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Redetermination of the crystal structure of 5,14-dihydro-6,17-dimethyl-8,15-diphenyldibenzo(b,i)(1,4,8,11) tetra-azacyclotetradecine, $C_{32}H_{28}N_4$

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Abstract

$C_{32}H_{28}N_4$, monoclinic, $P2_1/c$ (no. 14), a = 17.7218(4) Å, b = 20.7769(5) Å, c = 14.9434(3) Å, β = 113.598 (3)°, V = 5042.1(2) Å^3, Z = 8, $R_{gt}(F)$ = 0.0519, $wR_{ref}(F^2)$ = 0.1544, T = 294 K.

CCDC no.: 2256334

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

The brick-red free diphenyl macrocycle, (I), was prepared employing the same procedure described in a recent study [5] using benzoyl acetone (2.592 g) instead of 2,4-pentanedione. Suitable crystals for the X-ray crystallographic study were prepared by the slow evaporation of the solution of (I) in a

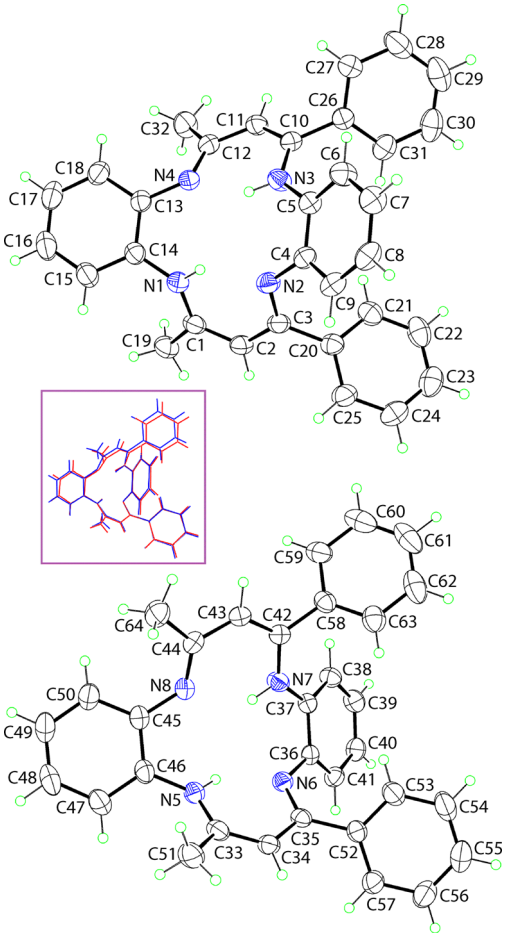

Table 1: Data collection and handling.

