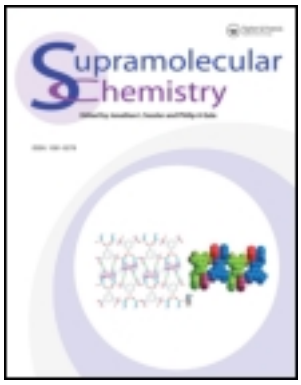

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New tetraaza[14]annulene receptors derived from 2,3-diaminonaphthalene: synthesis and crystal structures

Alicja Kaźmierska [a], Marlena Gryl [a], Katarzyna Stadnicka [a] & Julita Eilmes [a]
[a] Department of Chemistry, Jagiellonian University, Ingardena 3, Kraków, 30-060, Poland
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New tetraaza[14]annulene receptors derived from 2,3-diaminonaphthalene: synthesis and crystal structures

Alicja Kaźmierska, Marlena Gryl, Katarzyna Stadnicka and Julita Eilmes*

Department of Chemistry, Jagiellonian University, Ingardena 3, Kraków 30-060, Poland

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The first synthesis of the bis(2-hydroxybenzoyl)dinaphthotetraaza[14]annulene ligand and its *O,O*-bis-alkylated derivatives containing a decanedioxy bridging moiety, pendant bis-alkoxy groups as well as dicationic butoxypyridinium substituents is reported. The synthetic procedures, full analytical and spectroscopic characterisation (NMR, MS and IR) and crystal structures of the new products are described. The crystal structures show that naphthylene moieties incorporated into the investigated derivatives provide additional opportunities for non-covalent interactions between the molecules.

Keywords: dinaphthotetraaza[14]annulene; synthesis; receptors; crystal structure; non-covalent interactions

1. Introduction

Dibenzotetraaza[14]annulenes (DBTAAs) are interesting macrocycles for both theoretical and practical reasons. The publication of studies of their chemistry has been growing in recent years (*1–5*). Our laboratory has shown that DBTAAs exhibited remarkable peripheral reactivity, allowing the preparation of various derivatives with modified structures and properties (*2*). Thus, among other results, new DBTAA-based liquid crystals have been developed, as well as water-soluble derivatives with promising DNA/RNA-binding properties (*3, 4*). The latest progress made in this field concerns acid–base behaviour and tautomerism involving superstructured molecules produced by the peripheral derivatisation of simple DBTAA substrates (*5*).

In line with our previous results and the above-mentioned purposes, our present study focuses on a structurally related system containing 2,3-diamino-naphthalene moieties. The few previously published studies concerning the dinaphthotetraaza[14]annulene (DNTAA) system were mainly limited to the unsubstituted macrocycle and its transition metal complexes (*6*).

Compared with the DBTAA derivatives studied earlier in our group, the target molecule contains more extended aromatic moieties due to the incorporation of *o*-naphthylene units in the place of *o*-phenylene units. It is reasonable to presume that such a change in structure will influence the overall electronic system of the macrocyclic core, thus modifying properties that are crucial for potential applications. It is therefore expected that the features depending on π–π aromatic interactions, such as DNA-binding behaviour and the mesomorphic properties of materials derived from the DNTAA macrocycle, will differ remarkably from those corresponding to the *o*-phenylene-based analogues. Similarly, the acid–base behaviour of the free ligands is expected to be modified significantly. In addition, the new receptors are potential fluorescent probes based on the well-known fluorescence characteristics of *o*-diaminonaphthalene derivatives and their use for the detection and bioimaging of nitric oxide (*7*).

In this study, we report on the preparation of the previously unknown DNTAA ligand **1** and its derivatives, among which a bridged product **3** and water-soluble bis-pyridinium derivative **5** are of particular interest as a *lacunar*-type receptor and a potential DNA-binding agent, respectively. The crystal structures of **3**, **4** and **5** have been determined and analysed, paying special attention to non-covalent interactions. Scheme 1 outlines the reactions carried out.

