115]

Ethyl 5,5-dichloro-3-(4-chlorophenyl)-3a-methyl-4a-phenyl-3a,4,4a,5-tetrahydro-3H-aziridino[2,1-d][1,2,4]triazolo[4,3-a][1,5]benzodiazepine-1-carboxylate

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S1. Comment

In order to develop work carried out before in our laboratory we were interested in the synthesis of new derivatives benzodiazepinic (El Hazazi *et al.*, 2003). These reactions are either of the reactions of cycloadditions [2 + 1] realising generated carbenes *in situ* or reactions of transfer of methylene.

In the present work, we report the synthesis of new benzodiazepine derivatives *via* addition of dichlorocarbene to [1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine obtained stereospecifically by the addition of nitrilimines (Sharp *et al.*, 1946) on 1,5-benzodiazepine (Bartrop *et al.*, 1959).

Dichloroazacyclopropanation of [1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine occurs readily under phase transfer catalysis conditions (liquid-liquid) with chloroform, aqueous sodium hydroxide and benzyltriethylammonium chloride (TBA-Cl) to give the corresponding dichloroadduct 2 (Fig. 1). Thus, the reaction of [1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine 1 with dichlorocarbene in these conditions produce gem-dichloroaziridino[2,1-*d*][1,2,4] triazolo[4,3-*a*][1,5]benzodiazepine 2 in good yield.

The crystallographic study made it possible to determine the stereochemistry of the product 2. The crystalline structure confirms that the condensation of dichlorocarbene is carried out on double bond C=N substituted by the phenyl and shows that the product 2a obtained is of *trans* relative stereochemistry (Fig. 2). The main geometric features of this group are in good agreement with those observed in similar compound (Chiaroni *et al.*, 1995; El Hazazi *et al.*, 2000).

S2. Experimental

[1,2,4]Triazolo[4,3-*a*][1,5]benzodiazepine 1 (0.65 mmol) in 2 ml of chloroform were stirred with 2 ml of aqueous 50% NaOH solution and a catalytic amount of triethylbenzylammonium chloride (TBA-Cl). After 4 h the mixture was poured into 5 ml of water and extracted with ether. The organic phase was then dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was chromatographed on a silica gel column (eluent: hexane/ethyl acetate 95/5) and recrystallized from ethanol/chloroform to give a compound 2a

The observation to be noted is that the condensation of dichlorocarbene to [1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine is stereospecific. The structure elucidation of the compound 2 was determined on spectral data (¹H NMR, ¹³C NMR and mass spectroscopy). The compound revealed in their spectra of mass the molecular peak located at *m/z* = 541 compatible with their empirical formula. The NMR spectrum of this product shows that the change of the chemical shifts of different grouping from monoadduct. In the ¹³C NMR spectrum of compound, we remarked the absence of the signals attributed to the double bond C5=N6 of cycle diazepinic. The ¹³C NMR spectrum of product was consistent with the presence of only one diastereoisomer. These spectral analyses do not enable us to determine relative stereochemistry of

the aziridino[2,1-*d*][1,2,4]]triazolo[4,3-*a*][1,5]benzodiazepine (*trans* 2 α or *cis* 2 β).

S3. Refinement

All H atoms were located in a difference map and then refined using a riding model, with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₃, C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₂, and C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH.