Crystal:	Red block
Size	0.14 × 0.08 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	0.57 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	61,154, 8987, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 7152
$N(param)_{refined}$:	662
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N1	0.63057 (11)	0.21429 (9)	0.97094 (12)	0.0515 (4)
H1N	0.5858 (10)	0.2334 (11)	0.9335 (15)	0.062*
N2	0.53963 (10)	0.31781 (9)	0.88668 (12)	0.0517 (4)
N3	0.45995 (11)	0.25619 (9)	0.71711 (12)	0.0526 (4)
H3N	0.4877 (14)	0.2318 (10)	0.7655 (13)	0.063*
N4	0.55001 (10)	0.15062 (8)	0.79833 (11)	0.0456 (4)
C1	0.69313 (13)	0.25547 (11)	1.01063 (14)	0.0521 (5)
C2	0.68113 (14)	0.32139 (11)	0.99288 (15)	0.0555 (5)
H2	0.725192	0.348257	1.027389	0.067*
C3	0.60834 (13)	0.35110 (10)	0.92742 (14)	0.0503 (5)
C4	0.46386 (12)	0.34405 (10)	0.82207 (14)	0.0459 (4)
C5	0.42139 (12)	0.31133 (10)	0.73432 (14)	0.0463 (4)
C6	0.34326 (13)	0.33192 (12)	0.67237 (16)	0.0587 (5)
H6	0.314576	0.309940	0.614396	0.070*
C7	0.30793 (14)	0.38477 (12)	0.69627 (18)	0.0614 (6)
H7	0.255718	0.398349	0.654253	0.074*
C8	0.34964 (14)	0.41736 (11)	0.78193 (18)	0.0592 (6)
H8	0.325959	0.453294	0.797427	0.071*
C9	0.42695 (14)	0.39674 (10)	0.84525 (17)	0.0543 (5)
H9	0.454413	0.418393	0.903854	0.065*
C10	0.45917 (12)	0.23380 (10)	0.63292 (14)	0.0447 (4)
C11	0.49909 (13)	0.17745 (10)	0.63006 (14)	0.0495 (5)
H11	0.494599	0.163851	0.568840	0.059*
C12	0.54629 (12)	0.13794 (10)	0.71038 (14)	0.0473 (4)
C13	0.59362 (11)	0.11363 (10)	0.88233 (14)	0.0465 (4)
C14	0.63390 (12)	0.14656 (11)	0.97152 (14)	0.0488 (5)
C15	0.67159 (15)	0.11160 (13)	1.05728 (16)	0.0639 (6)
H15	0.696281	0.133264	1.116396	0.077*
C16	0.67291 (17)	0.04492 (14)	1.05598 (19)	0.0736 (7)
H16	0.699779	0.022136	1.113648	0.088*
C17	0.63464 (17)	0.01270 (13)	0.9697 (2)	0.0719 (7)
H17	0.635836	−0.032042	0.968731	0.086*
C18	0.59406 (14)	0.04654 (11)	0.88376 (17)	0.0594 (5)
H18	0.566599	0.024057	0.825942	0.071*
C19	0.77959 (14)	0.23247 (13)	1.06839 (17)	0.0651 (6)
H19A[a]	0.815677	0.268865	1.090823	0.098*
H19B[a]	0.781090	0.207909	1.123496	0.098*
H19C[a]	0.797174	0.205952	1.027726	0.098*
H19D[a]	0.780284	0.186286	1.070540	0.098*
H19E[a]	0.814870	0.247242	1.037867	0.098*
H19F[a]	0.798787	0.249199	1.133637	0.098*
C20	0.61502 (13)	0.41936 (11)	0.89907 (15)	0.0505 (5)
C21	0.60038 (14)	0.43395 (13)	0.80336 (16)	0.0603 (6)
H21	0.585579	0.401381	0.756791	0.072*
C22	0.60753 (16)	0.49659 (15)	0.7760 (2)	0.0728 (7)
H22	0.598641	0.505655	0.711624	0.087*
C23	0.62777 (15)	0.54555 (14)	0.8439 (2)	0.0727 (7)
H23	0.631307	0.587755	0.825198	0.087*
C24	0.64254 (17)	0.53162 (13)	0.9384 (2)	0.0733 (7)
H24	0.655760	0.564557	0.984328	0.088*
C25	0.63804 (16)	0.46908 (12)	0.96673 (17)	0.0646 (6)
H25	0.650630	0.460077	1.032114	0.078*
C26	0.42112 (13)	0.27138 (10)	0.54026 (14)	0.0484 (5)
C27	0.35835 (16)	0.24507 (13)	0.46017 (17)	0.0683 (6)
H27	0.337628	0.204657	0.464771	0.082*
C28	0.3262 (2)	0.27863 (18)	0.3731 (2)	0.0947 (10)
H28	0.283336	0.260832	0.319670	0.114*
C29	0.3567 (2)	0.33777 (18)	0.3647 (2)	0.0915 (10)
H29	0.334418	0.360313	0.306089	0.110*
C30	0.4202 (2)	0.36344 (14)	0.4432 (2)	0.0793 (8)
H30	0.442011	0.403191	0.437417	0.095*
C31	0.45229 (16)	0.33075 (12)	0.53086 (19)	0.0634 (6)
H31	0.495143	0.348807	0.583974	0.076*
C32	0.59283 (17)	0.08498 (13)	0.68721 (19)	0.0698 (7)
H32A[a]	0.580331	0.085081	0.618488	0.105*
H32B[a]	0.650852	0.091519	0.723044	0.105*
H32C[a]	0.577172	0.044361	0.705241	0.105*
H32D[a]	0.625239	0.062227	0.746027	0.105*
H32E[a]	0.554718	0.055788	0.641471	0.105*
H32F[a]	0.628397	0.102946	0.659275	0.105*
N5	0.85358 (11)	0.22182 (8)	0.83225 (13)	0.0510 (4)
H5N	0.8979 (10)	0.2418 (11)	0.8388 (17)	0.061*
N6	0.94547 (10)	0.32469 (8)	0.83876 (11)	0.0448 (4)
N7	1.01554 (11)	0.26686 (9)	0.73130 (12)	0.0506 (4)
H7N	0.9880 (13)	0.2453 (10)	0.7569 (16)	0.061*
N8	0.93210 (10)	0.15837 (8)	0.73492 (12)	0.0472 (4)
C33	0.79168 (13)	0.26388 (11)	0.81390 (14)	0.0497 (5)
C34	0.80484 (12)	0.32959 (10)	0.81409 (14)	0.0459 (4)
H34	0.761638	0.356465	0.810072	0.055*
C35	0.87906 (11)	0.35946 (10)	0.81993 (12)	0.0418 (4)
C36	1.02174 (11)	0.34914 (9)	0.84551 (13)	0.0401 (4)
C37	1.05892 (11)	0.31840 (9)	0.78982 (13)	0.0420 (4)
C38	1.13667 (12)	0.33829 (11)	0.79888 (15)	0.0501 (5)
H38	1.161355	0.318764	0.761440	0.060*
C39	1.17731 (13)	0.38686 (11)	0.86318 (15)	0.0543 (5)
H39	1.229049	0.400005	0.868318	0.065*
C40	1.14216 (13)	0.41601 (10)	0.91969 (15)	0.0522 (5)
H40	1.170388	0.448221	0.963535	0.063*
C41	1.06453 (12)	0.39726 (10)	0.91112 (14)	0.0469 (4)
H41	1.040814	0.416939	0.949458	0.056*
C42	1.01915 (12)	0.24155 (10)	0.65022 (14)	0.0461 (4)
C43	0.98189 (14)	0.18351 (10)	0.61373 (15)	0.0513 (5)
H43	0.986371	0.168880	0.557238	0.062*
C44	0.93749 (13)	0.14359 (10)	0.65261 (15)	0.0484 (5)
C45	0.89150 (12)	0.12105 (10)	0.78052 (14)	0.0476 (5)
C46	0.85081 (13)	0.15404 (10)	0.83057 (15)	0.0503 (5)
C47	0.81487 (17)	0.11901 (13)	0.88226 (19)	0.0697 (7)
H47	0.787946	0.140584	0.915489	0.084*
C48	0.81851 (19)	0.05206 (14)	0.8851 (2)	0.0783 (8)
H48	0.793666	0.029282	0.919594	0.094*
C49	0.85843 (17)	0.01985 (12)	0.8375 (2)	0.0701 (7)
H49	0.860548	−0.024882	0.839079	0.084*
C50	0.89547 (14)	0.05356 (11)	0.78708 (17)	0.0599 (6)
H50	0.923946	0.031159	0.756481	0.072*
C51	0.70504 (15)	0.24006 (13)	0.7823 (2)	0.0664 (6)
H51A	0.667922	0.276015	0.765134	0.100*
H51B	0.699751	0.216552	0.834778	0.100*
H51C	0.691937	0.212340	0.726669	0.100*
C52	0.87404 (12)	0.42957 (10)	0.79436 (13)	0.0439 (4)
C53	0.90029 (14)	0.45110 (12)	0.72398 (17)	0.0607 (6)
H53	0.921874	0.422078	0.693061	0.073*
C54	0.89453 (17)	0.51588 (14)	0.6993 (2)	0.0786 (8)
H54	0.912919	0.529947	0.652475	0.094*
C55	0.86205 (18)	0.55944 (13)	0.7433 (2)	0.0771 (7)
H55	0.858818	0.602803	0.726703	0.093*