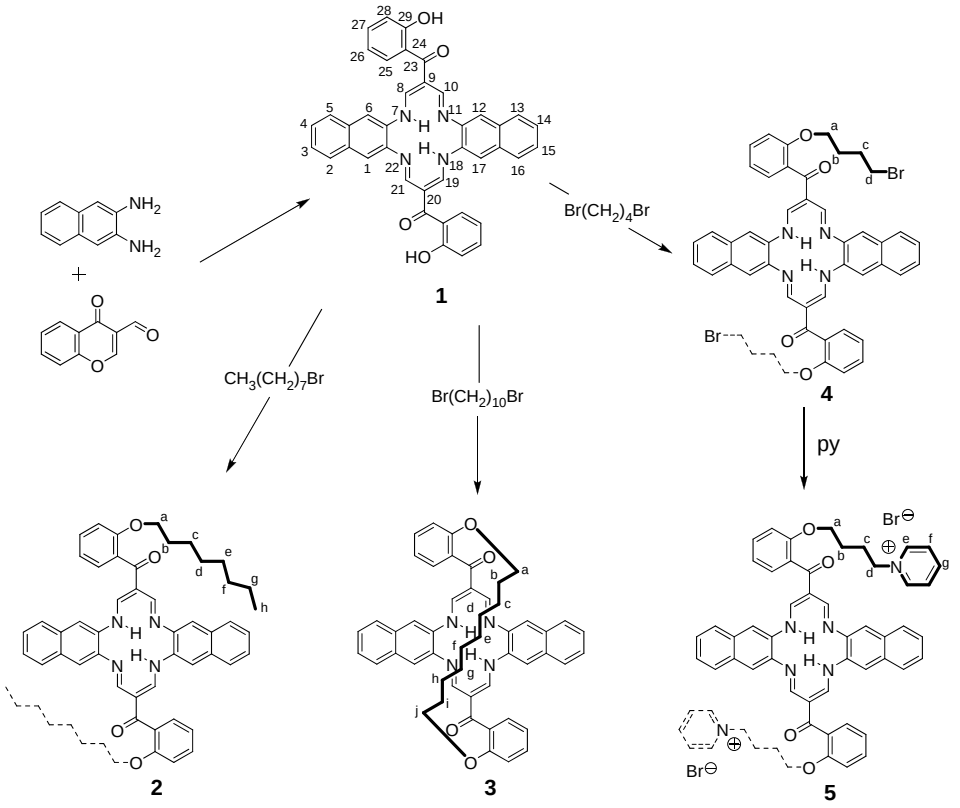
2. Results and discussion

2.1 Synthesis

9,20-Bis(2-hydroxybenzoyl)-7,18-dihydrodinaphtho[-b,i][1,4,8,11]tetraazacyclotetradecine (DNTAA) **1** was synthesised from 2,3-diaminonaphthalene and 3-formyl-chromone in 70% yield using a procedure analogous to that used earlier for the corresponding DBTAA ligand (*8*). To synthesise products **2**–**5** shown in Scheme 1, we used reactivity of OH groups at the *meso* benzoyl substituents of **1**.

Compounds **2**–**4** were synthesised via the alkylation of **1** with corresponding aliphatic bromides, carried out in anhydrous dimethylformamide (DMF) in the presence of anhydrous potassium carbonate. The lacunar product **3**

*Corresponding author. Email: jeilmes@chemia.uj.edu.pl



Scheme 1. Syntheses of DNTAA **1** and its *O*,*O*-bis-alkylated derivatives **2**–**5**.

was prepared by the bis-alkylation of **1** using 1,10-dibromodecane. To synthesise the dicationic derivative **5**, substrate **1** was transformed to dibromide **4**, which was subjected to the reaction with anhydrous pyridine.

All new products have been characterised by elemental analysis, HR-MS, ESI-MS, ^{1}H and ^{13}C NMR and IR spectroscopies. ^{1}H and ^{13}C NMR signals, their assignments and other spectroscopic and analytical data are collected in Section 3.

2.2 Crystallography

The structures of compounds **3**, **4** and **5** with the atom-numbering scheme are shown in Figures 1–3, respectively. Crystal data, data collection and structural refinement details are given in Table 1.

Compound **3** ($C_{50}H_{46}N_4O_4$) crystallises in space group $P2_1/c$ ($Z = 4$) with 0.90 $CHCl_3$ per lacunar molecule in the asymmetric part of the unit cell. Molecules of **3** occupy the general position of the space group. The chlorine atoms of the solvent molecules are disordered.

The conformation of the DNTAA moiety of **3** is not planar with the distortion from planarity of 0.1798(6) Å (rms deviation of the fitted atoms). The planes of two naphthalene rings: C6a-C22a and C11a-C17a, with the mean plane of the 14-membered ring form dihedral angles of 4.3(2)° and 14.0(1)°, respectively (Figure 1(a)). The dihedral angle between naphthalene rings themselves is 11.4(2)°. The benzoyl rings, C24-C29 and C42-C47, are at 53.5(1)° and 53.8(1)° dihedral angles against the tetraaza[14]annulene ring and at 73.4(2)° between themselves.

Crucial bond lengths and angles within the 14-membered ring are given in Table 2. The values of the appropriate valence angles at nitrogen atoms N7 and N18: C6a—N7—C8 = 124.0(5) and C17a—N18—C19 = 124.1(5)° confirmed H-atom localisations at the nitrogen atoms. On the contrary, the angles at N11 and N22: C10—N11—C11a = 120.3(5) and C21—N22—C22a = 121.5(5)° indicate the sp^2 hybridisation of the nitrogen atoms. The intramolecular H-bonds, N7—H7···N11 and N18—H18···N22, are described by the following geometrical parameters: 0.89(1), 2.07(4), 2.746(7) Å and 131(5)° and 0.89(1), 2.15(5), 2.764(8) Å and 126(5)°, respectively.

Packing of the molecules (Figure 1(b)) in the structure is governed by weak intermolecular C—H···O interactions (*9*) between benzoyl C—H and carbonyl groups: C43—H43···O23$^{x,-y+\frac{1}{2},z-\frac{1}{2}}$ and C44—H44···O48$^{-x+1,y+\frac{1}{2},-z-\frac{1}{2}}$, the geometrical parameters of which are given in Table 3. Relatively short distances between H-atoms and O-acceptors, 2.47 and 2.38 Å, respectively, and

