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A Direct Assembly Approach to the Synthesis of *N*,*N*′-Bridged Calix[4]pyrroles: The Synthesis of a 1,5-Diazacyclononatriene Locked in a Saddle Conformation

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Ring closure of 1,2-bis(1-pyrrolylmethyl)benzene in the acid-catalysed condensation with acetone yields the 1,5-diazacyclononatriene [o-$C_6H_4(CH_2NC_4H_3\text{-}2)_2C(CH_3)_2$] as the sole identifiable product. The twisted or saddle conformation of the 1,5-diazacyclononatriene, which was confirmed by X-ray crystal structure determination, is conformationally rigid in solution. The conformation of the 1,5-diazacyclononatriene prevents the formation of the target *N*,*N*′-bridged calix[4]pyrrole by further acid-catalysed condensation with acetone, the reaction affording unidentified oligomers/polymers instead. The acid-catalysed condensation of 1,3- and 1,4-bis(1-pyrrolylmethyl)benzene with acetone also yields unidentified oligomers/polymers.

Keywords: Calix[4]pyrrole; Porphyrinogen; Synthesis; Macrocycle; Pyrrole

INTRODUCTION

Porphyrinogens, **I** (also termed calix[4]pyrroles), are a class of macrocycle that have been known for over a century [1] but have only recently begun to attract interest in the arenas spanning separation science, supramolecular and organometallic chemistry [2]. The latter application usually involves the macrocycle in its tetradeprotonated form, and a great breadth of unique reactivities has been established in the past decade [3,4].

The synthesis of *N*-alkylated calix[4]pyrroles (**II**, for example) have been reported as separable mixtures by alkylation of the parent calix[4]pyrrole [5] and earlier biomimetic approaches have been used to prepare *N*,*N*′,*N*″,*N*‴-tetramethyl and *N*,*N*′-bridged species [6–9]. Partially *N*-substituted calix[4]pyrroles such as **II** are, in some ways, better suited to the needs of metals in lower oxidation states because of the reduced maximum anionic charge of the macrocycle when *N*-deprotonated. We have shown that *N*,*N*′-dimethyl derivatives allow better structural control in s- and f-block organometallic chemistry [10,11] and have led to both unusual reactivities [12] and the stabilization of otherwise reactive metal bound functionalities [13]. We also aim to access and exploit *N*,*N*′-bridged calix[4]pyrroles, **III**–**VI**, which will serve additionally to restrict the conformational possibilities of the macrocycles. In the case of **V** and **VI**, we aim to capitalise on the opportunities for studying metal reactivity within the inert solvent-like cavity of the metallated calix[4]pyrroles. For the calix[4]pyrroles **III** and **IV**, this strategy could lead to the possible encapsulation of metal ions or zero-valent metal complexes within the cavity of the completely *N*-substituted calix[4]pyrroles.

Herein we report preliminary results of our strategy towards the direct assembly of modified calix[4]pyrroles using bis (1-pyrrolylmethyl)benzene scaffolds (or templates [14]) on which to build the target macrocycles **III** and **IV** by the acid-catalysed condensation of ketones.

RESULTS AND DISCUSSION

Synthesis

The attempted synthesis of modified calix[4]pyrroles of types **III** and **IV** using bis(1-pyrrolylmethyl)benzene scaffolds is outlined in Scheme 1.

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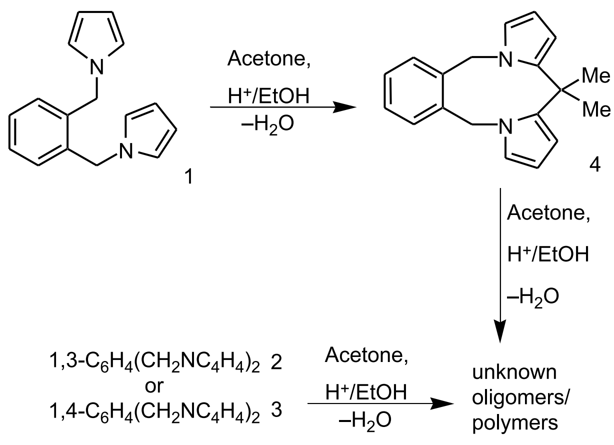

