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Synthesis, crystal structure and photophysical properties of 1,4-bis(1,3-diazaazulen-2-yl)benzene: a new π building block

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A dimerized 1,3-diazaazulene derivative, namely 1,4-bis(1,3-diazaazulen-2-vl)benzene [or 2,2'-(1,4-phenylene)bis(1,3-diazaazulene)], C₂₂H₁₄N₄, (I), has been synthesized successfully through the condensation reaction between 2-methoxytropone and benzene-1,4-dicarboximidamide hydrochloride, and was characterized by ¹H NMR and ¹³C NMR spectroscopies, and ESI-MS. X-ray diffraction analysis reveals that (I) has a nearly planar structure with good π -electron delocalization, indicating that it might serve as a π building block. The crystal belongs to the monoclinic system. One-dimensional chains were formed along the *a* axis through $\pi - \pi$ interactions and adjacent chains are stabilized by C- $H \cdots N$ interactions, forming a three-dimensional architecture. The solid emission of (I) in the crystalline form exhibited a 170 nm red shift compared with that in the solution state. The observed optical bandgap for (I) is 3.22 eV and a cyclic voltammetry experiment confirmed the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The calculated bandgap for (I) is 3.37 eV, which is very close to the experimental result. In addition, the polarizability and hyperpolarizability of (I) were appraised for its further application in second-order nonlinear optical materials.

1. Introduction

Organic functional materials have attracted much attention due to their potential applications in optoelectronics (Ostroverkhova, 2016; Gsänger *et al.*, 2016), semiconducting devices (Gsänger *et al.*, 2016) and chemical sensors (Bansal *et al.*, 2015). Aromatic conjugated skeletons are interesting since they serve as building blocks for organic functional materials (Zhang *et al.*, 2013; Jiang *et al.*, 2009). For example, azulene derivatives were reported to display tunable photophysical and optical behaviours and are candidates for optical materials owing to their unique polarized charge distribution on the fused seven- and five-membered rings (Xin *et al.*, 2016; Tsurui *et al.*, 2014).



Within many reported structures related to azulene, 1,3diazaazulene is a unique derivative in which two C atoms are replaced by N atoms, with a rather large dipole moment located within the heteroaromatic core (Braun *et al.*, 1973; Nozoe *et al.*, 1954). Studies show that 1,3-diazaazulene derivatives display promising performance in liquid crystal (Mori



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et al., 2003) and nonlinear optical materials (Ma *et al.*, 2011; Zhu *et al.*, 2007). As was reported, molecules with more N atoms in the conjugated system offer more possibilities for modulating stability, photophysical and electronic properties, and the generation of various structural backbones, and might display better photochemical stability and diverse properties (Zhou *et al.*, 2016; Liang *et al.*, 2011; Winkler & Houk, 2007). Thus, 1,3-diazaazulene is an interesting fragment for the construction of new π building blocks for organic optoelectronic materials.

In our previously published 1,3-diazaazulene derivatives, which have one 1,3-diazaazulene ring bonded to the arene ring, the rings are coplanar, forming a 16- π -electron conjugated structure (Rao *et al.*, 2017; Ma *et al.*, 2011; Zhu *et al.*, 2007). Hence, it can be deduced that it is possible to design conjugated molecules containing more N atoms by introducing further 1,3-diazaazulene groups to the arene ring.

We designed a dimerized 1,3-diazaazulene derivative, namely 1,4-bis(1,3-diazaazulen-2-yl)benzene, (I) (Scheme 1), with two 1,3-diazaazulene units connected through an arene bridge, which presents a larger conjugated system together with an increased number of N atoms. We report the synthesis and single-crystal X-ray structure characterization of (I), as well as an analysis of its photophysical and electrochemical properties. Theoretical calculations were also carried out to support the experimental studies.



