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

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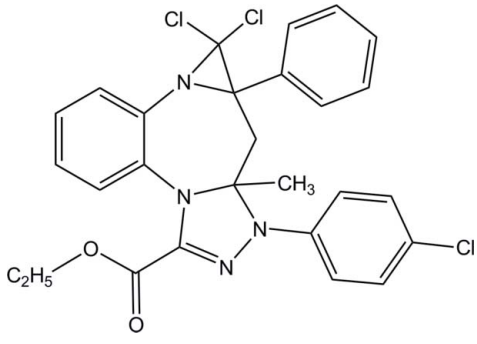
Key indicators: single-crystal X-ray study; $T$ = 300 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.036; $wR$ factor = 0.101; data-to-parameter ratio = 16.9.

In the title compound, $C_{27}H_{23}Cl_3N_4O_2$, 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

$C_{27}H_{23}Cl_3N_4O_2$
$M_r$ = 541.84
Triclinic, $P\overline{1}$
$a$ = 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) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.39 mm$^{-1}$
$T$ = 300 K
0.3 × 0.15 × 0.1 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
6860 measured reflections
5536 independent reflections
4616 reflections with $I > 2\sigma(I)$
$R_{int}$ = 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
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.33 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

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

**Aicha Boudina, Abdesselam Baouid, Mohamed Driss and El Hassane Soumhi**

## 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 methelyne.

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 (Barltrop *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 bichloroadduct 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 2*α* obtained is of *trans* relative stereochemistry (Fig. 2). The main geometric features of this group are in good agreement it 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 mm l) 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 chromatographied on a silica gel column (eluent: hexane/ethyl acetate 95/5) and recrystallized from ethanol/chloroform to give a compound 2*α*

The observation to be noted is that the condensation of dichlorocarbene to [1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine is streospecific. The structure elucidation of the compound 2 was determinate on spectral data ($^1$H NMR, $^{13}$C 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 decalage of the chemical shifts of different grouping from monoadduct. In the $^{13}$C NMR spectrum of compound, we remarked the absence of the signals attributed to the double bond C5=N6 of cycle diazepinic. The $^{13}$C NMR spectrum of product was consistent with the presence of only one diasterioisomer. 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 $U_{iso}$(H) = 1.2$U_{eq}$(C) for $CH_3$, C—H = 0.97 Å and $U_{iso}$(H) =1.2$U_{eq}$(C) for $CH_2$, and C—H = 0.93 Å and $U_{iso}$(H) =1.2$U_{eq}$(C) for CH.