SCHEME 1

In the case of the bis(1-pyrrolyl)-substituted *o*-xylene **1**, acid-catalysed condensation with acetone yields the 1,5-diazacyclononatriene **4**. The medium-sized ring intermediate **4** reacts further to give ill-defined oligomeric/polymeric products arising from electrophilic substitution of the pyrrolyl rings in the 5 position.[1] The formation of the desired *cis*,*cis*-dibridged calix[4]pyrrole **IV** is not observed because the twisted, or saddle, conformation of the heterocycle **4** prevents the final ring closure of the expected 5,5′-bis(pyrrolyl)-di(methyl)methane-coupled 1,5-diazacyclononatrienes, as can be seen from the projection given in Fig. 1. The earlier successful synthesis of a *cis*,*cis*-dibridged calix[4]pyrrole [6b] was shown to proceed through a structurally authenticated eight-membered cyclic bis(pyrrolyl)methane intermediate analogous to **4**, although in that case the intermediate exhibited a crown-type conformation that did not prohibit subsequent macrocyclization to give the calix[4]pyrrole. Variable-temperature ^{1}H NMR studies of the 1,5-diazacyclononatriene **4** show that the saddle conformation is locked at room temperature, with fluxional exchange of the inequivalent benzylic protons only occurring at above 150°C in d_6-DMSO. The formation of well-defined products is not observed in the analogous reactions involving the bis(1-pyrrolyl)-substituted *m*- and *p*-xylenes **2** and **3**.

Crystal Structure

The twist or saddle C_2 symmetric conformation of the 1,5-diazacyclononatriene **4** was confirmed in the solid state by X-ray crystal structure determination (Fig. 1). Of the possible conformations for cyclononatriene-related species, the saddle conformation observed here has only been reported previously for the thiophene-based cyclotris(dimethylthiophenylene) [15], the monoketone derivative of cyclotriveratrylene [16], and a cyclononatripyrrole [17] (the conformations of which are fluxional at room temperature in solution [18]). Far more common for cyclononatrienes is the so-called crown or bowl conformation adopted by cyclotriveratrylenes and related macrocycles without exception; these compounds are locked rigidly into this conformation even at elevated temperatures in solution [19]. This conformation has led to cyclotriveratrylene and related molecules having been exploited in recent years as host molecules for neutral [20–23] and anionic [24] guests within their shallow bowl-shaped cavity.

Relatively little strain in the medium-sized nine-membered ring of the 1,5-diazacyclononatriene **4** is apparent by the cyclic angles subtended at the saturated carbon centres, ranging from 111.2(1) to 116.3(1)°. Close contacts are observed across the ring between two of the benzylic protons and the nitrogen centres of the pyrrolyl rings [C7(13)···N14(8) = 3.061(2)–3.028(2) Å]. The reason for the stability of the saddle conformation of **4** is unclear, although cross-ring interactions between one of the geminal methyl groups and benzylic protons in the crown conformation are possibly influential, based on modelling studies. Summaries of important bond lengths, angles and ring torsion angles are given in the caption to Fig. 1.

MATERIALS AND METHODS

1,2-, 1,3- and 1,4-Bis(1-pyrrolylmethyl)benzene, **1–3**, were prepared by adaptations of the published procedure for **3** with yields of 84–90% [25]. Other chemicals were obtained from Aldrich and used as received. Solvents were used as received as technical-grade solvents. ^{1}H and ^{13}C NMR spectra were recorded on a JOEL JNM-GX 400 spectrometer in $CDCl_3$ or d_6-DMSO and referenced to the residual ^{1}H resonance or the ^{13}C resonance of the deuterated solvent. Mass spectra were recorded on a Varian MAT 311a spectrometer. GC–MS were recorded on a Hewlett-Packard 5890 instrument.