2. Experimental

2.1. Synthesis and crystallization

For the preparation of target compound (I), t-BuOK (191 mg, 4.0 equiv.) was added to a methanol solution of benzene-1,4-dicarboximidamide hydrochloride (100 mg, 1.0 equiv.), as shown in Scheme 2. The mixture was stirred for 30 min and cooled in an ice bath. A methanol solution of 2-methoxytropone (173 mg, 3.0 equiv.) was added carefully dropwise. The resulting solution was heated under reflux and the reaction was monitored by thin-layer chromatography $(R_{\rm F} = 0.1, \text{MeOH/CH}_2\text{Cl}_2 = 1:10 \text{ v/v})$. A light-yellow powder was obtained by flash-column chromatography with CH₃OH/ CH₂Cl₂ (1:50 v/v) as eluent. ¹H NMR (400 MHz, CDCl₃): δ 8.79-8.73 (m, 4H), 8.63 (s, 4H), 8.08 (d, J = 7.8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl₃): δ 174.60, 162.95, 162.46, 139.03, 135.18, 134.87, 129.56; HRMS (ESI): m/z [M]⁺ calculated for $[C_{22}H_{14}N_4 + H^+]$ 335.12912; found 335.12826. Elemental

Table	1	
Experi	mental	details

Crystal data	
Chemical formula	$C_{22}H_{14}N_4$
M _r	334.37
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	106
a, b, c (Å)	3.7610 (3), 13.2538 (9), 18 8657 (19)
β (°)	91 226 (9)
$V(\dot{A}^3)$	940 19 (14)
7	2
Radiation type	Μο Κα
(mm^{-1})	0.07
μ (mm) Γ	0.07 $0.40 \times 0.06 \times 0.03$
Crystal size (lillil)	0.40 × 0.00 × 0.05
Data collection	
Diffractometer	Agilent Xcalibur Eos Gemini
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2011)
T_{\min}, T_{\max}	0.974, 1.000
No. of measured, independent and	3520, 1846, 1396
observed $[I > 2\sigma(I)]$ reflections	, ,
R _{int}	0.030
$(\sin \theta/\lambda)_{\rm max}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.054, 0.155, 1.06
No. of reflections	1846
No. of parameters	118
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min}$ (e Å ⁻³)	0.20, -0.20

Computer programs: CrysAlis PRO (Agilent, 2011), SHELXS97 (Sheldrick, 2008), SHELXL97 (Sheldrick, 2008) and OLEX2 (Dolomanov et al., 2009).

analysis calculated (%): C 79.02, H 4.22, N 16.76; found: C 79.2, H 4.0, N 16.3; the absolute errors are 0.18% for C, 0.22% for H and 0.34% for N.

It should be noted that the solvent used for the condensation reaction should be methanol, not ethanol, since the use of ethanol would mostly convert 2-methoxytropone to 2-ethoxytropone and (I) would not be obtained. The preparation of benzene-1,4-dicarboximidamide hydrochloride, *i.e.* (4), and



Figure 1

Thermogravimetric analysis of (I). The heating rate was 10 K min $^{-1}$ under an N_{2} flow.

2-methoxytropone, (2), are described in the supporting information, as are their specific characterizations.

Yellow needle-shaped crystals of (I) suitable for singlecrystal X-ray analysis were grown *via* slow evaporation from a mixed solvent of dichloromethane and methanol (3:1 ν/ν) at room temperature for 3 d. Elemental analysis (vario EL elemental analyser) and themogravimetric differential scanning calorimetry (SDT Q600 analyser, under a nitrogen flow, 10 K min⁻¹) investigations were carried out to determine the amount of solvent in the crystal. Powder X-ray diffraction studies were also carried out (Shimadzu XRD-7000) with Cu K α radiation to analyse the phase purity of the bulk sample of (I).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. C-bound H atoms were placed in calculated positions and treated using a riding-model approximation, with C-H = 0.93 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. A region of electron density was removed using the SQUEEZE (Spek, 2015) procedure in *PLATON* (Spek, 2009). SQUEEZE calculated two voids with a volume of approximately 96 Å³ occupied by 16 electrons per unit cell.

2.3. Computational methods

The crystal structure parameters of (I) were used in the calculations without any optimization. All calculations were performed using *GAUSSIAN09* software (Revision A.02; Frisch *et al.*, 2009). Density functional theory (DFT) calculations were carried out at the B3LYP/6-311G(d,p) level for the gas state. The polarizability, the first hyperpolarizability tensor components, the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) were all displayed based on the crystal structure parameters without any optimization, and details are presented in the supporting information.