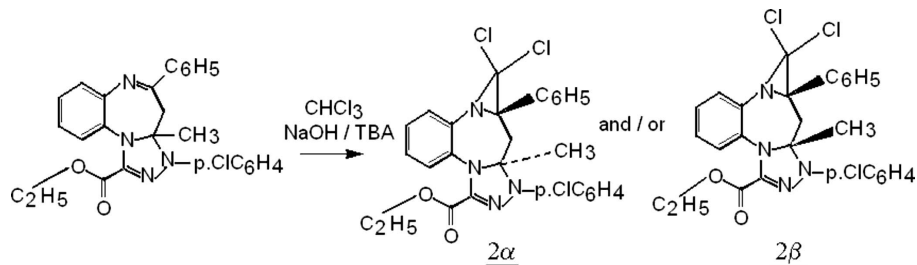


Figure 1

The reaction scheme of the title compound

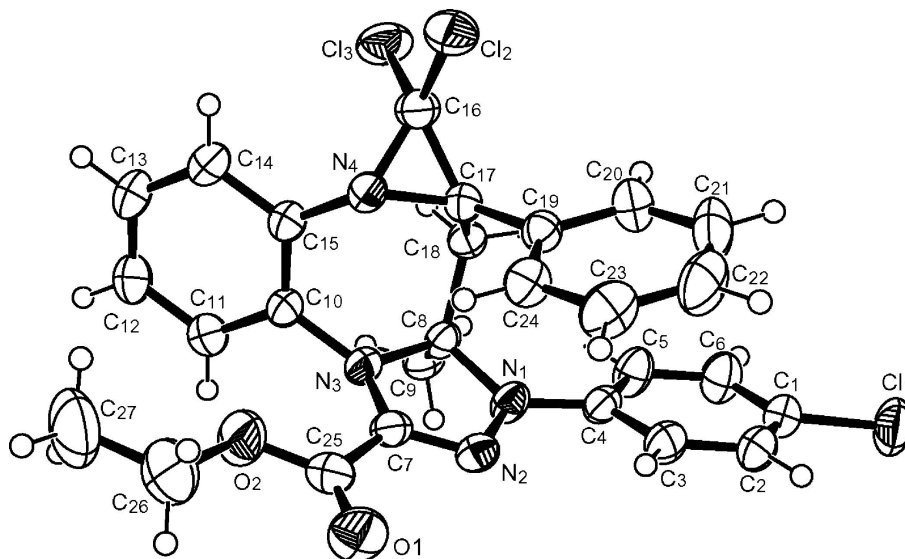


Figure 2

The molecular structure of the title compound, with 50% probability ellipsoids.

Ethyl 3,3-dichloro-7-(4-chlorophenyl)-6-methyl-4-phenyl-2,7,8,10-tetraazatetracyclo[9.4.0.0^{2,4}.0^{6,10}]pentadeca-1(11),8,12,14-tetraene- 9-carboxylate

Crystal data

C₂₇H₂₃Cl₃N₄O₂
 $M_r = 541.84$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 9.679$ (3) Å
 $b = 11.256$ (3) Å
 $c = 12.661$ (2) Å
 $\alpha = 79.09$ (2)°
 $\beta = 76.46$ (2)°
 $\gamma = 73.04$ (2)°
 $V = 1271.8$ (6) Å³

$Z = 2$
 $F(000) = 560$
 $D_x = 1.415$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 0.39$ mm⁻¹
 $T = 300$ K
 Prism, yellow
 $0.3 \times 0.15 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

6860 measured reflections

5536 independent reflections

4616 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.010$$

$$\theta_{\text{max}} = 27.0^\circ, \theta_{\text{min}} = 2.2^\circ$$

$$h = -12 \rightarrow 2$$

$$k = -14 \rightarrow 14$$

$$l = -16 \rightarrow 16$$

2 standard reflections every 60 min

intensity decay: 1.0%

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.036$$

$$wR(F^2) = 0.101$$

$$S = 1.05$$

5536 reflections

327 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.3226P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.31467 (5)	−0.06197 (4)	0.57617 (5)	0.06714 (16)
Cl2	0.74695 (5)	0.33836 (4)	0.03031 (4)	0.05465 (13)
Cl3	0.50575 (5)	0.37629 (5)	0.21522 (4)	0.05877 (14)
O1	1.09072 (14)	0.71899 (13)	0.20132 (12)	0.0619 (3)
O2	0.85011 (15)	0.79523 (12)	0.19906 (12)	0.0638 (4)
N1	0.94972 (12)	0.42660 (12)	0.40621 (10)	0.0369 (3)
N2	1.02302 (13)	0.51079 (12)	0.34036 (10)	0.0366 (3)
N3	0.78121 (13)	0.58997 (11)	0.34267 (10)	0.0354 (3)
N4	0.72403 (13)	0.50553 (11)	0.16401 (10)	0.0361 (3)
C1	1.20506 (17)	0.07966 (15)	0.52295 (14)	0.0444 (3)
C2	1.26875 (17)	0.15749 (15)	0.44036 (15)	0.0459 (4)
H2	1.3689	0.1335	0.4116	0.055*
C3	1.18305 (16)	0.27115 (15)	0.40070 (13)	0.0413 (3)
H3	1.2258	0.3230	0.3444	0.050*
C4	1.03279 (15)	0.30883 (13)	0.44432 (11)	0.0346 (3)
C5	0.97014 (17)	0.22829 (16)	0.52598 (14)	0.0470 (4)