Preparation of [*o*-$C_6H_4(CH_2NC_4H_3\text{-}2)_2C(CH_3)_2$], 4

To an ethanol solution (70 mL) of 1,2-bis(1-pyrrolylmethyl)benzene (200 mg, 0.85 mmol) were added acetone (500 mg, 8.6 mmol) and concentrated hydrochloric acid (5 drops of a 37% aqueous solution).[2]

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[1] By characteristic ^{1}H NMR resonances ($CDCl_3$) of 2,5-disubstituted pyrroles.

[2] The reaction carried out using a 1:1 1,2-bis(1-pyrrolylmethyl)benzene:acetone stoichiometry led to mixtures of **1**, **4** and unknown further condensed products from **4**. This stoichiometry represents a compromise between ease of isolation and product yield. GC/MS analysis of the crude reaction mixture indicates that there are no other detectable products besides **4**. Some decomposition of **4** occurs with sublimation to give **1** and other unidentified compounds.

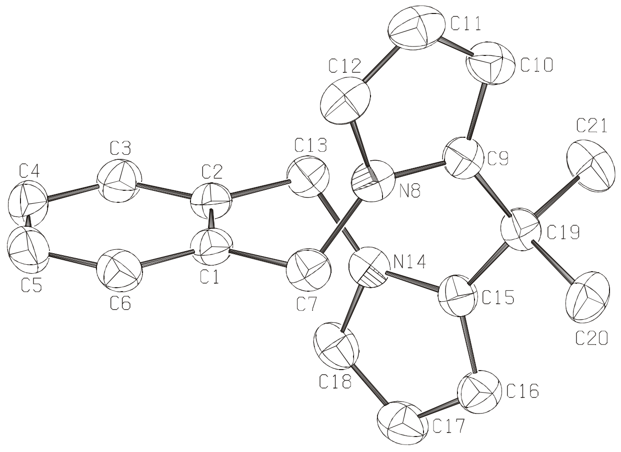

FIGURE 1 Molecular structure of [o-$C_6H_4(CH_2NC_4H_3\text{-}2)_2$-$C(CH_3)_2$] **4** showing the atom labelling scheme. Thermal ellipsoids were drawn at the 50% probability level. For clarity all hydrogen atoms are omitted. Selected bond distances (Å), angles (°) and ring torsion angles (°): C13···N8 3.028(2), C7···N14 3.061(2), H13B···N8 2.54(2), H7B···N14 2.61(2); C13—H13B···N8 109.7(4), C7—H7B···N14 107.6(4), C9—C19—C15 116.3(1), C1—C7—N8 112.4(1), C2—C13—N14 111.2(1); C7—C1—C2—C13 3.1(2), C1—C2—C13—N14 57.5(2), C2—C13—N14—C15 −106.3(2), C13—N14—C15—C19 −10.8(2), N14—C15—C19—C9 37.6(2), C15—C19—C9—N8 38.2(2), C19—C9—N8—C7 −7.6(2), C9—N8—C7—C1 −107.3(2), N8—C7—C1—C2 54.2(2).

The vessel was sealed and stirred at 50°C for 12 h to give a pale yellow solution and a small amount of white powder (unknown oligomer due to further condensation of the heterocycle **4**). The mixture was filtered and the solvent removed *in vacuo.* Hexane (100 mL) and water (100 mL) were then added to the pale brown oily residue. The hexane layer was separated and the aqueous layer extracted with hexane (2 × 100 mL). The hexane was removed *in vacuo* from the combined extracts, which were then purified by flash silica gel column chromatography (50:50% CH_2Cl_2:pentane), dried over anhydrous magnesium sulfate and evaporated to yield the product as a colourless oil that resisted crystallization. The product could be obtained as an analytically pure colourless crystalline solid in reduced yield by sublimation (110°C, 10^{-1} mbar), 100 mg (43%), mp 147°C. ^{1}H NMR ($CDCl_3$): δ 1.75 (s, 6H, Me), 4.48, 4.97 (d, AB, $^2J_{HH} = 15.36$ Hz, 2 × 2H, CH_2), 6.04, 6.13, 6.27 (m, ABC, 3 × 2H, CH(pyr.)), 7.13, 7.18 (m, AA′BB′, 2 × 2H, CH(benz.)). ^{13}C NMR ($CDCl_3$): δ 33.4 (Me), 35.9 (CMe_2), 49.7 (CH_2), 103.5, 108.5, 122.3, 127.7, 129.4 (5 × CH(pyr. and benz.)), 139.0, 140.9 (2 × C(pyr. and benz.)); MS (CI: m/z) 276 (M^+, 41%), 261 ($M^+ - Me$, 100%), 168 (90%). Anal. Calcd for $C_{19}H_{20}N_2$(%): C, 82.57; H, 7.29; N, 10.14. Found: C, 82.54; H, 7.31; N, 10.01.