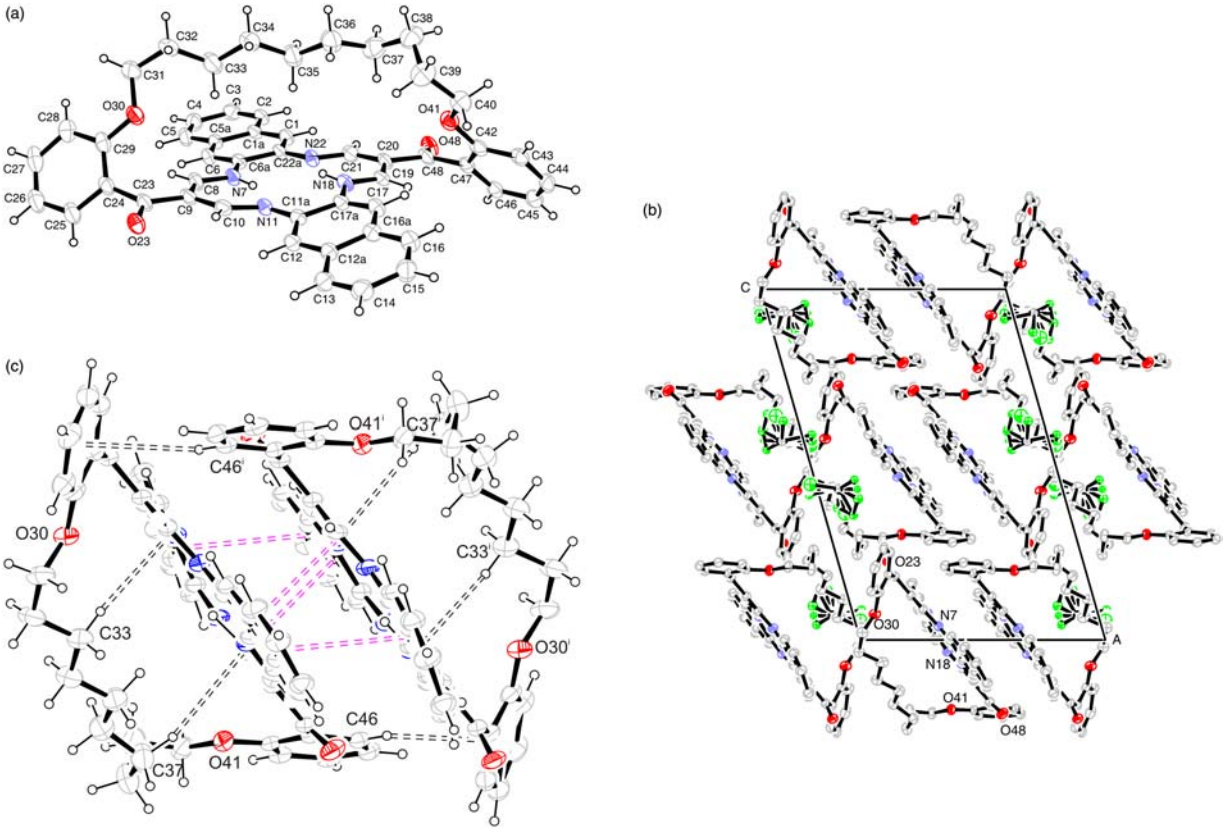


Figure 1. (a) Side view of **3** with the atom-numbering scheme. Atomic displacement ellipsoids are drawn at 30% probability level. The DNTAA ring is not planar, and the positions of H-atoms are localised at N7 and N18 nitrogen atoms. (b) Packing of **3** viewed in [0 1 0] direction. H-atoms were omitted for the clarity. The displacement ellipsoids are drawn at 30% probability level. The disordered molecules of chloroform are shown. (c) The pair of **3** related by the centre of symmetry at (1/2, 0, 0) due to π–π (dashed lines in magenta) and C—H···π (dashed lines in black) interactions (compare Table 3). The displacement ellipsoids are drawn at 50% probability level. Symmetry code i: $1-x, -y, -z$.

C—H···O angles close to 163° (almost linear H-bonds) seem to be significant for the crystal structure stability. Apart from mentioned H-bonds, the assembly is controlled by π–π interactions between naphthalene rings $Cg2\cdots Cg3^{-x+1,-y,-z}$ and between the naphthalene ring and pentanediimine system $Cg1\cdots Cg6^{-x+1,-y,-z}$ (Table 3), with the centroid–centroid distance of 3.709 and 3.742 Å, respectively. It is worth noting that Cg—Cg distances are considered to be in the range of 3.4–4.0 Å (*9*), whereas the distance of one ring centroid to the plane of another ring interacting via π–π should be *ca*. 3.40 Å. In the case of the dimer of **3**, the appropriate distances are as follows: $Cg6^{-x+1,-y,-z}$ to (C1 ∧ C6a) ring plane = 3.407(3) and $Cg3^{-x+1,-y,-z}$ to (C2 ∧ C5a) ring plane = 3.464 Å.

Packing of the molecules, shown in Figure 1(b),(c), also revealed intramolecular C—H···π interactions between alkyl CH_2 groups and pentanediimine system, the most significant of which are C33—H33a···Cg5 and C37—H37b···Cg6, with relatively short H···Cg distances of 3.12 and 3.13 Å and nearly linear CHCg angles of 175° and 157°, respectively.

Compound **4** crystallises in space group $P2_1/n$ with two centrosymmetric molecules of $C_{48}H_{42}Br_2N_4O_4$ in the unit cell (the asymmetric part contains one-half of the molecule). Conformation of **4** with the atom-numbering scheme is shown in Figure 2(a).

Essential bond lengths are given in Table 2. H-atoms at N2 and N9 are found to be disordered with the site occupancy factor of 0.5. The conformation of the DNTAA ring is chair like. The naphthalene moieties are parallel to each other and form the angles of 4.3(1)° with the inner fragment of the 14-membered ring, i.e. N2—C2a—C8a—N9—$N2^i$—$C2a^i$—$C8a^i$—$N9^i$ {(i) $-x+1, -y+1, -z+1$}, whereas the pentanediimine moiety forms the angle of 14.7(1)° against the naphthalene best planes.

Side chains in *meso* positions are antiperiplanar with dihedral angle of 88.47(5)° between 14-membered ring and the benzoyl best plane.

