Crystal structure of (1Z,4Z)-2,4-dimethyl-3H-benzo[b][1,4]diazepine

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The title compound, $C_{11}H_{12}N_2$, is not planar due to the folding of the seven-membered ring. In the crystal, molecules are packed opposite each other to minimize the electronic repulsion but the long intermolecular distances indicate that no directional contacts are found.

1. Chemical context

(1Z,4Z)-2,4-Dimethyl-3H-benzo[b][1,4]diazepine, $C_{11}H_{12}N_2$ (Me, Me) (**1**), also called a 1,5-benzodiazepine, is a molecule situated at the crossroad of many avenues of chemistry. This compound is associated with the names of Douglas Lloyd and Donald R. Marshall of the University of St Andrews in Scotland (Gibson *et al.*, 2002). These authors reported the synthesis of **1**, determined that its tautomeric structure is **1** and not **1'**, and also determined that the protonation of **1** yields the cation **1H⁺** (Lloyd *et al.*, 2002). For molecules such as **1H⁺** they introduced the term 'quasi-aromatic' (Lloyd & Marshall, 1971), a term that has not survived the authors (Claramunt *et al.*, 2013). The inversion barrier of the seven-membered ring of **1** was measured to be 48.9 kJ mol⁻¹ (Mannschreck *et al.*, 1967); our calculated value is 43.4 kJ mol⁻¹ (Claramunt *et al.*, 2013).
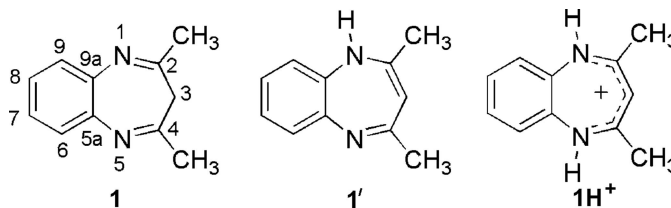
Benzo[b][1,4]diazepines continue to be the subject of many studies, but with other substituents (Bonacorso *et al.*, 1996; El-Azab, 2013; Aastha *et al.*, 2013; Solan *et al.*, 2014; Young *et al.*, 2016). Of the different procedures existing in the literature to prepare compound **1**, we used the reaction of acetylacetone with *o*-phenylenediamine using silica-supported sulfuric acid as catalyst under solvent-free conditions (Chen *et al.*, 2009). In spite of what the authors described in the paper, the reaction was not complete at room temperature and it was necessary to heat up to 273 K to attain a quantitative yield of the product,

https://doi.org/10.1107/S2056989017004972 **647**
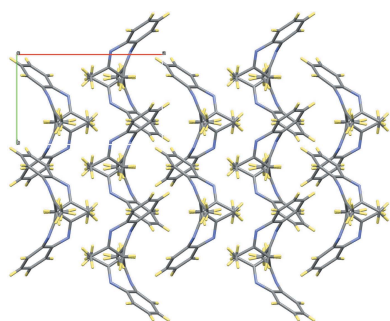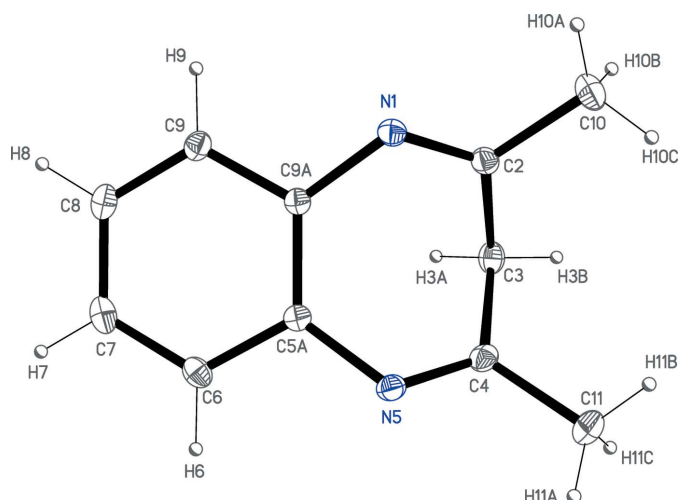
Figure 1
ORTEP plot (20% probability displacement ellipsoids) of **1**.

which was purified by column chromatography on silica gel and crystallized from ethyl acetate/hexane solution presenting a melting point of 408 K. We report herein on its characterization by ^{1}H, ^{13}C and ^{15}N NMR in solution and solid state spectroscopy and, since its X-ray molecular structure is unknown, we decided to complete the panorama of compound **1** determining it. Note that the structures of the monomethyl compound (Me, H) and the parent compound (H, H) are unknown, as well as those of their salts.