Crystal Structure of [o-$C_6H_4(CH_2NC_4H_3\text{-}2)_2C(CH_3)_2$], 4

$C_{19}H_{20}N_2$, $M = 276.38$, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.6174(3)$, $b = 10.8429(3)$, $c = 13.0022(4)$ Å, $\beta = 92.677(2)°$, $V = 1495.22(7)$ Å^3, $Z = 4$, $D_{calc} = 1.228\ g\,cm^{-3}$, $F(000) = 592$, monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 0.7\ cm^{-1}$, $T = 193$ K. Colourless crystal (0.3 × 0.1 × 0.1 mm) grown by sublimation at 110°C (10^{-1} mbar). A total of 2936 unique reflections were measured on a Kappa CCD diffractometer, 2102 reflections with $F > 4.0\sigma(F)$. The structure was solved by direct methods using SHELXS-86 [26] and refined using SHELXL-93 [27]. PLATON was used for the molecular projection diagram [28]. Anisotropic thermal parameters were refined for all non-hydrogen atoms in the structure determination. Hydrogen atom positions were located and refined in x, y, z and U_{iso}. The final residuals were $R = 0.0446$ [$F > 4.0\sigma(F)$], 0.0717 (all data), $R_w = 0.1076$ (all data), $s = 1.035$, with 270 parameters. A final difference map had extreme values of $+0.14$ and -0.21 e Å^{-3}. Selected structural parameters are given in the caption to Fig. 1. CCDC 268197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

CONCLUSION

The direct assembly approach to the synthesis of N,N'-bridged calix[4]pyrroles has previously been shown to be a feasible methodology [6b]; however, we have established that the methodology is hindered by the appropriate choice of alkyl or aryl N,N'-bridges to complete the specific acid-catalysed ring closures necessary. These must dictate, in the case of *cis*-N,N'-bridging, that the intermediately formed cyclic bis(pyrrolyl)methane intermediate has a crown conformation for the successful completion of the subsequent assembly of the calix[4]pyrrole. We are continuing to explore the possible syntheses of N-modified calix[4]pyrroles, such as **III–VI**, for their application in organometallic and supramolecular synthesis.