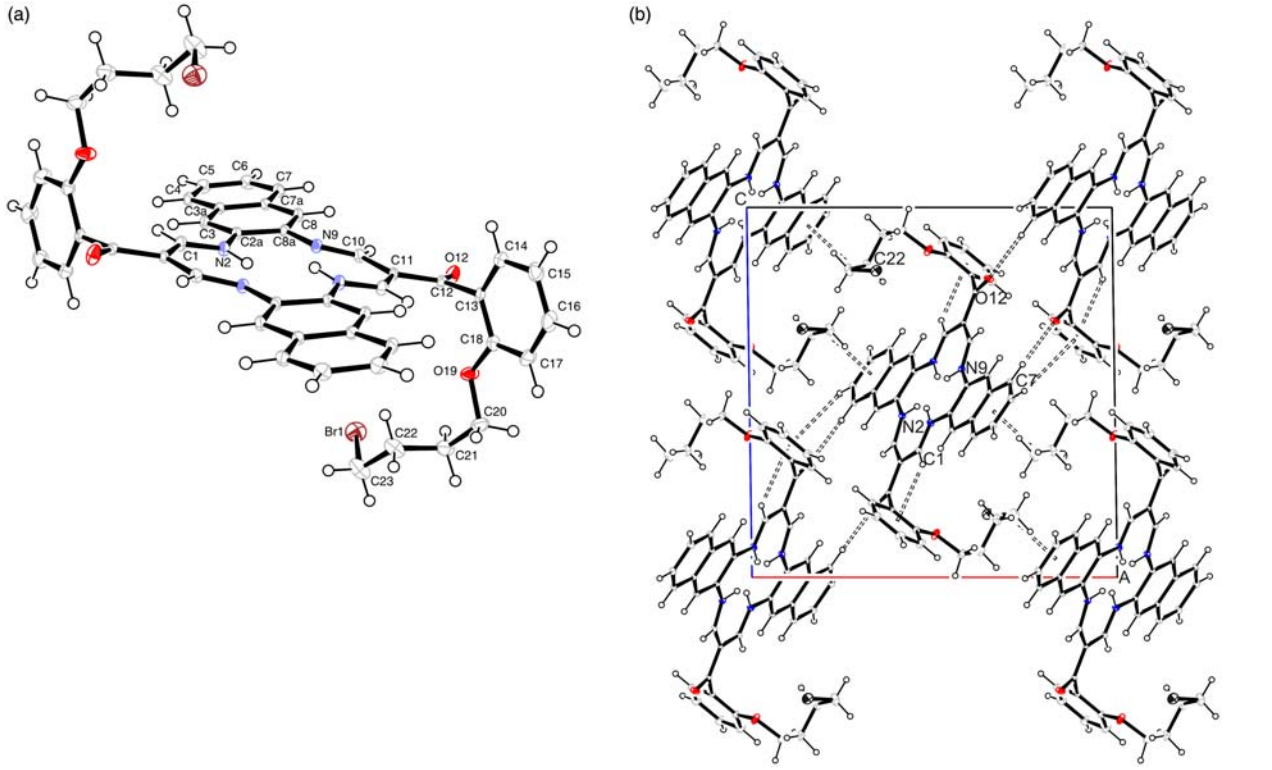


Figure 2. (a) View of **4** showing the conformation of DNTAA ring and antiperiplanar side chains with their atom-numbering scheme. Atomic displacement ellipsoids are drawn at 50% probability level. The molecule is centrosymmetric: $\bar{1}$ ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). H-atoms at nitrogen N2 and N9 are disordered with the side occupancy factor of 0.5. The H-atom at N9 is not shown. (b) Packing of **4** viewed in [010] direction. Note that H-atoms at nitrogen N2 and N9 are disordered with the side occupancy factor of 0.5. C—H···π interactions are marked by dashed lines (compare Table 3).

Packing of the molecules, shown in Figure 2(b), revealed weak interactions of C—H···O, C—H···π and π–π types, the geometrical parameters of which are given in Table 3. The structure is stabilised by intermolecular interactions between the aromatic C—H group and the oxygen atom of carbonyl group, with H7···O12$^{-x+1\frac{1}{2},y-\frac{1}{2},-z+1\frac{1}{2}}$ distance of 2.50 Å, between methine C1—H1 and benzoyl ring, with H1···Cg3$^{-x+1,-y+1,-z+1}$ distance of 2.92 Å and between the adjacent naphthalene rings Cg2···Cg2$^{-x+1,-y,-z+1}$, with the centroid–centroid distance of 3.542 Å.

In conclusion, the pseudo-hexagonal packing of the molecules in both **3** and **4** crystal structures is governed by weak interactions between C-H from benzoyl group (in **3**) or from naphthalene part (in **4**) and carbonyl C=O as well as by π–π interactions (in the mode face-to-face) between both naphthalene rings from one side and, either pentanediimine or naphthalene moieties. The behaviour of benzoyl fragment, together with edge-to-face interaction between the methine C1—H1 and the gravity centre of benzoyl ring as (Table 3), seems to play a significant role in intermolecular interactions of the molecules.

Compound **5** crystallises in space group $P\bar{1}$ ($Z=1$) with one tetraaza cation $C_{58}H_{52}N_6O_4^{2+}$, two bromide anions and two methanol molecules in the unit cell (the asymmetric part contains half of the contents).

Conformation of **5** with the atom-numbering scheme is shown in Figure 3(a),(b). Compound **5** is centrosymmetric: -1 ($\frac{1}{2}$,0,0). The values of bond lengths and angles for pentanediimine system in 14-membered ring are given in Table 2. H-atom at N9 and also that at N9$^{-x+1,-y,-z}$, are localised. The value of valence angle C10—N9—C8a = 125.7(1) in contrary to C1—N9—C2a = 118.2(1) confirms H-atom assignment. The geometrical parameters of intramolecular H-bond N9—H9···N2$^{-x+1,-y,-z}$ within 14-membered ring are as follows: 0.86(1), 2.09(2), 2.766(2) Å and 136(2)°. An intermolecular H-bond, O37—H37···Br1$^{x-2,y,z+1}$, is observed between the bromide anion and the methanol molecule, and has the following parameters: 0.82(1), 2.44(1), 3.253(1) Å and 169(2)°.

The conformation of the DNTAA ring is chair like and is similar to that found for compound **4**. Two naphthalene rings are parallel to each other. The dihedral angle between the inner fragment, N2—C2a—C8a—N9—N2^{ii}—C2a^{ii}—C8a^{ii}—N9^{ii} {(ii) $-x+1,-y,-z$}, of 14-membered ring and the naphthalene ring is 5.2(1)° and the pentanediimine system is inclined at 18.3(1) to the naphthalene ring best