2. Structural commentary

The title compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 1). As expected, the derivative is not planar due to the folding of the seven-membered ring. According to the electronic distribution for the two imine groups N1—C2 and N5—C4 [bond distances = 1.283 (3) and 1.281 (3) Å, respectively], atoms C2, C3 and C4 together with the two methyl groups of the diazepine ring deviate from the phenyl ring plane: atom C3 shows the largest displacement at 1.495 (1) Å while C2 and C4 are situated symmetrically at about 0.58 Å from it. The dihedral angle between the phenyl ring and C2/C3/C4 fragment of the diazepine ring is 87.8 (2)°, giving rise to a boat conformation for the diazepine ring.
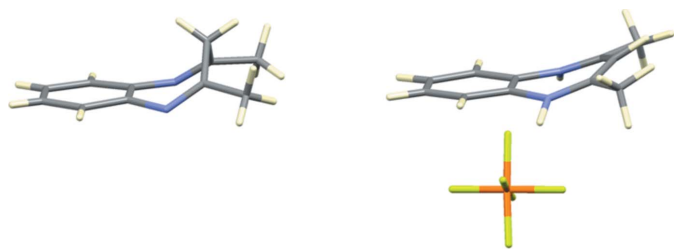
Figure 2
Comparative views of the seven-membered rings in **1** (left) and **1H⁺** (right) in the salt $C_{11}H_{13}N_2^+ \cdot PF_6^-$ (Blake *et al.*, 1991).

It is noteworthy that this is the only example found in the CSD database (Groom *et al.*, 2016) of a neutral diazepine derivative. For this reason, this structure is compared with the reported cationic diazepines $C_{11}H_{13}N_2^+ \cdot X^-$ [$X = PF_6^-$ (Blake *et al.*, 1991), Cl^- (Speakman *et al.*, 1976; Svensson & Timby, 1981) and ZnI_4^{2-} (Orioli & Lip, 1974)] showing relevant structural differences. In the latter compounds, there is electronic delocalization in the N1/C2/C3/C4/N5 moiety that results in an almost planar geometry of this part of the seven-membered ring. However, in the neutral species, the C3 atom keeps both hydrogen atoms in an sp^3 conformation, leading to localization of the double bonds between the nitrogen atoms and their adjacent carbon atoms, which induces a great deviation of this moiety from planarity (Fig. 2).

3. Supramolecular features

In the crystal, the molecules are packed opposite each other to minimize electronic repulsion but the long intermolecular distances indicate that no relevant contacts are found (Fig. 3). This feature differs from the salts previously mentioned, where the presence of the hydrogen atoms on the nitrogen atoms allows the formation of N—H···X hydrogen bonds, leading to different supramolecular networks. The absence of these atoms in **1**, along with the boat conformation described above, prevents the formation of any supramolecular structure.