Acknowledgements

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SUPPORTING INFORMATION

TABLE S1 Non-hydrogen atom parameters for **4**

Atom	x	y	z	sof	U_{eq}
C1	0.19321	0.80947	0.12976	1.00000	0.03027
	0.00013	0.00013	0.00011	0.00000	0.00035
C2	0.13069	0.92385	0.12451	1.00000	0.02991
	0.00013	0.00013	0.00011	0.00000	0.00034
C3	0.20028	1.03038	0.10960	1.00000	0.03772
	0.00015	0.00015	0.00012	0.00000	0.00039
C4	0.32962	1.02587	0.09915	1.00000	0.04344
	0.00015	0.00017	0.00012	0.00000	0.00043
C5	0.39132	0.91422	0.10541	1.00000	0.04378
	0.00016	0.00017	0.00012	0.00000	0.00044
C6	0.32316	0.80728	0.12054	1.00000	0.03732
	0.00014	0.00015	0.00012	0.00000	0.00039
C7	0.12376	0.68910	0.14445	1.00000	0.03305
	0.00014	0.00014	0.00013	0.00000	0.00036
N8	0.02053	0.67131	0.06756	1.00000	0.03151
	0.00011	0.00011	0.00009	0.00000	0.00030
C9	−0.10859	0.67848	0.07876	1.00000	0.03042
	0.00013	0.00012	0.00011	0.00000	0.00035
C10	−0.16437	0.66149	−0.01755	1.00000	0.03850
	0.00017	0.00014	0.00012	0.00000	0.00039
C11	−0.06945	0.64587	−0.08814	1.00000	0.04452
	0.00017	0.00015	0.00013	0.00000	0.00044
C12	0.04297	0.65260	−0.03450	1.00000	0.03888
	0.00017	0.00014	0.00012	0.00000	0.00040
C13	−0.00963	0.93525	0.13844	1.00000	0.03150
	0.00014	0.00014	0.00012	0.00000	0.00036
N14	−0.04368	0.88542	0.23796	1.00000	0.02967
	0.00010	0.00011	0.00009	0.00000	0.00030
C15	−0.10528	0.77647	0.25945	1.00000	0.02960
	0.00012	0.00013	0.00011	0.00000	0.00034
C16	−0.10171	0.76515	0.36487	1.00000	0.03703
	0.00014	0.00016	0.00012	0.00000	0.00039
C17	−0.03573	0.86724	0.40796	1.00000	0.04140
	0.00015	0.00016	0.00013	0.00000	0.00041
C18	−0.00058	0.93858	0.32896	1.00000	0.03705
	0.00015	0.00016	0.00012	0.00000	0.00038
C19	−0.17123	0.69284	0.18078	1.00000	0.03198
	0.00013	0.00013	0.00011	0.00000	0.00036
C20	−0.18361	0.56302	0.22828	1.00000	0.04248
	0.00018	0.00016	0.00015	0.00000	0.00042
C21	−0.30507	0.74526	0.15913	1.00000	0.04498
	0.00015	0.00018	0.00016	0.00000	0.00045

TABLE S2 Anisotropic non-hydrogen atom thermal parameters for **4**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.03230	0.03406	0.02448	0.00052	0.00163	0.00149
	0.00078	0.00084	0.00076	0.00063	0.00061	0.00063
C2	0.03280	0.03223	0.02450	0.00176	−0.00078	−0.00150
	0.00078	0.00081	0.00078	0.00063	0.00060	0.00065
C3	0.04288	0.03468	0.03537	0.00189	−0.00051	−0.00476
	0.00093	0.00090	0.00090	0.00071	0.00072	0.00076
C4	0.04333	0.05110	0.03585	−0.00072	0.00132	−0.01891
	0.00098	0.00109	0.00094	0.00081	0.00075	0.00089
C5	0.03115	0.06481	0.03548	−0.00512	0.00267	−0.00728
	0.00089	0.00126	0.00095	0.00083	0.00071	0.00085
C6	0.03347	0.04709	0.03143	−0.00289	0.00180	0.00336
	0.00085	0.00100	0.00086	0.00074	0.00066	0.00077
C7	0.03238	0.03071	0.03614	0.00154	0.00237	0.00709
	0.00079	0.00084	0.00093	0.00070	0.00070	0.00068
N8	0.03771	0.02621	0.03071	−0.00129	0.00268	0.00122
	0.00070	0.00063	0.00070	0.00052	0.00054	0.00053
C9	0.03375	0.02272	0.03460	−0.00055	−0.00033	−0.00067
	0.00079	0.00072	0.00085	0.00063	0.00064	0.00063
C10	0.04641	0.03042	0.03777	−0.00133	−0.00765	−0.00197
	0.00098	0.00083	0.00095	0.00068	0.00079	0.00074
C11	0.06789	0.03461	0.03087	−0.00459	0.00033	−0.00023
	0.00118	0.00092	0.00096	0.00075	0.00090	0.00081
C12	0.05153	0.03130	0.03459	−0.00348	0.01024	0.00223
	0.00107	0.00083	0.00093	0.00070	0.00082	0.00076
C13	0.03404	0.02353	0.03666	0.00273	−0.00136	0.00147
	0.00081	0.00076	0.00091	0.00069	0.00070	0.00066
N14	0.02996	0.02859	0.03039	−0.00233	0.00061	0.00148
	0.00064	0.00064	0.00069	0.00053	0.00053	0.00052
C15	0.02621	0.02997	0.03270	−0.00084	0.00218	0.00238
	0.00073	0.00077	0.00083	0.00064	0.00060	0.00062
C16	0.03614	0.04188	0.03323	0.00148	0.00339	0.00057
	0.00086	0.00094	0.00091	0.00075	0.00069	0.00074
C17	0.03993	0.05182	0.03204	−0.00729	−0.00265	0.00392
	0.00091	0.00105	0.00095	0.00083	0.00074	0.00079
C18	0.03444	0.03755	0.03883	−0.01011	−0.00191	−0.00080
	0.00081	0.00088	0.00094	0.00076	0.00069	0.00074
C19	0.02999	0.03089	0.03493	−0.00094	0.00015	−0.00091
	0.00075	0.00081	0.00085	0.00065	0.00064	0.00063
C20	0.04985	0.03458	0.04375	0.00112	0.00991	−0.00911
	0.00108	0.00089	0.00105	0.00080	0.00091	0.00083
C21	0.03242	0.05109	0.05092	−0.01067	−0.00364	0.00337
	0.00089	0.00115	0.00113	0.00096	0.00084	0.00081