H5	0.8699	0.2514	0.5548	0.056*
C6	1.05614 (19)	0.11349 (16)	0.56493 (15)	0.0507 (4)
H6	1.0135	0.0596	0.6191	0.061*
C7	0.92343 (15)	0.60263 (13)	0.30379 (11)	0.0345 (3)
C8	0.78887 (14)	0.46551 (13)	0.40868 (11)	0.0322 (3)
C9	0.69700 (16)	0.47994 (15)	0.52411 (12)	0.0405 (3)
H9A	0.7524	0.5014	0.5681	0.049*
H9B	0.6731	0.4025	0.5568	0.049*
H9C	0.6079	0.5450	0.5197	0.049*
C10	0.65238 (15)	0.65391 (13)	0.29762 (12)	0.0355 (3)
C11	0.55573 (18)	0.75943 (15)	0.34035 (15)	0.0464 (4)
H11	0.5753	0.7887	0.3978	0.056*
C12	0.43014 (19)	0.82118 (16)	0.29742 (17)	0.0555 (4)
H12	0.3658	0.8918	0.3259	0.067*
C13	0.40124 (19)	0.77727 (16)	0.21230 (17)	0.0567 (5)
H13	0.3171	0.8187	0.1837	0.068*
C14	0.49615 (18)	0.67216 (16)	0.16904 (15)	0.0492 (4)
H14	0.4760	0.6436	0.1115	0.059*
C15	0.62242 (15)	0.60913 (13)	0.21222 (12)	0.0366 (3)
C16	0.68332 (17)	0.39468 (14)	0.15834 (13)	0.0403 (3)
C17	0.78959 (15)	0.38713 (12)	0.23111 (11)	0.0333 (3)
C18	0.73573 (15)	0.37907 (13)	0.35398 (11)	0.0336 (3)
H18A	0.7696	0.2931	0.3866	0.040*
H18B	0.6290	0.4013	0.3692	0.040*
C19	0.94952 (15)	0.32550 (13)	0.19097 (11)	0.0351 (3)
C20	0.99906 (19)	0.19656 (15)	0.21963 (14)	0.0483 (4)
H20	0.9342	0.1518	0.2625	0.058*
C21	1.1452 (2)	0.13472 (18)	0.18427 (17)	0.0628 (5)
H21	1.1776	0.0486	0.2031	0.075*
C22	1.2422 (2)	0.2009 (2)	0.12121 (17)	0.0644 (5)
H22	1.3402	0.1597	0.0985	0.077*
C23	1.19335 (19)	0.3282 (2)	0.09202 (15)	0.0570 (4)
H23	1.2588	0.3726	0.0494	0.068*
C24	1.04672 (17)	0.39071 (15)	0.12584 (12)	0.0427 (3)
H24	1.0141	0.4763	0.1046	0.051*
C25	0.96658 (18)	0.71092 (15)	0.22958 (13)	0.0422 (3)
C26	0.8773 (3)	0.9023 (2)	0.1207 (2)	0.0818 (7)
H26A	0.9327	0.8752	0.0512	0.098*
H26B	0.9332	0.9448	0.1478	0.098*
C27	0.7316 (4)	0.9875 (2)	0.1068 (3)	0.0985 (9)
H27A	0.6806	1.0179	0.1751	0.118*
H27B	0.6750	0.9428	0.0844	0.118*
H27C	0.7451	1.0570	0.0520	0.118*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0493 (3)	0.0441 (2)	0.0967 (4)	0.00124 (19)	−0.0208 (2)	0.0058 (2)