2.4. UV-Vis absorption and fluorescence studies

The general photophysical properties of (I) in solution were characterized in dichloromethane, including the UV–Vis absorption (8 × 10^{-5} mol l⁻¹) and fluorescence excitation/ emission (1 × 10^{-5} mol l⁻¹) spectra. The UV–Vis absorption spectrum was recorded on a Varian Cary 50 UV–Vis spectrophotometer and the fluorescence spectra were recorded on an FLS980 steady-state and time-resolved fluorescence spectrophotometer.

The solid-state photophysical properties of (I) were also studied. The UV–Vis absorption spectrum was recorded on a Shimazu UV3600Plus UV–Vis–NIR (NIR is near IR) spectrophotometer equipped with an integrating sphere. The fluorescence emission spectrum was recorded on an FLS980 steady-state and time-resolved fluorescence spectrophotometer.

2.5. Electrochemical study

The electrochemical properties of (I) in acetonitrile (CH₃CN) were studied on a CHI 660D workstation (CH Instruments Inc., China) with tetrabutylammonium hexa-fluorophosphate (Bu₄NPF₆) (0.1 mol l⁻¹) as electrolyte. A traditional three-electrode system, consisting of a bare GC ($\Phi = 3.0$ mm) working electrode, an Ag/AgCl (in 3.0 mol l⁻¹ KCl) reference electrode and a platinum wire auxiliary electrode, was used. The scan rate was 100 mV s⁻¹.

3. Results and discussion

3.1. Synthesis and characterization

Compound (I) was obtained in good yield as a pale-yellow powder through the condensation reaction of one equivalent of benzene-1,4-dicarboximidamide hydrochloride and three equivalents of 2-methoxytropone. The chemical structure was identified by ¹H NMR and ¹³C NMR spectroscopies, and ESI– MS (see supporting information). Compound (I) exhibits a low solubility in most solvents, except dichloromethane, chloroform and methanol, due to its expanded π -conjugated structure with no hydrophilic substitutions.

The elemental analysis results (see §2.1) are well within the margin of error, suggesting that almost no solvent molecules exist in the crystal. Thermogravimetric analysis (TGA) shows that there is a weight loss of only 0.8% below 473 K, confirming the presence of little or no solvent in the crystal (Fig. 1). From the powder X-ray diffraction (PXRD) results, we found that the patterns matched with the simulated results very well, confirming the phase purity of the bulk sample used for the other measurements (Fig. 2).



Comparison of the experimental PXRD pattern (red line) with the simulated pattern from the single-crystal structure (black line) for compound (I).

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Table 0

Selected geometric parameters (Å, °).							
1.353 (3)	C7-C8	1.393 (3)					
1.354 (3)	C7-C6	1.393 (3)					
1.359 (3)	C8-C9	1.387 (3)					
1.360 (3)	C5-C6	1.462 (3)					
1.468 (3)	C5-C11	1.397 (3)					
1.403 (3)	C10-C11	1.390 (3)					
1.399 (3)	C10-C9	1.393 (3)					
1.393 (3)							
12.0 (3)	C3-C2-C1-N2	-169.12 (17)					
-167.08 (18)	C3-C2-C1-N1	11.8 (3)					
	e parameters (Å, 1.353 (3) 1.354 (3) 1.359 (3) 1.360 (3) 1.468 (3) 1.403 (3) 1.399 (3) 1.393 (3) 12.0 (3) -167.08 (18)	$\begin{array}{c} \mbox{: parameters (Å, °).} \\ \hline 1.353 (3) & C7-C8 \\ 1.354 (3) & C7-C6 \\ 1.359 (3) & C8-C9 \\ 1.360 (3) & C5-C6 \\ 1.468 (3) & C5-C11 \\ 1.403 (3) & C10-C11 \\ 1.399 (3) & C10-C9 \\ 1.393 (3) \\ \hline 12.0 (3) & C3-C2-C1-N2 \\ -167.08 (18) & C3-C2-C1-N1 \\ \end{array}$					

Symmetry code: (i) -x + 1, -y + 1, -z.