TABLE S3 Hydrogen atom parameters for **4**

Atom	x	y	z	sof	U_{eq}
H3	0.15588	1.10935	0.10698	1.00000	0.04118
	0.00141	0.00153	0.00121	0.00000	0.00431
H4	0.37580	1.10137	0.09108	1.00000	0.04078
	0.00144	0.00152	0.00118	0.00000	0.00424
H5	0.48296	0.91044	0.09700	1.00000	0.04704
	0.00162	0.00148	0.00121	0.00000	0.00447
H6	0.36813	0.72383	0.12295	1.00000	0.04398
	0.00144	0.00157	0.00119	0.00000	0.00432
H7A	0.18213	0.62088	0.13671	1.00000	0.03264
	0.00135	0.00139	0.00108	0.00000	0.00387
H7B	0.08720	0.68494	0.21378	1.00000	0.02786
	0.00126	0.00122	0.00118	0.00000	0.00370
H10	−0.25376	0.66139	−0.03383	1.00000	0.03998
	0.00147	0.00141	0.00120	0.00000	0.00429
H11	−0.08021	0.63063	−0.16201	1.00000	0.05388
	0.00155	0.00157	0.00144	0.00000	0.00490
H12	0.12877	0.64558	−0.05620	1.00000	0.04624
	0.00155	0.00150	0.00125	0.00000	0.00465
H13A	−0.03214	1.02585	0.13772	1.00000	0.04022
	0.00134	0.00156	0.00112	0.00000	0.00413
H13B	−0.06079	0.89048	0.08358	1.00000	0.03653
	0.00139	0.00137	0.00120	0.00000	0.00406
H16	−0.14041	0.69941	0.40236	1.00000	0.04583
	0.00150	0.00153	0.00129	0.00000	0.00463
H17	−0.01989	0.88553	0.48278	1.00000	0.04988
	0.00149	0.00150	0.00136	0.00000	0.00472
H18	0.04846	1.01809	0.32491	1.00000	0.04809
	0.00146	0.00163	0.00121	0.00000	0.00452
H20A	−0.23118	0.50742	0.17770	1.00000	0.04420
	0.00142	0.00154	0.00123	0.00000	0.00439
H20B	−0.23097	0.56585	0.29464	1.00000	0.04476
	0.00145	0.00146	0.00132	0.00000	0.00445
H20C	−0.09777	0.52554	0.24484	1.00000	0.06437
	0.00183	0.00176	0.00141	0.00000	0.00552
H21A	−0.35698	0.68707	0.11295	1.00000	0.05265
	0.00160	0.00160	0.00138	0.00000	0.00487
H21B	−0.29977	0.82827	0.12193	1.00000	0.05054
	0.00151	0.00173	0.00130	0.00000	0.00484
H21C	−0.34946	0.75463	0.22593	1.00000	0.05185
	0.00157	0.00153	0.00145	0.00000	0.00482