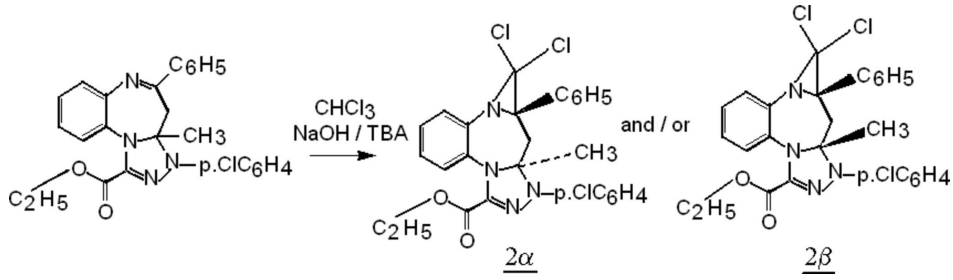


**Figure 1**

The reaction scheme of the title compound

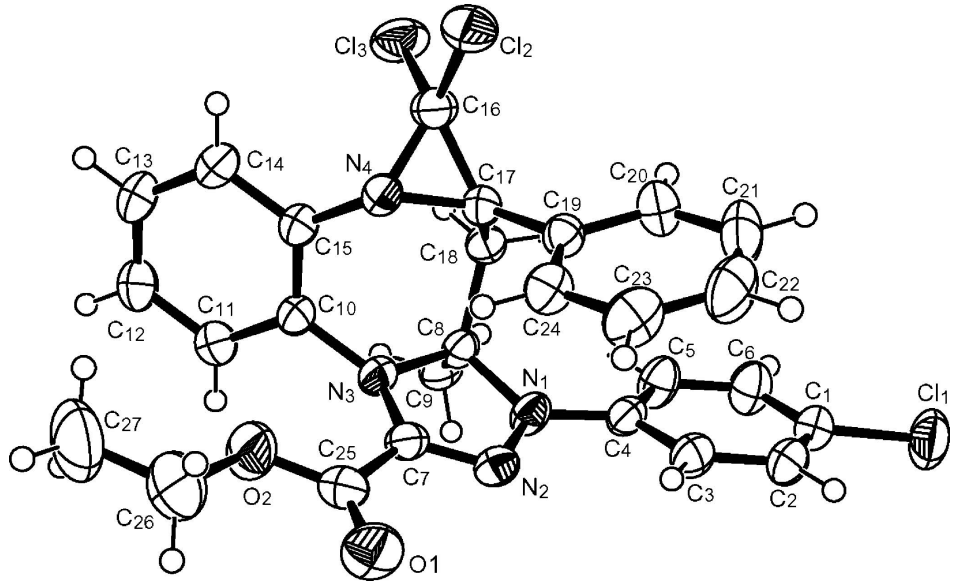


**Figure 2**

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*

$C_{27}H_{23}Cl_3N_4O_2$
$M_r$ = 541.84
Triclinic, $P\overline{1}$
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) Å$^3$
$Z$ = 2
$F$(000) = 560
$D_x$ = 1.415 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 10–15°
$\mu$ = 0.39 mm$^{-1}$

$T$ = 300 K
Prism, yellow

0.3 × 0.15 × 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 $I > 2\sigma(I)$

$R_{int}$ = 0.010
$\theta_{max}$ = 27.0°, $\theta_{min}$ = 2.2°
$h$ = −12→2
$k$ = −14→14
$l$ = −16→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
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.3226P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.33 e Å$^{-3}$

*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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0493 (3) | 0.0441 (2) | 0.0967 (4) | 0.00124 (19) | −0.0208 (2) | 0.0058 (2) |
| Cl2 | 0.0623 (3) | 0.0590 (3) | 0.0487 (2) | −0.0108 (2) | −0.01682 (19) | −0.02154 (19) |
| Cl3 | 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, º)*

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| Cl1—C1 | 1.7500 (17) | C10—C11 | 1.392 (2) |
| Cl2—C16 | 1.7614 (16) | C10—C15 | 1.395 (2) |
| Cl3—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 |

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| 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 |

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| 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—Cl3 | 121.86 (11) |
| C10—N3—C8 | 119.40 (11) | C17—C16—Cl3 | 120.64 (11) |
| C15—N4—C16 | 122.29 (12) | N4—C16—Cl2 | 114.44 (11) |
| C15—N4—C17 | 122.26 (12) | C17—C16—Cl2 | 120.61 (11) |
| C16—N4—C17 | 62.05 (9) | Cl3—C16—Cl2 | 110.44 (8) |
| C6—C1—C2 | 120.55 (15) | N4—C17—C19 | 116.19 (12) |
| C6—C1—Cl1 | 119.73 (14) | N4—C17—C16 | 56.97 (9) |
| C2—C1—Cl1 | 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 |

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| 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) | | |

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| 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) |
| Cl1—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—Cl3 | −2.34 (19) |
| C2—C3—C4—N1 | 177.17 (14) | C17—N4—C16—Cl3 | 109.96 (14) |
| N2—N1—C4—C5 | 168.12 (14) | C15—N4—C16—Cl2 | 134.90 (12) |
| C8—N1—C4—C5 | −25.5 (2) | C17—N4—C16—Cl2 | −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) |

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| 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) |
| Cl1—C1—C6—C5 | 177.27 (14) | Cl3—C16—C17—N4 | −111.90 (13) |
| C4—C5—C6—C1 | 0.6 (3) | Cl2—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) | Cl3—C16—C17—C19 | 143.09 (12) |
| C10—N3—C7—N2 | −161.35 (14) | Cl2—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) | Cl3—C16—C17—C18 | −7.28 (18) |
| C8—N3—C7—C25 | 176.90 (13) | Cl2—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) |