C12	0.0623 (3)	0.0590 (3)	0.0487 (2)	−0.0108 (2)	−0.01682 (19)	−0.02154 (19)
C13	0.0403 (2)	0.0739 (3)	0.0728 (3)	−0.0232 (2)	−0.0127 (2)	−0.0197 (2)
O1	0.0495 (7)	0.0679 (8)	0.0696 (8)	−0.0300 (6)	−0.0053 (6)	0.0043 (7)
O2	0.0588 (8)	0.0488 (7)	0.0836 (9)	−0.0227 (6)	−0.0257 (7)	0.0213 (6)
N1	0.0249 (5)	0.0414 (6)	0.0421 (6)	−0.0082 (5)	−0.0074 (5)	0.0008 (5)
N2	0.0305 (6)	0.0423 (6)	0.0388 (6)	−0.0127 (5)	−0.0072 (5)	−0.0041 (5)
N3	0.0284 (6)	0.0341 (6)	0.0449 (7)	−0.0084 (5)	−0.0116 (5)	−0.0022 (5)
N4	0.0338 (6)	0.0364 (6)	0.0382 (6)	−0.0048 (5)	−0.0115 (5)	−0.0060 (5)
C1	0.0385 (8)	0.0380 (8)	0.0562 (9)	−0.0028 (6)	−0.0162 (7)	−0.0068 (7)
C2	0.0280 (7)	0.0452 (8)	0.0620 (10)	−0.0033 (6)	−0.0075 (7)	−0.0117 (7)
C3	0.0298 (7)	0.0439 (8)	0.0488 (8)	−0.0096 (6)	−0.0050 (6)	−0.0060 (6)
C4	0.0282 (6)	0.0395 (7)	0.0364 (7)	−0.0055 (5)	−0.0094 (5)	−0.0066 (6)
C5	0.0310 (7)	0.0518 (9)	0.0487 (9)	−0.0049 (7)	−0.0032 (6)	0.0020 (7)
C6	0.0421 (9)	0.0482 (9)	0.0530 (9)	−0.0075 (7)	−0.0071 (7)	0.0056 (7)
C7	0.0316 (7)	0.0377 (7)	0.0377 (7)	−0.0113 (6)	−0.0083 (6)	−0.0078 (6)
C8	0.0250 (6)	0.0347 (7)	0.0359 (7)	−0.0057 (5)	−0.0073 (5)	−0.0038 (5)
C9	0.0301 (7)	0.0508 (9)	0.0400 (8)	−0.0079 (6)	−0.0041 (6)	−0.0116 (6)
C10	0.0286 (6)	0.0324 (7)	0.0460 (8)	−0.0061 (5)	−0.0114 (6)	−0.0038 (6)
C11	0.0435 (8)	0.0382 (8)	0.0587 (10)	−0.0036 (6)	−0.0152 (7)	−0.0137 (7)
C12	0.0436 (9)	0.0403 (8)	0.0784 (12)	0.0061 (7)	−0.0183 (8)	−0.0160 (8)
C13	0.0401 (9)	0.0470 (9)	0.0814 (13)	0.0042 (7)	−0.0291 (9)	−0.0072 (9)
C14	0.0435 (9)	0.0478 (9)	0.0594 (10)	−0.0026 (7)	−0.0256 (8)	−0.0093 (7)
C15	0.0307 (7)	0.0343 (7)	0.0444 (8)	−0.0049 (5)	−0.0102 (6)	−0.0056 (6)
C16	0.0369 (7)	0.0444 (8)	0.0428 (8)	−0.0098 (6)	−0.0095 (6)	−0.0123 (6)
C17	0.0313 (7)	0.0313 (7)	0.0374 (7)	−0.0071 (5)	−0.0073 (5)	−0.0053 (5)
C18	0.0293 (6)	0.0347 (7)	0.0371 (7)	−0.0098 (5)	−0.0047 (5)	−0.0046 (5)
C19	0.0335 (7)	0.0362 (7)	0.0340 (7)	−0.0049 (6)	−0.0063 (5)	−0.0077 (5)
C20	0.0481 (9)	0.0363 (8)	0.0540 (9)	−0.0037 (7)	−0.0067 (7)	−0.0052 (7)
C21	0.0583 (11)	0.0456 (9)	0.0701 (12)	0.0122 (8)	−0.0128 (9)	−0.0124 (9)
C22	0.0386 (9)	0.0769 (13)	0.0635 (12)	0.0086 (9)	−0.0027 (8)	−0.0211 (10)
C23	0.0388 (9)	0.0767 (13)	0.0500 (10)	−0.0136 (8)	0.0024 (7)	−0.0103 (9)
C24	0.0395 (8)	0.0464 (8)	0.0393 (8)	−0.0090 (7)	−0.0050 (6)	−0.0052 (6)
C25	0.0466 (9)	0.0430 (8)	0.0424 (8)	−0.0187 (7)	−0.0096 (7)	−0.0062 (6)
C26	0.0976 (18)	0.0566 (12)	0.0926 (17)	−0.0362 (12)	−0.0307 (14)	0.0282 (11)
C27	0.129 (2)	0.0516 (12)	0.104 (2)	−0.0106 (14)	−0.0397 (18)	0.0166 (13)