3.2. Crystal structure of compound (I)

Short and straight golden needle-shaped crystals of (I) were obtained. The molecular structure is shown in Fig. 3(*a*). Selected geometric parameters are presented in Table 2. The single-crystal X-ray results indicate that (I) crystallizes in the monoclinic system (space group $P2_1/n$) (Fig. 3*a*) and that the unit cell consists of two molecules (Fig. 3*b*). The molecular structure of (I) shows that the two diazaazulene rings are coplanar, but there is a torsion angle of 11.8 (3)° (C3-C2-C1-N1; Table 2) between the diazaazulene and arene rings. This value is larger than that of the anologue previously reported by our group, namely 2-(4-aminophenyl)-6-nitro-1,3-diazaazulene (Ma *et al.*, 2011), whose twist is only 1.1° between the diazaazulene rings to the arene ring led to an increase of the



Figure 3

(a) The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. (b) The unit cell (colour key: C atoms dark grey, N atoms blue and H atoms light grey). [Symmetry code: (i) -x + 1, -y + 1, -z.]



Figure 4

Crystal packing diagrams of (I), showing (a) chains formed through π - π interactions along the *a* axis and (b) the three-dimensional architecture (the grey dashed lines represent weak C-H···N interactions).

dihedral angle between the conjugated rings in the crystal structure. In addition, the C-C bond lengths range from 1.387 (3) to 1.468 (3) Å (Table 2), falling in the range of typical C-C single (1.54 Å) and C-C aryl bonds (1.36 Å), and the C–N bond lengths range from 1.353(3) to 1.360(3) Å (Table 2), falling in the range of typical C–N single (1.47 Å)and double bonds (1.27 Å) (Zarei et al., 2017). These observations indicate good π -electron delocalization across the molecule of (I). In the crystal packing structure, one-dimensional chains are formed along the *a* axis through π - π interactions, with a centroid-centroid distance of 3.761 (1) Å and a centroid-plane distance of 3.465 (1) Å (Fig. 4a). Adjacent chains were stabilized by weak $C-H \cdots N$ interactions (Nobukuni et al., 2007), with a C···N distance of 3.548 (?) Å, forming a three-dimensional architecture (Fig. 4b). The wellorganized stacking performance of (I) through intermolecular interactions makes (I) promising as a π building block.

3.3. Photophysical properties

To illuminate the optical properties, the UV–Vis absorption and fluorescence spectra of (I) are shown in Fig. 5. Compound

Table 3 Summary of the energy properties of (I).

$E_{1/2}^{red}$ (V) ^a	LUMO $(eV)^b$	HOMO $(eV)^c$	$E_{\rm gap}/\lambda_{\rm max}$ [(eV) ^d /nm]	LUMO $(eV)^e$	$HOMO (eV)^e$	$E_{ m gap}$ (eV)
-1.67	-2.73	-5.95	3.22/385	-2.85	-6.02	3.37

Notes: (a) obtained from cyclic voltammograms; (b) calculated from cyclic voltammograms; (c) calculated according to the formula $E_{HOMO} = E_{LUMO} - E_{gap}$; (d) optical bandgap, $E_{gap} = 1240/\lambda_{max}$; (e) obtained from theoretical calculations.

(I) exhibited a main absorption peak at 385 nm with a shoulder at 405 nm in dichloromethane. In the crystal, (I) exhibited a broader absorption coverage ranging from 200 to 800 nm (Fig. 5a) due to the intermolecular interactions in the crystalline state. Absorption spectra were also recorded in other solvents with different polarities, and no obvious peakshape changes were observed, except for a slight red shift of the maximum absorption peak with decreasing solvent polarity (Fig. 1S of the supporting information). This is in good agreement with the results reported for 1,3-diazaazulene (Jinguji et al., 1985), indicating that the dipole moment of the ground state (μ_{e}) is larger than that of the excited state (μ_{e}) for (I) and that the ground state is difficult to polarize.

The fluorescence emission spectrum of (I) in solution indicates a main $S_1 \rightarrow S_0$ emission at 480 nm, with a Stokes shift



Figure 5 Normalized (a) absorption spectra and (b) fluorescence emission spectra of (I) in dichloromethane solution (black) and in the crystalline state

(red).