4. Synthesis and crystallization

All chemicals cited in the synthetic procedures are commercial compounds. Melting points were determined by DSC and thermograms (sample size 0.002–0.004 g) were recorded with a scan rate of 5.0 K min^{-1}. Column chromatography was performed on silica gel 70–230 mesh. The NMR solution spectra were recorded on a 9.4 Tesla spectrometer
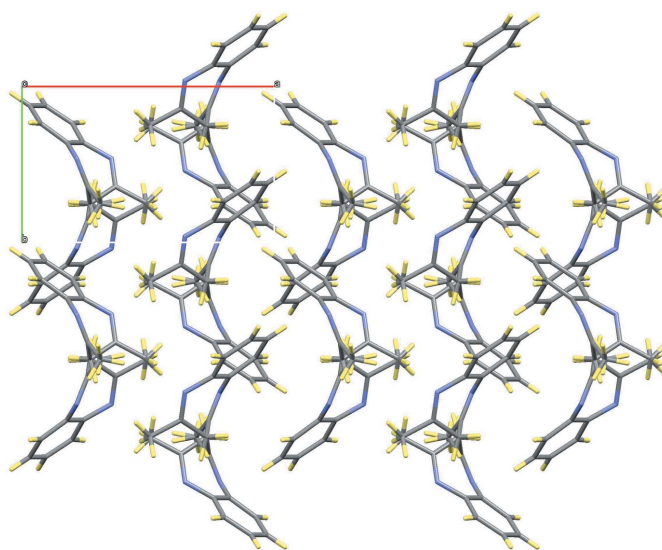
Figure 3
View of the crystal packing of **1**.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{12}N_2$
M_r	172.23
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	11.8226 (16), 6.6305 (9), 13.3557 (19)
β (°)	114.531 (3)
V (Å^3)	952.4 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	$0.18 \times 0.13 \times 0.10$
Data collection	
Diffractometer	Bruker SMART CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7529, 1876, 878
R_{int}	0.072
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.146, 0.99
No. of reflections	1876
No. of parameters	118
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.15

Computer programs: *SMART* and *SAINT* (Bruker, 2004), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

(400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and 40.54 MHz for ^{15}N) at 300 K with a 5 mm inverse detection H—X probe equipped with a z-gradient coil. Chemical shifts (δ in p.p.m.) are given from internal solvents: CDCl$_3$ 7.26 for ^{1}H and 77.0 for ^{13}C. Nitromethane was used for ^{15}N as external reference. CPMAS NMR spectra were obtained on a 9.4 Tesla spectrometer at 300 K (100.73 MHz for ^{13}C and 40.60 MHz for ^{15}N) using a 4 mm DVT probehead at spinning rates of 12 and 6 kHz, respectively. ^{13}C spectra were originally referenced to a glycine sample and then the chemical shifts were recalculated to the Me$_4$Si (for the glycine carbonyl atom δ = 176.1 p.p.m.) and ^{15}N spectra to ^{15}NH$_4$Cl and then converted to the nitromethane scale using the relationship: δ ^{15}N (nitromethane) = δ ^{15}N (ammonium chloride) − 338.1 p.p.m.. Samples were spun at the magic angle at rates of 25 kHz and the experiments were carried out at 300 K.

Synthesis of (1Z,4Z)-2,4-dimethyl-3H-benzo[b][1,4]diazepine (1): To a mixture of 2,4-pentanedione (100.12 mg, 1 mmol) and *o*-phenylenediamine (108.14 mg, 1 mmol), H$_2$SO$_4$·SiO$_2$ (20 mg) was added. The mixture was heated with magnetic stirring at 373 K for 1 h. After completion of the reaction, the resulting black oil was purified using silica gel column chromatography (ethyl acetate/petroleum ether, 60:40) and crystallized from ethyl acetate/hexane solution to give colourless prisms (90%). R_f (ethyl acetate/petroleum ether 80:20): 0.25. M.p (DSC) 408 K (Nishio *et al.*, 1985, 403–405 K) ^{1}H NMR (400.13 MHz, CDCl$_3$) δ 7.36 (*dd*, ^3J = 6.0, ^4J = 3.5, 2H, H7, H8), 7.21 (*dd*, ^3J = 6.0, ^4J = 3.5 Hz, 2H, H6, H9), 2.82 (*br*, 2H, H3), 2.35 (*s*, 6H, CH$_3$). ^{13}C NMR (100.62 MHz, CDCl$_3$) δ 157.6 (*q*, ^2J = 6.4 Hz, C2), 140.2 (*dd*, ^3J = 3 J = 7.0 Hz, C5a, C9a), 127.5 (*dddd* ^1J = 160.4, ^3J = 7.4, ^2J = ^2J = 3.5 Hz, C7,