Geometric parameters (Å, °)

C11—C1	1.7500 (17)	C10—C11	1.392 (2)
C12—C16	1.7614 (16)	C10—C15	1.395 (2)
C13—C16	1.7570 (17)	C11—C12	1.389 (2)
O1—C25	1.196 (2)	C11—H11	0.9300
O2—C25	1.327 (2)	C12—C13	1.381 (3)
O2—C26	1.455 (2)	C12—H12	0.9300
N1—N2	1.3830 (17)	C13—C14	1.385 (2)
N1—C4	1.3979 (18)	C13—H13	0.9300
N1—C8	1.4837 (17)	C14—C15	1.399 (2)
N2—C7	1.2878 (19)	C14—H14	0.9300

N3—C7	1.3886 (18)	C16—C17	1.509 (2)
N3—C10	1.4326 (18)	C17—C19	1.5081 (19)
N3—C8	1.4804 (18)	C17—C18	1.5148 (19)
N4—C15	1.4209 (19)	C18—H18A	0.9700
N4—C16	1.4322 (19)	C18—H18B	0.9700
N4—C17	1.4936 (18)	C19—C24	1.384 (2)
C1—C6	1.379 (2)	C19—C20	1.394 (2)
C1—C2	1.381 (2)	C20—C21	1.390 (3)
C2—C3	1.382 (2)	C20—H20	0.9300
C2—H2	0.9300	C21—C22	1.380 (3)
C3—C4	1.397 (2)	C21—H21	0.9300
C3—H3	0.9300	C22—C23	1.378 (3)
C4—C5	1.390 (2)	C22—H22	0.9300
C5—C6	1.389 (2)	C23—C24	1.393 (2)
C5—H5	0.9300	C23—H23	0.9300
C6—H6	0.9300	C24—H24	0.9300
C7—C25	1.491 (2)	C26—C27	1.484 (4)
C8—C9	1.533 (2)	C26—H26A	0.9700
C8—C18	1.5506 (19)	C26—H26B	0.9700
C9—H9A	0.9600	C27—H27A	0.9600
C9—H9B	0.9600	C27—H27B	0.9600
C9—H9C	0.9600	C27—H27C	0.9600
C25—O2—C26	117.07 (16)	C13—C14—H14	120.1
N2—N1—C4	118.46 (11)	C15—C14—H14	120.1
N2—N1—C8	113.24 (11)	C10—C15—C14	119.52 (14)
C4—N1—C8	127.07 (12)	C10—C15—N4	120.50 (12)
C7—N2—N1	106.12 (12)	C14—C15—N4	119.84 (14)
C7—N3—C10	127.78 (12)	N4—C16—C17	60.97 (9)
C7—N3—C8	108.57 (11)	N4—C16—C13	121.86 (11)
C10—N3—C8	119.40 (11)	C17—C16—C13	120.64 (11)
C15—N4—C16	122.29 (12)	N4—C16—C12	114.44 (11)
C15—N4—C17	122.26 (12)	C17—C16—C12	120.61 (11)
C16—N4—C17	62.05 (9)	C13—C16—C12	110.44 (8)
C6—C1—C2	120.55 (15)	N4—C17—C19	116.19 (12)
C6—C1—C11	119.73 (14)	N4—C17—C16	56.97 (9)
C2—C1—C11	119.71 (12)	C19—C17—C16	117.06 (12)
C1—C2—C3	119.74 (14)	N4—C17—C18	116.74 (11)
C1—C2—H2	120.1	C19—C17—C18	117.07 (12)
C3—C2—H2	120.1	C16—C17—C18	119.10 (12)
C2—C3—C4	120.61 (15)	C17—C18—C8	113.50 (11)
C2—C3—H3	119.7	C17—C18—H18A	108.9
C4—C3—H3	119.7	C8—C18—H18A	108.9
C5—C4—C3	118.81 (14)	C17—C18—H18B	108.9
C5—C4—N1	121.63 (13)	C8—C18—H18B	108.9
C3—C4—N1	119.55 (13)	H18A—C18—H18B	107.7
C6—C5—C4	120.48 (14)	C24—C19—C20	119.32 (14)
C6—C5—H5	119.8	C24—C19—C17	122.92 (13)