Figure 6

Cyclic voltammetry curve of (I) in acetonitrile.

of 95 nm, which is larger than for reported molecules with only one 1,3-diazaazulene component (Ma et al., 2011). However, the emission peak of (I) in the crystal is red shifted by 170 nm compared with that in solution, with a value of 650 nm; the peak shapes are similar. Results of lifetime studies show that (I) in dichloromethane solution displays a shorter lifetime of 1.03 ns, while (I) in the crystal displays an average lifetime of 1.89 ns (see Fig. 2S in the supporting information). This might be caused by the restricted motional freedom for (I) in the crystal (Chosrowjan et al., 2007).

3.4. Electrochemical properties

As shown in Fig. 6, (I) displays a pair of reduction/reoxidation peaks under negative voltage. When the potential scan moved towards positive voltage, no oxidation peak was observed. Therefore, (I) should be an inherent *n*-type organic semiconductor. The half-wave reduction potential for (I) is -1.67 V, in agreement with the LUMO energy level of -2.73 V, obtained according to the empirical equation $E_{\text{LUMO}} = -[4.4 + E^{\text{red}}] \text{ eV}$ (Hong *et al.*, 2011). The optical bandgap was obtained based on the wavelength of the observed maximum absorption peak. The HOMO energy level could then be calculated from the optical bandgap and the LUMO level, as shown in Table 3.

3.5. Calculation results

The theoretically calculated HOMO and LUMO energies were analyzed based on the crystal structure parameters (Fig. 3S and Table 1S of the supporting information). Data are listed in Table 3 and compared with the experimental electrochemical results. As can be seen, the calculated HOMO and LUMO energies are very close to the observed results and the calculated energy gap was 3.37 eV, in good agreement with the experimental data (3.22 eV), with a small difference of 0.15 eV. In addition, the polarizability and hyperpolarizability parameters of (I) are gathered in Table 2S of the supporting information according to the x, y and z components defined by Zarei et al.. (2017). However, (I) exhibited no nonlinear optical (NLO) properties due to its centrosymmetric nature.

4. Conclusion

In summary, 1,4-bis(1,3-diazaazulen-2-yl)benzene, (I), a novel chromophore based on 1.3-diazaazulene, was synthesized successfully in excellent yield using methanol as solvent. To the best of our knowledge, this is the first case where the synthesis and crystal structure of dimerized 1,3-diazaazulene have been discussed. Single-crystal X-ray diffraction results show that (I) is a centrosymmetric molecule, with the atoms arranged almost in a plane and forming a conjugation structure with 26- π electrons; it could thus serve as a π building block. One-dimensional chains are formed based on intermolecular π - π interactions and adjacent chains are stabilized by C-H···N interactions, forming a well-organized threedimensional architecture. In addition, the calculated HOMO, LUMO and bandgaps for (I) are very close to the experimental electrochemical results. Even though the first hyperpolarizability was zero due to its centrosymmetric characteristic according our calculations, it is believed that a good nonlinear optic performance could be expected if electron-donor/acceptor substituents were introduced to this novel π -conjugation backbone.

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Synthesis, crystal structure and photophysical properties of 1,4-bis(1,3-diazaazulen-2-yl)benzene: a new π building block

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO* (Agilent, 2011); data reduction: *CrysAlis PRO* (Agilent, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

2-[4-(Cyclohepta[d]imidazol-2-yl)phenyl]cyclohepta[d]imidazole

Crystal data

 $C_{22}H_{14}N_4$ $M_r = 334.37$ Monoclinic, $P2_1/n$ a = 3.7610 (3) Å b = 13.2538 (9) Å c = 18.8657 (19) Å $\beta = 91.226$ (9)° V = 940.19 (14) Å³ Z = 2

Data collection

Agilent Xcalibur Eos Gemini diffractometer Radiation source: Enhance (Mo) X-ray Source Graphite monochromator Detector resolution: 16.0971 pixels mm⁻¹ ω scans Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011) $T_{\min} = 0.974, T_{\max} = 1.000$

Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.054$ $wR(F^2) = 0.155$ S = 1.061846 reflections 118 parameters 0 restraints F(000) = 348 $D_x = 1.181 \text{ Mg m}^{-3}$ Mo *Ka* radiation, $\lambda = 0.7107 \text{ Å}$ Cell parameters from 868 reflections $\theta = 3.2-29.1^{\circ}$ $\mu = 0.07 \text{ mm}^{-1}$ T = 106 KNeedle, yellow $0.40 \times 0.06 \times 0.03 \text{ mm}$