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C56	0.83443 (18)	0.53852 (12)	0.81182 (18)	0.0706 (7)
H56	0.812592	0.567794	0.842117	0.085*
C57	0.83897 (15)	0.47399 (11)	0.83599 (15)	0.0578 (5)
H57	0.818240	0.460048	0.880828	0.069*
C58	1.05683 (13)	0.27752 (10)	0.59236 (14)	0.0496 (5)
C59	1.11143 (15)	0.24678 (13)	0.56110 (17)	0.0635 (6)
H59	1.127636	0.204675	0.580478	0.076*
C60	1.14202 (18)	0.27870 (18)	0.5009 (2)	0.0813 (9)
H60	1.178443	0.257886	0.479838	0.098*
C61	1.1186 (2)	0.34059 (19)	0.47263 (19)	0.0916 (10)
H61	1.139330	0.361902	0.432608	0.110*
C62	1.0648 (2)	0.37138 (16)	0.50287 (19)	0.0831 (9)
H62	1.048891	0.413458	0.482996	0.100*
C63	1.03398 (16)	0.34053 (12)	0.56257 (16)	0.0636 (6)
H63	0.997649	0.361973	0.583081	0.076*
C64	0.89527 (18)	0.08669 (12)	0.58934 (19)	0.0705 (7)
H64A[a]	0.908291	0.085711	0.532875	0.106*
H64B[a]	0.913944	0.047643	0.625927	0.106*
H64C[a]	0.836771	0.090570	0.569054	0.106*
H64D[a]	0.864380	0.063571	0.619029	0.106*
H64E[a]	0.858727	0.101640	0.525978	0.106*
H64F[a]	0.935900	0.058713	0.582850	0.106*