TABLE S4 Bond lengths (Å) and angles (°) for **44**

C1—				
C6	1.391 (0.002)			
C2	1.407 (0.002)	118.60 (0.13)		
C7	1.516 (0.002)	119.12 (0.13)	122.28 (0.12)	
	C1—	C6	C2	
C2—				
C3	1.390 (0.002)			
C1	1.407 (0.002)	119.13 (0.13)		
C13	1.514 (0.002)	118.78 (0.13)	122.06 (0.13)	
	C2—	C3	C1	
C3—				
C4	1.387 (0.002)			
C2	1.390 (0.002)	121.31 (0.16)		
H3	0.977 (0.016)	120.37 (0.89)	118.32 (0.90)	
	C3—	C4	C2	
C4—				
C5	1.377 (0.002)			
C3	1.387 (0.002)	119.71 (0.16)		
H4	0.963 (0.016)	120.72 (0.91)	119.50 (0.92)	
	C4—	C5	C3	
C5—				
C4	1.377 (0.002)			
C6	1.386 (0.002)	119.60 (0.15)		
H5	0.985 (0.016)	119.98 (0.97)	120.40 (0.97)	
	C5—	C4	C6	
C6—				
C5	1.386 (0.002)			
C1	1.391 (0.002)	121.65 (0.15)		
H6	1.023 (0.017)	119.90 (0.87)	118.43 (0.87)	
	C6—	C5	C1	
C7—				
N8	1.461 (0.002)			
C1	1.516 (0.002)	112.41 (0.12)		
H7A	0.973 (0.015)	106.84 (0.82)	109.00 (0.83)	
H7B	0.999 (0.015)	107.51 (0.76)	111.37 (0.77)	109.58 (1.15)
	C7—	N8	C1	H7A
N8—				
C12	1.374 (0.002)			
C9	1.388 (0.002)	109.04 (0.13)		
C7	1.461 (0.002)	121.45 (0.13)	129.34 (0.12)	
	N8—	C12	C9	
C9—				
C10	1.372 (0.002)			
N8	1.388 (0.002)	106.44 (0.13)		
C19	1.519 (0.002)	128.51 (0.14)	124.90 (0.12)	
	C9—	C10	N8	
C10—				
C9	1.372 (0.002)			
C11	1.405 (0.002)	108.68 (0.15)		
H10	0.963 (0.015)	125.43 (0.95)	125.89 (0.95)	
	C10—	C9	C11	
C11—				
C12	1.356 (0.002)			
C10	1.405 (0.002)	107.37 (0.15)		
H11	0.976 (0.018)	125.10 (1.01)	127.51 (1.00)	
	C11—	C12	C10	
C12—				
C11	1.356 (0.002)			
N8	1.374 (0.002)	108.45 (0.15)		
H12	0.969 (0.016)	131.51 (0.94)	120.04 (0.95)	
	C12—	C11	N8	
C13—				
N14	1.463 (0.002)			
C2	1.514 (0.002)	111.15 (0.11)		
H13A	1.011 (0.016)	107.39 (0.85)	108.16 (0.84)	
H13B	1.002 (0.016)	107.62 (0.85)	112.27 (0.85)	110.14 (1.17)
	C13—	N14	C2	H13A
N14—				
C18	1.375 (0.002)			
C15	1.385 (0.002)	108.98 (0.12)		
C13	1.463 (0.002)	121.34 (0.12)	129.19 (0.12)	
	N14—	C18	C15	
C15—				
C16	1.375 (0.002)			