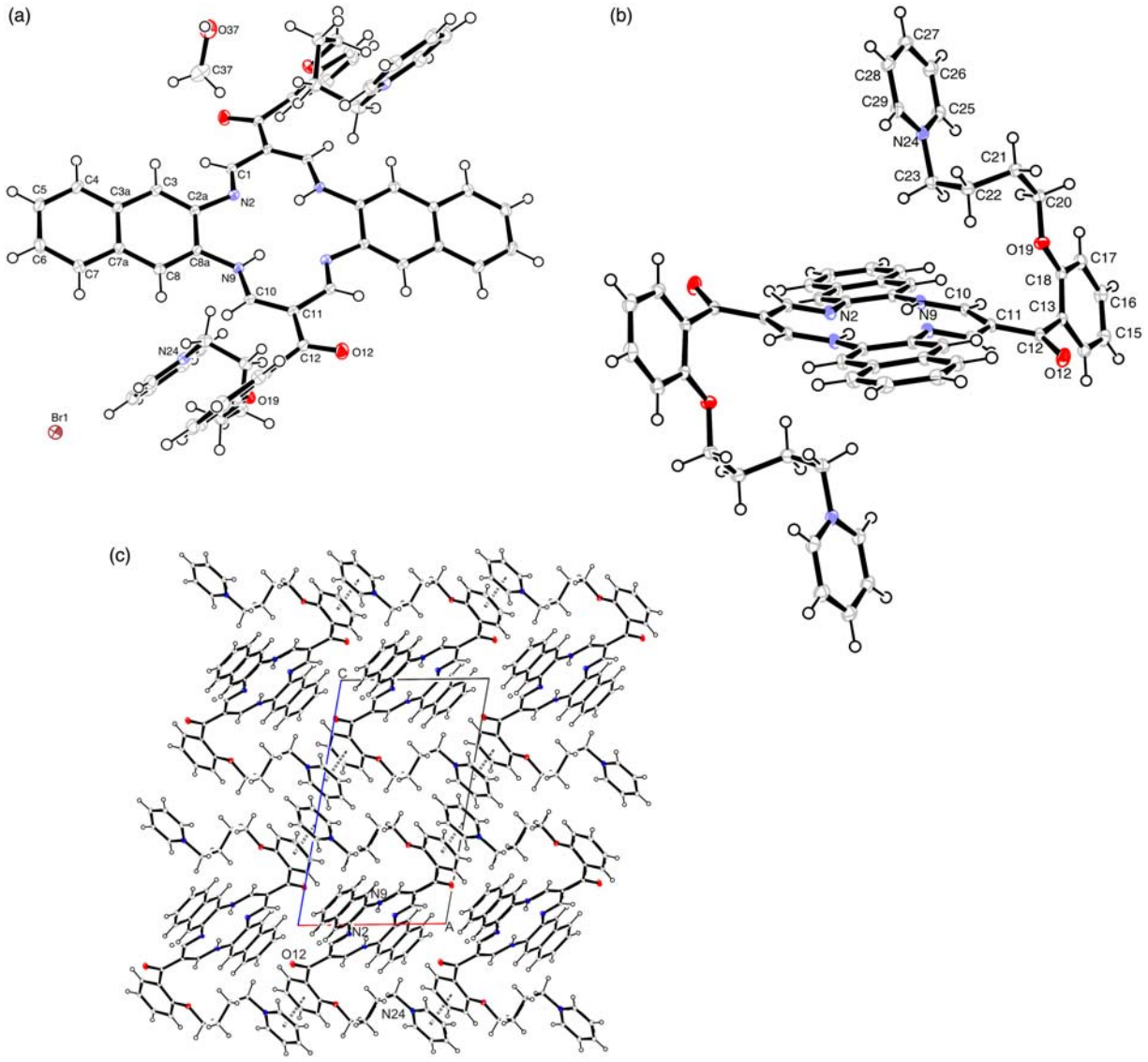


Figure 3. (a) View of **5** onto DNTAA ring with the atom-numbering scheme. Atomic displacement ellipsoids are drawn at 50% probability level. (b) View of **5** showing the conformation of tetraaza[14]annulene ring and antiperiplanar side chains with their atom-numbering scheme. Atomic displacement ellipsoids are drawn at 50% probability level. (c) Packing of **5** viewed in [010] direction. Methanol molecules and Br^- anions are omitted for clarity. $\pi-\pi$ interactions between the benzoyl and pyridine rings are marked by dashed lines (compare Table 3).

plane. The side chains (related by the centre of symmetry) are bent above and below the 14-membered ring with the angle of 69.34(3)° between the macro ring and the benzoyl ring.

Packing of the molecules, shown in Figure 3(c), revealed C—H···π and π−π interactions. The most significant were those between pyridine and benzoyl rings, with the Cg3···Cg4$^{-x+1,y,z}$ distance of 3.518 Å, and between naphthalene rings with the distances of Cg1···Cg2$^{-x+1,-y+1,-z}$ and Cg2···Cg2$^{-x+1,-y+1,-z}$ equal to 3.863 and 3.721 Å, respectively. The geometrical parameters characterising the intermolecular interactions are given in Table 3.

In comparison to **3** and **4**, **5** has additionally the pyridine moiety which also interacts with the benzoyl group in face-to-face mode despite being involved in C—H···Cg edge-to-face interaction (Table 3).

3. Experimental

3.1 General

2,3-Diaminonaphthalene, 3-formylchromone, 1-bromo-octane and 1,10-dibromodecane were purchased from commercial sources (Sigma-Aldrich), and were used as received. Solvents were dried using standard methods, and were freshly distilled before use.

Table 1. Crystal data, measurement details and structure refinement conditions.