[a]Occupancy: 0.5.

solvent mixture of chloroform and xylene in the ratio of 1:1. X-ray crystallography proved the structure to be a known compound [6, 7].

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = 1.2–1.5 U_{eq}(C). The N-bound H atom was located in a difference map and refined with N–H = 0.86 ± 0.01 Å. The hydrogen atoms of three methyl groups, i.e. the C19-, C32- and C64-methyl groups, were modelled over two positions of equal weight and rotated 60° to each other. A number of reflections were omitted from the final cycles of refinement owing to poor agreement; see the CIF for details.

3 Comment

The crystal structure of the title macrocycle, (I), has been reported previously [6]; the molecule has also been characterised crystallographically as its 1:1 1,2-dichloroethane solvate [7]. In a recent study, the crystal structure [8] of the all methyl derivative of (I) was re-investigated [5]. The new data allowed a definitive analysis of the nature of the bonding in the N=C–C(H) = C–N(H) residue. The improved data reported here for (I) has similarly allowed a resolution of the bonding in the four N=C–C(H)–C–N(H) residues in the two independent molecules of (I).

Two independent molecules comprise the crystallographic asymmetric-unit of (I); their molecular structures are shown in the figure (35 % probability ellipsoids). To a first approximation, the molecular conformations of the independent molecules are equivalent (see below). The four nitrogen atoms define an approximate plane and feature intramolecular secondary-amine–N–H···N(imine) hydrogen bonds [N1–H1n···N2: H1n···N2 = 1.94(2) Å, N1···N2 = 2.680(3) Å with angle at H1n = 143 (2)°; N3–H3n···N4: H3n···N4 = 1.97(2) Å, N3···N4 = 2.698(3) Å with angle at H3n = 142.3 (18)°; N5–H5n···N6: H5n···N6 = 1.92(2) Å, N5···N6 = 2.665(3) Å with angle at H5n = 145 (2)°; and N7–H7n···N8: H7n···N8 = 2.02(2) Å, N7···N8 = 2.708(3) Å with angle at H7n = 136 (2)°] which close six-membered {···NC_3NH} synthons. When viewed side-on through the N_4 plane, the N-bound phenyl rings and the two methyl substituents lie to one side of the plane and the remaining chemistry lies to the other side of the plane. Thus, the molecule has the shape of a flattened bowl.