3520 measured reflections 1846 independent reflections 1396 reflections with $I > 2\sigma(I)$ $R_{int} = 0.030$ $\theta_{max} = 26.0^\circ, \theta_{min} = 3.3^\circ$ $h = -4 \rightarrow 4$ $k = -16 \rightarrow 9$ $l = -23 \rightarrow 23$

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0762P)^{2} + 0.1696P] \qquad \Delta\rho$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3 \qquad \Delta\rho$ $(\Delta/\sigma)_{max} < 0.001$

 $\begin{array}{l} \Delta \rho_{\rm max} = 0.20 \ {\rm e} \ {\rm \AA}^{-3} \\ \Delta \rho_{\rm min} = -0.20 \ {\rm e} \ {\rm \AA}^{-3} \end{array}$

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 ($(Å^2)$
				p	· /

	x	У	Z	$U_{ m iso}$ */ $U_{ m eq}$	
N2	0.1546 (4)	0.52343 (13)	0.18448 (8)	0.0228 (4)	
N1	0.2047 (4)	0.68447 (13)	0.13999 (9)	0.0218 (4)	
C2	0.3804 (5)	0.54193 (16)	0.06353 (10)	0.0194 (5)	
C1	0.2471 (5)	0.58368 (16)	0.12997 (10)	0.0199 (5)	
C4	0.3503 (5)	0.43798 (16)	0.05077 (10)	0.0202 (5)	
H4	0.2500	0.3965	0.0847	0.024*	
C3	0.5311 (5)	0.60383 (15)	0.01219 (10)	0.0206 (5)	
Н3	0.5522	0.6729	0.0201	0.025*	
C7	-0.0754 (5)	0.55841 (17)	0.30062 (11)	0.0288 (5)	
H7	-0.0712	0.4894	0.3096	0.035*	
C8	-0.1973 (5)	0.61972 (18)	0.35492 (12)	0.0293 (5)	
H8	-0.2623	0.5862	0.3960	0.035*	
C5	0.0698 (5)	0.69108 (16)	0.20612 (11)	0.0218 (5)	
C6	0.0408 (5)	0.58873 (16)	0.23432 (10)	0.0220 (5)	
C10	-0.1619 (5)	0.79588 (17)	0.30496 (11)	0.0285 (5)	
H10	-0.2142	0.8622	0.3171	0.034*	
C11	-0.0212 (5)	0.78228 (17)	0.23809 (11)	0.0261 (5)	
H11	0.0165	0.8404	0.2117	0.031*	
С9	-0.2352 (5)	0.72377 (18)	0.35631 (11)	0.0289 (5)	
Н9	-0.3238	0.7495	0.3983	0.035*	

Atomic displacement parameters $(Å^2)$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U ²³
N2	0.0260 (9)	0.0237 (9)	0.0190 (9)	0.0004 (7)	0.0034 (7)	-0.0031 (7)
N1	0.0227 (8)	0.0240 (9)	0.0187 (8)	0.0019 (7)	0.0006 (7)	-0.0017 (7)
C2	0.0156 (9)	0.0254 (11)	0.0170 (10)	0.0012 (8)	-0.0021 (7)	-0.0007 (8)
C1	0.0165 (9)	0.0245 (10)	0.0187 (10)	-0.0008 (8)	-0.0019 (7)	-0.0015 (8)
C4	0.0189 (9)	0.0244 (11)	0.0174 (9)	0.0001 (8)	0.0002 (8)	0.0005 (9)
C3	0.0200 (9)	0.0202 (10)	0.0214 (10)	0.0016 (8)	-0.0012 (8)	-0.0008 (8)
C7	0.0334 (11)	0.0285 (12)	0.0248 (11)	-0.0039 (9)	0.0037 (9)	-0.0016 (10)
C8	0.0300 (11)	0.0368 (13)	0.0215 (11)	-0.0048 (10)	0.0066 (9)	-0.0045 (10)