C8), 124.8 (*dd*, ^1J = 161.8, ^2J = 8.7 Hz, C6, C9), 43.2 (*tsep*, ^1J = 134.5, 3 J = 2.8 Hz, C3), 27.6 (*qt*, ^1J = 128.0, ^3J = 2.5 Hz, CH$_3$). ^{15}N NMR (40.54 MHz, CDCl$_3$) δ −74.1. ^{13}C SSNMR (100.76 MHz, CPMAS) δ 162.9 and 161.5 (C2, C6), 142.2 (C5a, C9a), 128.0 (C7, C8), 125.5 and 124.6 (C6/C9), 43.1 (C3), 27.6 (CH$_3$). ^{15}N SSNMR (40.60 MHz, CPMAS) δ −69.7.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Hydrogen atoms were included in their calculated positions (C—H = 0.93–0.97Å) and refined riding on the respective carbon atoms with $U_{iso}(H)$ = $1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl H atoms.

References

Aastha, P., Navneet, K., Anshu, A., Pratima, S. & Dharma, K. (2013). *Res. J. Chem. Sci.* **3**, 90–103.
Blake, A. J., Schröder, M. & Sorbie, R. J. (1991). *Z. Kristallogr.* **194**, 148–151.
Bonacorso, H. G., Bittencourt, S. T., Wastowski, A. D., Wentz, A. P., Zanatta, N., Martins, A. P. M. (1996). *Tetrahedron Lett.* **37**, 9155–9156.
Bruker (2004). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, X., She, J., Shang, Z.-C., Wu, J. & Zhang, P. (2009). *Synth. Commun.* **39**, 947–957.
Claramunt, R. M., Alkorta, I. & Elguero, J. (2013). *Comput. Theor. Chem.* **1019**, 108–115.
El-Azab, I. H. (2013). *J. Heterocycl. Chem.* **50**, E178–E188.
Gibson, J. F., Mackie, R. K. & Marshall, D. R. (2002). *Arkivoc*, **iii**, 1–18.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Lloyd, D. & Marshall, D. R. (1971). *The Jerusalem Symposia on Quantum Chemistry and Biochemistry*. Vol. III, *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity*. Jerusalem: The Israel Academy of Sciences and Humanities.
Lloyd, D., McDougall, R. H. & Marshall, D. R. (2002). *J. Chem. Soc.* 3785–3792.
Mannschreck, A., Rissmann, G., Vögtle, F. & Wild, D. (1967). *Chem. Ber.* **100**, 335–346.
Nishio, T., Tokunaga, T. & Omote, Y. (1985). *J. Heterocycl. Chem.* **22**, 405–407.
Orioli, P. L. & Lip, H. C. (1974). *Cryst. Struct. Commun.* **3**, 477.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

research communications

Solan, A., Nişanci, B., Belcher, M., Young, J., Schäfer, C., Wheeler, K. A., Török, B. & Dembinski, R. (2014). *Green Chem.* **16**, 1120–1124.

Speakman, J. C. & Wilson, F. B. (1976). *Acta Cryst.* B**32**, 622–624.

Svensson, C. & Timby, L. (1981). *Cryst. Struct. Commun.* **10**, 429.

Young, J., Schäfer, C., Solan, A., Baldrica, A., Belcher, M., Nişanci, B., Wheeler, K. A., Trivedi, E. R., Török, B. & Dembinski, R. (2016). *RSC Adv.* **6**, 107081–107093.

Crystal structure of (1*Z*,4*Z*)-2,4-dimethyl-3*H*-benzo[*b*][1,4]diazepine

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Computing details

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(1*Z*,4*Z*)-2,4-dimethyl-3*H*-benzo[*b*][1,4]diazepine

Crystal data

$C_{11}H_{12}N_2$	$F(000) = 368$
$M_r = 172.23$	$D_x = 1.201$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.8226$ (16) Å	Cell parameters from 974 reflections
$b = 6.6305$ (9) Å	$\theta = 3.1$–20.1°
$c = 13.3557$ (19) Å	$\mu = 0.07$ mm^{-1}
$\beta = 114.531$ (3)°	$T = 296$ K
$V = 952.4$ (2) Å^3	Prismatic, colorless
$Z = 4$	$0.18 \times 0.13 \times 0.10$ mm

Data collection

Bruker SMART CCD diffractometer	878 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.072$
Graphite monochromator	$\theta_{max} = 26.0°$, $\theta_{min} = 1.9°$
phi and ω scans	$h = -13 \rightarrow 14$
7529 measured reflections	$k = -8 \rightarrow 8$
1876 independent reflections	$l = -16 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.146$	
$S = 0.99$	H-atom parameters constrained
1876 reflections	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2]$
118 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.18$ e Å^{-3}
	$\Delta\rho_{min} = -0.15$ 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.