C4—C5—H5	119.8	C20—C19—C17	117.74 (14)
C1—C6—C5	119.76 (16)	C21—C20—C19	120.20 (17)
C1—C6—H6	120.1	C21—C20—H20	119.9
C5—C6—H6	120.1	C19—C20—H20	119.9
N2—C7—N3	113.87 (13)	C22—C21—C20	120.11 (17)
N2—C7—C25	119.72 (13)	C22—C21—H21	119.9
N3—C7—C25	126.39 (13)	C20—C21—H21	119.9
N3—C8—N1	97.86 (10)	C23—C22—C21	119.85 (17)
N3—C8—C9	110.22 (12)	C23—C22—H22	120.1
N1—C8—C9	113.22 (11)	C21—C22—H22	120.1
N3—C8—C18	111.80 (11)	C22—C23—C24	120.47 (18)
N1—C8—C18	113.43 (11)	C22—C23—H23	119.8
C9—C8—C18	109.85 (11)	C24—C23—H23	119.8
C8—C9—H9A	109.5	C19—C24—C23	120.03 (16)
C8—C9—H9B	109.5	C19—C24—H24	120.0
H9A—C9—H9B	109.5	C23—C24—H24	120.0
C8—C9—H9C	109.5	O1—C25—O2	125.08 (15)
H9A—C9—H9C	109.5	O1—C25—C7	123.70 (16)
H9B—C9—H9C	109.5	O2—C25—C7	111.22 (13)
C11—C10—C15	119.98 (13)	O2—C26—C27	107.1 (2)
C11—C10—N3	119.99 (14)	O2—C26—H26A	110.3
C15—C10—N3	120.01 (13)	C27—C26—H26A	110.3
C12—C11—C10	120.18 (16)	O2—C26—H26B	110.3
C12—C11—H11	119.9	C27—C26—H26B	110.3
C10—C11—H11	119.9	H26A—C26—H26B	108.6
C13—C12—C11	119.76 (16)	C26—C27—H27A	109.5
C13—C12—H12	120.1	C26—C27—H27B	109.5
C11—C12—H12	120.1	H27A—C27—H27B	109.5
C12—C13—C14	120.77 (15)	C26—C27—H27C	109.5
C12—C13—H13	119.6	H27A—C27—H27C	109.5
C14—C13—H13	119.6	H27B—C27—H27C	109.5
C13—C14—C15	119.79 (16)		
C4—N1—N2—C7	170.77 (12)	C16—N4—C15—C10	123.80 (15)
C8—N1—N2—C7	2.53 (16)	C17—N4—C15—C10	48.67 (19)
C6—C1—C2—C3	1.1 (3)	C16—N4—C15—C14	−60.6 (2)
C11—C1—C2—C3	−177.96 (13)	C17—N4—C15—C14	−135.70 (15)
C1—C2—C3—C4	0.8 (2)	C15—N4—C16—C17	−112.30 (14)
C2—C3—C4—C5	−2.0 (2)	C15—N4—C16—C13	−2.34 (19)
C2—C3—C4—N1	177.17 (14)	C17—N4—C16—C13	109.96 (14)
N2—N1—C4—C5	168.12 (14)	C15—N4—C16—C12	134.90 (12)
C8—N1—C4—C5	−25.5 (2)	C17—N4—C16—C12	−112.80 (12)
N2—N1—C4—C3	−11.0 (2)	C15—N4—C17—C19	−141.09 (13)
C8—N1—C4—C3	155.43 (14)	C16—N4—C17—C19	106.56 (14)
C3—C4—C5—C6	1.3 (2)	C15—N4—C17—C16	112.35 (15)
N1—C4—C5—C6	−177.85 (15)	C15—N4—C17—C18	3.56 (18)
C2—C1—C6—C5	−1.8 (3)	C16—N4—C17—C18	−108.79 (14)
C11—C1—C6—C5	177.27 (14)	C13—C16—C17—N4	−111.90 (13)