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C5	0.0180 (9)	0.0269 (11)	0.0202 (10)	-0.0007 (8)	-0.0023 (8)	-0.0026 (9)
C6	0.0215 (9)	0.0248 (10)	0.0198 (10)	-0.0014 (8)	-0.0006 (8)	-0.0038 (9)
C10	0.0262 (10)	0.0301 (12)	0.0290 (12)	0.0048 (9)	-0.0023 (9)	-0.0119 (10)
C11	0.0266 (10)	0.0242 (10)	0.0276 (11)	0.0025 (9)	-0.0009 (9)	-0.0034 (9)
C9	0.0264 (10)	0.0393 (13)	0.0212 (11)	0.0020 (10)	0.0009 (9)	-0.0114 (10)

Geometric parameters (Å, °)

N2—C1	1.353 (3)	С7—С8	1.393 (3)
N2—C6	1.354 (3)	C7—C6	1.393 (3)
N1—C1	1.359 (3)	C8—H8	0.9300
N1—C5	1.360 (3)	C8—C9	1.387 (3)
C2—C1	1.468 (3)	C5—C6	1.462 (3)
C2—C4	1.403 (3)	C5—C11	1.397 (3)
C2—C3	1.399 (3)	C10—H10	0.9300
C4—H4	0.9300	C10—C11	1.390 (3)
C4C3 ⁱ	1.393 (3)	C10—C9	1.393 (3)
C3—C4 ⁱ	1.393 (3)	C11—H11	0.9300
С3—Н3	0.9300	С9—Н9	0.9300
С7—Н7	0.9300		
C1—N2—C6	103.92 (17)	C9—C8—C7	129.0 (2)
C1—N1—C5	103.78 (17)	C9—C8—H8	115.5
C4—C2—C1	119.27 (17)	N1—C5—C6	107.83 (17)
C3—C2—C1	121.40 (19)	N1—C5—C11	123.49 (19)
C3—C2—C4	119.32 (17)	C11—C5—C6	128.68 (19)
N2—C1—N1	116.20 (16)	N2—C6—C7	123.3 (2)
N2—C1—C2	121.62 (19)	N2—C6—C5	108.26 (17)
N1—C1—C2	122.17 (18)	C7—C6—C5	128.43 (19)
C2—C4—H4	119.6	C11—C10—H10	115.6
C3 ⁱ —C4—C2	120.73 (18)	C11—C10—C9	128.8 (2)
C3 ⁱ —C4—H4	119.6	C9-C10-H10	115.6
С2—С3—Н3	120.0	C5—C11—H11	116.4
C4 ⁱ —C3—C2	119.95 (18)	C10-C11-C5	127.3 (2)
C4 ⁱ —C3—H3	120.0	C10-C11-H11	116.4
С8—С7—Н7	116.3	C8—C9—C10	130.3 (2)
C8—C7—C6	127.4 (2)	С8—С9—Н9	114.8
С6—С7—Н7	116.3	С10—С9—Н9	114.8
С7—С8—Н8	115.5		
N1C5	-0.7 (2)	C3—C2—C4—C3 ⁱ	0.1 (3)
N1—C5—C6—C7	178.37 (19)	C7—C8—C9—C10	-0.4(4)
N1—C5—C11—C10	179.60 (19)	C8—C7—C6—N2	-179.84 (19)
C1—N2—C6—C7	-178.87 (18)	C8—C7—C6—C5	1.3 (3)
C1—N2—C6—C5	0.2 (2)	C5—N1—C1—N2	-0.7 (2)
C1—N1—C5—C6	0.8 (2)	C5—N1—C1—C2	178.42 (16)
C1-N1-C5-C11	-178.90 (19)	C6—N2—C1—N1	0.3 (2)
$C1-C2-C4-C3^{i}$	178.97 (16)	C6—N2—C1—C2	-178.84 (16)

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C1-C2-C3-C4 ⁱ	-178.94 (16)	C6—C7—C8—C9	0.6 (4)	
C4—C2—C1—N2	12.0 (3)	C6—C5—C11—C10	0.0 (4)	
C4—C2—C1—N1	-167.08 (18)	C11—C5—C6—N2	178.99 (19)	
$C4$ — $C2$ — $C3$ — $C4^{i}$	-0.1 (3)	C11—C5—C6—C7	-2.0 (3)	
C3—C2—C1—N2	-169.12 (17)	C11—C10—C9—C8	-1.6 (4)	
C3—C2—C1—N1	11.8 (3)	C9—C10—C11—C5	2.1 (4)	

Symmetry code: (i) -x+1, -y+1, -z.