N14	1.385 (0.002)	106.62 (0.13)		
C19	1.514 (0.002)	127.62 (0.14)	125.62 (0.13)	
	C15—	C16	N14	
C16—				
C15	1.375 (0.002)			
C17	1.412 (0.002)	108.40 (0.15)		
H16	0.966 (0.017)	125.20 (0.97)	126.38 (0.97)	
	C16—	C15	C17	
C17—				
C18	1.352 (0.002)			
C16	1.412 (0.002)	107.25 (0.15)		
H17	0.999 (0.017)	125.88 (0.95)	126.85 (0.95)	
	C17—	C18	C16	
C18—				
C17	1.352 (0.002)			
N14	1.375 (0.002)	108.74 (0.14)		
H18	1.010 (0.017)	133.58 (0.91)	117.68 (0.91)	
	C18—	C17	N14	
C19—				
C15	1.514 (0.002)			
C9	1.519 (0.002)	116.34 (0.12)		
C21	1.544 (0.002)	107.18 (0.12)	108.37 (0.13)	
C20	1.545 (0.002)	108.72 (0.13)	107.73 (0.12)	108.27 (0.14)
	C19—	C15	C9	C21
C20—				
C19	1.545 (0.002)			
H20A	1.010 (0.017)	109.44 (0.88)		
H20B	1.019 (0.017)	111.44 (0.91)	108.53 (1.24)	
H20C	1.012 (0.019)	111.00 (1.07)	108.47 (1.38)	107.88 (1.38)
	C20—	C19	H20A	H20B
C21—				
C19	1.544 (0.002)			
H21A	1.016 (0.018)	110.39 (0.94)		
H21B	1.025 (0.018)	109.82 (0.93)	107.87 (1.35)	
H21C	1.012 (0.019)	109.99 (0.95)	107.94 (1.37)	110.79 (1.37)
	C21—	C19	H21A	H21B

Selected torsion angles

C6—C1—C2—C3	0.46 (0.20)
C7—C1—C2—C3	− 179.18 (0.13)
C6—C1—C2—C13	− 177.28 (0.13)
C7—C1—C2—C13	3.08 (0.21)
C1—C2—C3—C4	0.45 (0.22)
C13—C2—C3—C4	178.26 (0.14)
C2—C3—C4—C5	− 1.18 (0.24)
C3—C4—C5—C6	0.97 (0.24)
C4—C5—C6—C1	− 0.06 (0.24)
C2—C1—C6—C5	− 0.66 (0.22)
C7—C1—C6—C5	178.99 (0.14)
C6—C1—C7—N8	− 125.47 (0.14)
C2—C1—C7—N8	54.17 (0.19)
C1—C7—N8—C12	67.58 (0.17)
C1—C7—N8—C9	− 107.27 (0.16)
C12—N8—C9—C10	1.14 (0.15)
C7—N8—C9—C10	176.49 (0.13)
C12—N8—C9—C19	177.06 (0.12)
C7—N8—C9—C19	− 7.60 (0.22)
N8—C9—C10—C11	− 0.94 (0.16)
C19—C9—C10—C11	− 176.65 (0.13)
C9—C10—C11—C12	0.39 (0.18)
C10—C11—C12—N8	0.32 (0.17)
C9—N8—C12—C11	− 0.92 (0.17)
C7—N8—C12—C11	− 176.70 (0.13)
C3—C2—C13—N14	− 120.22 (0.14)
C1—C2—C13—N14	57.52 (0.18)
C2—C13—N14—C18	64.72 (0.17)
C2—C13—N14—C15	− 106.32 (0.16)
C18—N14—C15—C16	1.31 (0.16)
C13—N14—C15—C16	173.22 (0.13)
C18—N14—C15—C19	177.25 (0.13)
C13—N14—C15—C19	− 10.84 (0.22)
N14—C15—C16—C17	− 0.84 (0.16)
C19—C15—C16—C17	− 176.68 (0.13)
C15—C16—C17—C18	0.07 (0.17)
C16—C17—C18—N14	0.74 (0.17)
C15—N14—C18—C17	− 1.29 (0.17)

C13—N14—C18—C17	−173.95 (0.12)
C16—C15—C19—C9	−147.33 (0.15)
N14—C15—C19—C9	37.58 (0.19)
C16—C15—C19—C21	91.26 (0.18)
N14—C15—C19—C21	−83.83 (0.17)
C16—C15—C19—C20	−25.56 (0.20)
N14—C15—C19—C20	159.36 (0.13)
C10—C9—C19—C15	−146.81 (0.14)
N8—C9—C19—C15	38.20 (0.19)
C10—C9—C19—C21	−26.03 (0.20)
N8—C9—C19—C21	158.98 (0.13)
C10—C9—C19—C20	90.90 (0.18)
N8—C9—C19—C20	−84.09 (0.16)

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