Identification code	**3**	**4**	**5**
Crystal data			
Chemical formula	$C_{50}H_{46}N_4O_4$ 0.90 $CHCl_3$	$C_{48}H_{42}Br_2N_4O_4$	$C_{58}H_{52}N_6O_4^{2+}2Br^-\cdot 2CH_3OH$
Mr	874.34	898.66	1120.94
Temperature (K)	110(2)	110(2)	113(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	$a = 13.8790(8)$ $b = 15.7021(10)$ $c = 20.6126(12)$ $\beta = 105.886(6)$	$a = 15.8211(3)$ $b = 7.9364(1)$ $c = 16.0007(3)$ $\beta = 90.832(2)$	$a = 9.0889(2)$ $b = 9.3100(2)$ $c = 15.4082(4)$ $\alpha = 82.966(2)$ $\beta = 79.175(2)$ $\gamma = 87.680(2)$
V (Å^3)	4320.5(4)	2008.88(6)	1270.76(5)
$Z(Z')$, Dx (Mg/m^3)	4(1), 1.344	2(0.5), 1.486	1(0.5), 1.465
μ (mm^{-1})	0.246	2.069	1.656
F (0 0 0)	1833	920	580
Crystal size (mm)	0.48 × 0.44 × 0.13	0.37 × 0.13 × 0.06	0.35 × 0.25 × 0.10
Crystal form, colour	Plate, orange	Needle, orange	Plate, yellow
Data collection			
θ Range (°)	3.01–25.00	3.15–30.00	3.14–30.00
Data collection method	*CrysAlisPro1.171.35.15*[a]	*CrysAlisPro1.171.35.15*[a]	*CrysAlisPro1.171.35.15*[a]
Limiting indices	h, −16, 15; k, −18,16; l, −24, 20	h, −18, 22; k, −11, 11, l, −22, 22	h, −12,12; k, −12, 13, l, 0, 21
Reflections collected	12588	11134	26037
Reflections unique, R(int)	7597, 0.0742	5835, 0.0223	7398, 0.0366
Reflections $I > 2\sigma(I)$	5056	3859	6565
Completeness (%) to θ_{max}	0.998	0.997	0.999
T_{min}, T_{max}	0.8912, 0.9688	0.5148, 0.8859	0.7330, 0.7893
Refinement			
Data/restraints/parameters	7597/0/610	5835/2/268	7398/2/342
Goodness of fit	1.024	0.954	1.060
Final R indices [$I > 2\sigma(I)$]	$R^1 = 0.1001$, $wR^2 = 0.2286$	$R^1 = 0.0403$, $wR^2 = 0.1086$	$R^1 = 0.0331$, $wR^2 = 0.0846$
R indices (all data)	$R^1 = 0.1450$, $wR^2 = 0.2603$	$R^1 = 0.0632$, $wR^2 = 0.1124$	$R^1 = 0.0389$, $wR^2 = 0.0874$
Weighting scheme w[b]: A, B	0.0887, 11.0746	0.0648, 0.0000	0.0423, 0.5242
$\Delta\rho_{max}$, $\Delta\rho_{min}$, rms (e Å^{-3})	0.635, −0.327, 0.069	0.631, −0.565, 0.086	0.561, −0.921, 0.068

[a] CrysAlisPro, Agilent Technologies, CrysAlis171.NET.
[b] $w = 1/[\sigma^2(F_o^2) + AP^2 + BP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Bond lengths (Å) and angles (°) characteristic for pentanediimine system in 14-membered ring.

3		**4**		**5**	
N7—C8	1.333(6)	N9—C10	1.298(3)	C1—N2	1.297(2)
C6a—N7	1.409(7)	C8a—N9	1.407(3)	N2—C2a	1.416(2)
C10—N11	1.311(6)	C1—N2	1.308(3)	N9—C10	1.336(2)
N11—C11a	1.401(8)	N2—C2a	1.418(2)	C8a—N9	1.412(2)
C19—N18	1.317(6)	$N9^{i}$—$C10^{i}$	1.298(3)	$C1^{ii}$—$N2^{ii}$	1.297(2)
N18—C17a	1.400(8)	$C8a^{i}$—$N9^{i}$	1.407(3)	$N2^{ii}$—$C2a^{ii}$	1.416(2)
C8—N7(C6a	124.0(5)	C8a—N9(C10	122.6(2)	C1—N2—C2a	118.2(1)
C10—N11—C11a	120.3(5)	C1—N2—C2a	122.2(2)	C8a—N9—C10	125.7(1)
C19—N18—C17a	124.1(5)	$C8a^{i}$ —$N9^{i}$ —$C10^{i}$	122.6(2)	$C1^{ii}$—$N2^{ii}$—$C2a^{ii}$	118.2(1)
C21—N22—C22a	121.5(5)	$C1^{i}$—$N2^{i}$—$C2a^{i}$	122.2(2)	$C8a^{ii}$ —$N9^{ii}$—$C10^{ii}$	125.7(1)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y, -z$.

Elemental analyses were carried out on an Elementar vario MICRO cube analyser. ^{1}H and ^{13}C NMR spectroscopy was carried out using a Bruker AVANCE II 300 spectrometer. Chemical shifts (δ) are expressed in parts per million and J values in Hz. Signal multiplicities are denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). ESI mass spectra were taken on a Bruker Daltonics Esquire 3000 spectrometer. HR-MS spectra were taken on a Waters Micromass Quattro LC apparatus. The IR spectra were recorded with a Thermo

Table 3. The geometrical parameters (Å, °) for weak interactions.

D-H···A	D-H	H···A	D···A	D-H···A
3		±0.01	±0.005	±1
C26—H26···$Cg1^{x, -y-\frac{1}{2}, z+\frac{1}{2}}$	0.95	3.36	4.197	147
C25—H25···$Cg2^{x, -y-\frac{1}{2}, z+\frac{1}{2}}$	0.95	3.18	4.010	147
C31—H31a···Cg3	0.99	3.65	4.325	128
C32—H32b···$Cg3^{-x, -y, -z}$	0.99	3.52	4.189	127
C31—H31b···$Cl5^{-x, -y, -z}$	0.99	2.66	3.617	164
C33—H33a···Cg5	0.99	3.12	4.108	175
C37—H37b···Cg6	0.99	3.13	4.061	157
C38—H38a···$Cg7^{-x, -y, -z}$	0.99	3.32	4.051	132
C45—H45···$Cg7^{-x+1, -y, -z}$	0.95	3.38	4.002	125
C46—H46···$Cg7^{-x+1, -y, -z}$	0.95	3.18	3.908	135
C2—H2···$Cg8^{-x+1, y-\frac{1}{2}, -z-\frac{1}{2}}$	0.95	3.22	4.154	169
C43—H43···$O23^{x, -y+\frac{1}{2}, z-\frac{1}{2}}$	0.95	2.47	3.388	163
C44—H44···$O48^{-x+1, y+\frac{1}{2}, -z-\frac{1}{2}}$	0.95	2.38	3.295	163
Cg1···$Cg6^{-x+1, -y, -z}$			3.742	
Cg2···$Cg3^{-x+1, -y, -z}$			3.709	
4		±0.01	±0.002	±2
C1—H1···$Cg3^{-x+1, -y+1, -z+1}$	0.95	2.92	3.644	134
C6—H6···$Cg3^{-x+1\frac{1}{2}, y-1\frac{1}{2}, -z+1\frac{1}{2}}$	0.95	3.60	4.480	155
C21—H21a···$Cg5^{x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}}$	0.99	3.29	3.961	127
C22—H22a···$Cg1^{x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}}$	0.99	3.08	3.852	136
C23—Br1···$Cg3^{x, y-1, z}$	1.954(3)	4.35	6.126	155
C7—H7···$O12^{-x+1\frac{1}{2}, y-\frac{1}{2}, -z+1\frac{1}{2}}$	0.95	2.50	3.435	169
Cg1···$Cg4^{-x+1, -y, -z+1}$			3.632	
Cg2···$Cg2^{-x+1, -y, -z+1}$			3.542	
5		±0.01	±0.002	±2
C14—H14···Cg2	0.95	2.78	3.672	156
C15—H15···Cg1	0.95	3.06	3.706	127
C37—H37b···$Cg3^{-x+1, -y+1, -z}$	0.91	3.37	4.075	136
Cg1···$Cg2^{-x+1, -y+1, -z}$			3.863	
Cg2···$Cg2^{-x+1, -y+1, -z}$			3.721	
Cg3···$Cg4^{-x+1, y, z}$			3.518	
O37—H37···$Br1^{x-2, y, z+1}$	0.82(1)	2.44	3.253(1)	169