C4—C5—C6—C1	0.6 (3)	C12—C16—C17—N4	102.80 (13)
N1—N2—C7—N3	1.62 (16)	N4—C16—C17—C19	−105.01 (14)
N1—N2—C7—C25	179.78 (12)	C13—C16—C17—C19	143.09 (12)
C10—N3—C7—N2	−161.35 (14)	C12—C16—C17—C19	−2.21 (18)
C8—N3—C7—N2	−5.08 (17)	N4—C16—C17—C18	104.62 (14)
C10—N3—C7—C25	20.6 (2)	C13—C16—C17—C18	−7.28 (18)
C8—N3—C7—C25	176.90 (13)	C12—C16—C17—C18	−152.58 (11)
C7—N3—C8—N1	5.69 (13)	N4—C17—C18—C8	−70.59 (15)
C10—N3—C8—N1	164.27 (12)	C19—C17—C18—C8	73.75 (15)
C7—N3—C8—C9	124.04 (12)	C16—C17—C18—C8	−135.88 (13)
C10—N3—C8—C9	−77.37 (15)	N3—C8—C18—C17	41.51 (15)
C7—N3—C8—C18	−113.48 (12)	N1—C8—C18—C17	−67.98 (15)
C10—N3—C8—C18	45.10 (16)	C9—C8—C18—C17	164.20 (12)
N2—N1—C8—N3	−5.08 (14)	N4—C17—C19—C24	24.5 (2)
C4—N1—C8—N3	−172.10 (13)	C16—C17—C19—C24	88.97 (18)
N2—N1—C8—C9	−121.11 (13)	C18—C17—C19—C24	−120.05 (15)
C4—N1—C8—C9	71.87 (18)	N4—C17—C19—C20	−154.13 (13)
N2—N1—C8—C18	112.84 (13)	C16—C17—C19—C20	−89.64 (17)
C4—N1—C8—C18	−54.18 (18)	C18—C17—C19—C20	61.34 (18)
C7—N3—C10—C11	−97.33 (19)	C24—C19—C20—C21	0.9 (3)
C8—N3—C10—C11	108.64 (16)	C17—C19—C20—C21	179.56 (16)
C7—N3—C10—C15	83.81 (19)	C19—C20—C21—C22	0.5 (3)
C8—N3—C10—C15	−70.22 (18)	C20—C21—C22—C23	−1.0 (3)
C15—C10—C11—C12	−0.7 (3)	C21—C22—C23—C24	0.1 (3)
N3—C10—C11—C12	−179.54 (15)	C20—C19—C24—C23	−1.7 (2)
C10—C11—C12—C13	0.2 (3)	C17—C19—C24—C23	179.67 (15)
C11—C12—C13—C14	0.0 (3)	C22—C23—C24—C19	1.2 (3)
C12—C13—C14—C15	0.3 (3)	C26—O2—C25—O1	3.4 (3)
C11—C10—C15—C14	1.0 (2)	C26—O2—C25—C7	−176.14 (17)
N3—C10—C15—C14	179.86 (14)	N2—C7—C25—O1	−0.4 (2)
C11—C10—C15—N4	176.65 (14)	N3—C7—C25—O1	177.46 (15)
N3—C10—C15—N4	−4.5 (2)	N2—C7—C25—O2	179.06 (14)
C13—C14—C15—C10	−0.8 (3)	N3—C7—C25—O2	−3.0 (2)
C13—C14—C15—N4	−176.51 (16)	C25—O2—C26—C27	−175.3 (2)