An overlay diagram of the N1-containing molecule (red image) and the inverse of the N5-containing molecule (blue image) is included as an insert in the figure. This diagram illustrates the closeness in conformation between the independent molecules. The differences between the molecules are not chemically significant and are best illustrated by the sequence of C4–C9/C13–C14 [44.06 (12)° cf. 50.62 (11)° for the equivalent angle in the N5-containing molecule], C4–C9/C20–C25 [63.02 (13)° cf. 59.86 (11)°], C4–C9/C26–C31 [64.99 (14)° cf. 65.34 (13)°], C13–C14/C20–C25 [21.56 (13)° cf. 10.43 (13)°], C13–C14/C26–C31 [28.54 (14)° cf. 17.27 (13)°] and C20–C25/C26–C31 [33.34 (15)° cf. 15.73 (13)°] dihedral angles.

Considerable delocalisation of π-electron density is noted in the formally N=C–C(H)=C–N(H) residues. Using the C14–N1(H)–C1–C2–C3=N2–C4 sequence as an example for the three remaining residues, the C3=N2 bond of 1.318(3) Å is consistent with a formal double bond. However, the experimentally equivalent C1–C2 and C2–C3 bond lengths, at 1.395(3) and 1.411(3) Å, respectively, are longer and shorter than formal double and single bonds, respectively. Further, the C1–N1 bond is shorter, at 1.337(3) Å, than that expected for a C–N single bond. The delocalisation extends to the fused six-membered rings as seen in the C4–N2 and C14–N1 bond lengths of 1.412(3) and 1.408(3) Å, respectively. Thus, with the possible exception of the C3=N2 bond, the bonding in the remaining atoms of the C14–N1(H)–C1–C2–C3=N2–C4 sequence more closely resembles the bonding, i.e. with extensive

delocalisation of π-electron density over this residue, when doubly-deprotonated (I) complexes to M = copper(II) [9] and M = nickel(II) [10], defining square-planar MN_4 geometries.

A search for directional interactions in the crystal of (I), with the aid of PLATON [11], only revealed a weak N-bound-phenyl–C–H···π(terminal phenyl) [C16–H16···Cg(C52–C57)^{i}: H16···Cg(C52–C57)^{i} = 2.96 Å, C16···Cg(C52–C57)^{i} = 3.723(3) Å and angle at H16 = 140° for symmetry operation (i): x, 1/2 – y, 1/2 + z] contact. These interactions occur between the independent molecules within a helical arrangement of molecules along the *b*-axis. This conclusion is supported by an analysis of the calculated Hirshfeld surfaces. Thus, with the program suite CrystalExplorer [12] and following standard procedures [13], the surface contacts were evaluated. Previous work [14] has shown how useful such an approach can be in distinguishing independent molecules in a crystal and how these results can confirm space group assignment.

The analysis of surface contacts in (I) indicates shows that 64.1 % of all surface contacts are due to H···H contacts. These are complimented by contributions by C···H/H···C [29.9 %] and N···H/N···N [4.0 %] along with very small contributions from C···C [1.5 %] and N···C/C···N [0.6 %] contacts. In terms of the individual molecules, the nature of the surface contacts closely resemble each other. The greatest difference is noted for H···H contacts where, for the N1-containing molecule, these account for 61.8 % of contacts which is less than 63.1 % for the N5-containing molecule. Smaller differences are noted for the C···H/H···C [32.0 % cf. 31.0 %] and N···H/N···N [4.7 % cf. 3.0 % contacts].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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