Notes: The appropriate ring gravity centres are defined as follows: for compound **3** Cg1, (C1 ∧ C6a); Cg2, (C2 ∧ C5a); Cg3, (C17 ∧ C12a); Cg4, (C16a ∧ C13); Cg5, (N7-C8-C9-C10-N11); Cg6, (N18-C19-C20-C21-N22); Cg7, (C29 ∧ C25); Cg8, (C46 ∧ C44); for compound **4** Cg1, (C3a ∧ C7a); Cg2, (C2a ∧ C8a); Cg3, (C13 ∧ C18); Cg4, (N2—C1—$C11^{i}$—$C10^{i}$—$N9^{i}$) with (i) $=(-x+1, -y+1, -z+1)$; Cg5, (C2a—C3—C3a—C4—C5—C6—C7—C7a—C8—C8a) and for compound **5** Cg1, (C3a ∧ C7a); Cg2, (C2a ∧ C8a); Cg3, (C13 ∧ C18); Cg4, (N24 ∧ C29).

Fisher Scientific Nicolet IR200. Melting points were measured using a Boethius apparatus, and were not corrected.

3.2 Syntheses

3.2.1 9,20-Bis(2-hydroxybenzoyl)-7,18-dihydrodinaphtho[b,i][1,4,8,11]tetraazacyclotetradecine (**1**)

A reaction mixture consisting of 2,3-diaminonaphthalene (0.12 g, 0.75 mmol) and 3-formylchromone (0.125 g, 0.75 mmol) in chloroform (20 mL) was refluxed with stirring for 1 h. A yellow-orange, fairly insoluble precipitate was collected and washed thoroughly with hot butanol and chloroform. Yellow-orange powder, yield 0.175 g (70%), mp 233–234°C. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): 7.00 (t, $J = 7.4$, 2H, $H^{26,26'}$), 7.04 (d, $J = 8.4$, 2H, $H^{28,28'}$), 7.42–7.47 (m, 8H, $H^{3,4,14,15,25,25',27,27'}$), 7.84 (m, 4H, $H^{2,5,13,16}$), 7.88 (s, 4H, $H^{1,6,12,17}$), 8.85 (d, 4H, $J = 6.4$,=NCH), 10.32 (s, 2H, OH), 13.87 (t, $J = 6.4$, 2H, NH); IR (ATR) ν_{max}(cm^{-1}): 3046, 1636, 1619, 1562, 1478, 1314, 1292, 1222. Anal. Calcd for $C_{40}H_{28}N_4O_4$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.30; H, 4.56; N, 8.99%.

3.2.2 9,20-Bis[2-(octoxy)benzoyl]-7,18-dihydrodinaphtho[b,i][1,4,8,11]tetraazacyclotetradecine (**2**)

A reaction mixture consisting of **1** (0.126 g, 0.2 mmol), anhydrous potassium carbonate (0.5 g) and *n*-octyl bromide (0.11 mL, 0.6 mmol) in anhydrous DMF (75 mL) was heated with stirring for 5 h at 80°C. During this time, the colour of the solution changed slowly from orange to brown. The reaction mixture was cooled to room temperature and then transferred to a separatory funnel and partitioned between chloroform (50 mL) and water (50 mL). The organic layer was separated, washed with water (5 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the oily residue was chromatographed on a silica gel column using toluene–acetone (10:1) as eluent. The main yellow fraction was collected and concentrated into a small volume. The product was precipitated with *n*-hexane (5 mL). Yellow powder, yield 0.077 g (44%), mp 143°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.62 (t, $J = 6.9$ Hz, 6H, CH_3), 0.96–1.09 (m, 16H, CH_2), 1.23 (m, 4H, CH_2), 1.62 (m, 4H, CH_2), 3.98 (t, $J = 6.6$ Hz, 4H, CH_2O), 6.99–7.69 (m, 20H, Ar-H), 8.84 (br s, 4H, =CHN), 13.92 (br s, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.54, 22.98, 26.57, 29.74, 29.75, 29.85, 69.37, 111.68, 112.99, 113.25, 121.63; 126.71, 128.05, 130.27, 132.13, 132.53, 137.39, 154.11, 193.90; IR (ATR) ν_{max}(cm^{-1}): 3165, 3095, 2954, 2888, 1607, 1580, 1487, 1252, 1156; ESI-HR-MS (*m/z*) 875.4503 (M + Na$^+$).