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$
N1	0.3543 (2)	0.4619 (3)	0.32401 (16)	0.0491 (6)
C2	0.3699 (2)	0.6414 (4)	0.2963 (2)	0.0490 (7)
C3	0.2695 (3)	0.7496 (4)	0.2027 (2)	0.0551 (8)
H3A	0.1911	0.7421	0.2095	0.066*
H3B	0.2911	0.8904	0.2011	0.066*
C4	0.2606 (2)	0.6429 (4)	0.1002 (2)	0.0511 (7)
C5A	0.1784 (2)	0.3600 (4)	0.1489 (2)	0.0415 (6)
N5	0.21672 (19)	0.4640 (3)	0.07648 (17)	0.0498 (6)
C6	0.0737 (2)	0.2360 (4)	0.0995 (2)	0.0542 (7)
H6	0.0330	0.2313	0.0231	0.065*
C7	0.0299 (3)	0.1214 (4)	0.1614 (3)	0.0631 (8)
H7	−0.0415	0.0439	0.1274	0.076*
C8	0.0930 (3)	0.1223 (4)	0.2750 (3)	0.0602 (8)
H8	0.0635	0.0462	0.3176	0.072*
C9	0.1986 (3)	0.2348 (4)	0.3245 (2)	0.0502 (7)
H9	0.2428	0.2284	0.4005	0.060*
C9A	0.2416 (2)	0.3593 (3)	0.2635 (2)	0.0402 (6)
C10	0.4921 (3)	0.7461 (5)	0.3555 (3)	0.0776 (10)
H10A	0.5475	0.6599	0.4125	0.116*
H10B	0.4795	0.8690	0.3875	0.116*
H10C	0.5277	0.7765	0.3043	0.116*
C11	0.3111 (3)	0.7471 (5)	0.0277 (2)	0.0799 (10)
H11A	0.3008	0.6616	−0.0335	0.120*
H11B	0.3979	0.7752	0.0692	0.120*
H11C	0.2671	0.8713	0.0011	0.120*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0538 (15)	0.0523 (13)	0.0416 (13)	−0.0049 (12)	0.0203 (11)	−0.0059 (11)
C2	0.0515 (18)	0.0539 (17)	0.0451 (16)	−0.0062 (16)	0.0236 (14)	−0.0099 (15)
C3	0.0600 (19)	0.0378 (14)	0.073 (2)	0.0002 (14)	0.0327 (16)	0.0001 (15)
C4	0.0464 (17)	0.0558 (17)	0.0468 (17)	0.0072 (15)	0.0151 (13)	0.0147 (15)
C5A	0.0424 (16)	0.0413 (14)	0.0422 (16)	0.0054 (13)	0.0191 (13)	−0.0004 (13)
N5	0.0508 (14)	0.0570 (14)	0.0399 (13)	0.0007 (12)	0.0173 (11)	0.0043 (12)
C6	0.0423 (18)	0.0525 (16)	0.0603 (19)	0.0003 (14)	0.0138 (15)	−0.0073 (15)

C7	0.0497 (19)	0.0468 (17)	0.090 (3)	−0.0045 (14)	0.0267 (19)	−0.0044 (17)
C8	0.069 (2)	0.0457 (17)	0.080 (2)	−0.0021 (16)	0.0448 (19)	0.0037 (16)
C9	0.062 (2)	0.0426 (15)	0.0522 (17)	0.0007 (14)	0.0304 (15)	0.0014 (13)
C9A	0.0424 (15)	0.0377 (13)	0.0438 (16)	0.0018 (12)	0.0211 (13)	−0.0043 (13)
C10	0.064 (2)	0.080 (2)	0.081 (2)	−0.0249 (17)	0.0227 (18)	−0.0128 (18)
C11	0.089 (2)	0.087 (2)	0.069 (2)	−0.0131 (19)	0.0372 (19)	0.0183 (18)

Geometric parameters (Å, º)

N1—C2	1.283 (3)	C6—H6	0.9300
N1—C9A	1.412 (3)	C7—C8	1.385 (4)
C2—C10	1.499 (4)	C7—H7	0.9300
C2—C3	1.502 (3)	C8—C9	1.367 (4)
C3—C4	1.505 (3)	C8—H8	0.9300
C3—H3A	0.9700	C9—C9A	1.396 (3)
C3—H3B	0.9700	C9—H9	0.9300
C4—N5	1.281 (3)	C10—H10A	0.9600
C4—C11	1.500 (4)	C10—H10B	0.9600
C5A—C9A	1.396 (3)	C10—H10C	0.9600
C5A—N5	1.407 (3)	C11—H11A	0.9600
C5A—C6	1.402 (3)	C11—H11B	0.9600
C6—C7	1.373 (4)	C11—H11C	0.9600
C2—N1—C9A	119.7 (2)	C6—C7—H7	120.3
N1—C2—C10	120.0 (3)	C9—C8—C7	120.1 (3)
N1—C2—C3	121.7 (2)	C9—C8—H8	120.0
C10—C2—C3	118.3 (3)	C7—C8—H8	120.0
C4—C3—C2	105.4 (2)	C8—C9—C9A	121.4 (3)
C4—C3—H3A	110.7	C8—C9—H9	119.3
C2—C3—H3A	110.7	C9A—C9—H9	119.3
C4—C3—H3B	110.7	C5A—C9A—C9	118.9 (2)
C2—C3—H3B	110.7	C5A—C9A—N1	125.0 (2)
H3A—C3—H3B	108.8	C9—C9A—N1	115.8 (2)
N5—C4—C3	121.9 (2)	C2—C10—H10A	109.5
N5—C4—C11	119.7 (3)	C2—C10—H10B	109.5
C3—C4—C11	118.3 (3)	H10A—C10—H10B	109.5
C9A—C5A—N5	125.2 (2)	C2—C10—H10C	109.5
C9A—C5A—C6	118.7 (2)	H10A—C10—H10C	109.5
N5—C5A—C6	115.9 (2)	H10B—C10—H10C	109.5
C4—N5—C5A	119.8 (2)	C4—C11—H11A	109.5
C7—C6—C5A	121.4 (3)	C4—C11—H11B	109.5
C7—C6—H6	119.3	H11A—C11—H11B	109.5
C5A—C6—H6	119.3	C4—C11—H11C	109.5
C8—C7—C6	119.4 (3)	H11A—C11—H11C	109.5
C8—C7—H7	120.3	H11B—C11—H11C	109.5
C9A—N1—C2—C10	−176.0 (2)	C5A—C6—C7—C8	−2.4 (4)
C9A—N1—C2—C3	1.9 (3)	C6—C7—C8—C9	−0.7 (4)

N1—C2—C3—C4	−70.2 (3)	C7—C8—C9—C9A	3.6 (4)
C10—C2—C3—C4	107.8 (3)	N5—C5A—C9A—C9	−174.3 (2)
C2—C3—C4—N5	70.2 (3)	C6—C5A—C9A—C9	0.3 (3)
C2—C3—C4—C11	−106.6 (3)	N5—C5A—C9A—N1	−0.5 (4)
C3—C4—N5—C5A	−1.8 (4)	C6—C5A—C9A—N1	174.1 (2)
C11—C4—N5—C5A	175.0 (2)	C8—C9—C9A—C5A	−3.3 (4)
C9A—C5A—N5—C4	−41.4 (4)	C8—C9—C9A—N1	−177.7 (2)
C6—C5A—N5—C4	143.8 (2)	C2—N1—C9A—C5A	42.0 (3)
C9A—C5A—C6—C7	2.6 (4)	C2—N1—C9A—C9	−144.0 (2)
N5—C5A—C6—C7	177.7 (2)		