3.2.3 Lacunar compound (**3**)

A reaction mixture consisting of **1** (0.15 g, 0.24 mmol), 1,10-dibromodecane (0.08 g, 0.26 mmol), potassium carbonate (0.5 g) and DMF (75 mL) was stirred for 48 h at room temperature and then transferred to a separatory funnel and partitioned between chloroform (50 mL) and water (50 mL). The organic layer was separated, washed with water (5 × 50 mL) and then dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum, and the oily residue was chromatographed on a silica gel column using toluene–acetone (20:1) as eluent. The main yellow fraction was collected and evaporated to dryness. A solid residue was recrystallised from chloroform–hexane (1:3). Yellow crystals were filtered off and washed with *n*-hexane. Yellow prisms, yield 0.047 g (26%), mp > 300°C.

Crystals suitable for X-ray measurements were grown from $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.78 (m, 4H, CH_2), 0.93 (m, 4H, CH_2), 1.12 (m, 4H, CH_2), 1.53 (m, 4H, CH_2), 3.93 (t, $J = 5.2$ Hz, 4H, OCH_2), 6.98–7.65 (m, 20H, ArH), 8.81 (d, $J = 6.6$, 4H, =CHN), 13.74 (t, $J = 6.6$, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 27.2, 30.3, 30.4, 30.8, 69.4, 111.9, 112.4, 112.7, 121.9, 126.6, 128.1, 130.1, 130.6, 132.4, 136.9, 153.4, 156.7, 194.0; IR (ATR) ν_{max}(cm^{-1}): 3052, 2925, 2851, 1650, 1610, 1592, 1560, 1290, 1249; ESI-HR-MS (*m/z*) 789.3423 (M + Na$^+$).

3.2.4 9,20-Bis[2-(4-bromobutoxy)benzoyl]-7,18-dihydrodinaphtho[b,i][1,4,8,11]tetraazacyclotetradecine (**4**)

A reaction mixture consisting of **1** (0.14 g, 0.22 mmol), 1,4-dibromobutane (0.26 mL, 2.2 mmol), potassium carbonate (0.12 g) and DMF (35 mL) was stirred for 48 h at room temperature and then transferred to a separatory funnel and partitioned between chloroform (50 mL) and water (50 mL). The organic layer was separated, washed with water (5 × 50 mL) and then dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum, and the oily residue was chromatographed on a silica gel column using toluene–acetone (40:1) as eluent. The main yellow fraction was collected, concentrated to a small volume and left to crystallise in air. Deep-orange crystals were collected and washed with *n*-hexane. Yield 0.044 g (22%), mp 263°C. Crystals suitable for X-ray measurements were grown from toluene. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.83 (m, 8H, —CH_2CH_2—), 3.23 (t, $J = 6.3$ Hz, 4H, CH_2Br), 4.02 (t, $J = 6.3$ Hz, 4H, CH_2O), 6.99–7.69 (m, 20H, ArH), 8.82 (d, $J = 7.1$ Hz, 4H, =CHN), 13.94 (t, $J = 7.1$ Hz, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 28.35, 29.95, 33.97, 68.37, 111.74, 113.10, 113.39, 121.96, 126.81, 128.13, 130.23, 132.13, 132.57, 137.36, 154.00, 156.39, 193.68; IR (ATR) ν_{max}(cm^{-1}): 3053, 2954, 2930, 2870, 1657, 1609, 1562, 1286, 1254; ESI-MS (*m/z*) 897.20 (M$^+$). Anal. Calcd for

$C_{48}H_{42}Br_2N_4O_4$: C, 64.15; H, 4.71; N, 6.23. Found: C, 64.31; H, 4.64; N, 6.15%.

*3.2.5 9,20-Bis{2-[4-(N-pyridinium-1-yl)butoxy]benzoyl}-7,18-dihydrodinaphtho[b,i][1,4,8,11]tetraazacyclotetradecine dibromide pentahydrate (**5**)*

Pyridine (20 mL) was added to 4-bromobutoxy derivative **4** (0.08 g, 0.09 mmol), and the mixture was heated with stirring for 8 h at 45°C. The solution was then cooled to room temperature, and the precipitate was collected by filtration and washed with *n*-hexane. Yellow powder, yield 0.082 g (86%), mp 256–258°C. Crystals suitable for X-ray measurements were grown from methanol–pyridine (1:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.60 (m, 4H, CH_2), 1.85 (m, 4H, CH_2), 4.12 (t, $J = 6.3$ Hz, 4H, CH_2O), 4.43 (t, $J = 7.5$ Hz, 4H, CH_2N^+), 7.10 (t, $J = 7.5$ Hz, 2H, $H^{27,27'}$), 7.21 (d, $J = 8.4$ Hz, 2H, $H^{29,29'}$), 7.40 (m, 6H, $H^{3,4,26,26',14,15}$), 7.53 (dt, $J = 1.6$, 7.5 Hz, 2H, $H^{28,28'}$), 7.72 (m, 4H, $H^{f,f'}$), 7.73 (m, 4H, $H^{1,6,12,17}$), 7.82 (m, 4H, $H^{2,5,13,16}$), 8.26 (tt, $J = 1.2$, 7.9 Hz, 2H, $H^{g,g'}$), 8.73 (d, $J = 6.5$ Hz, 4H, =CHN), 8.79 (dd, $J = 1.2$, 6.9 Hz, 4H, $H^{e,e'}$), 13.51 (t, $J = 6.5$ Hz, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 26.26, 29.08, 61.22, 68.49, 111. 60, 113.87, 114.14, 127.41, 128.66, 128.80, 129.82, 130.51, 132.59, 132.82, 136.89, 145.35, 146.18, 154.51, 156.40, 170.31, 192.83; IR (ATR) ν_{max}(cm^{-1}): 3470, 3407, 3126, 3052, 2940, 2868, 1649, 1588, 1562, 1483, 1416, 1289, 1256; ESI-MS (*m/z*) 448.40 (M^{2+}/2). Anal. Calcd for $C_{58}H_{52}Br_2N_6O_4{\cdot}5\ H_2O$: C, 60.74; H, 5.45; N, 7.33. Found: C, 61.12; H, 5.18; N, 7.34%.

3.3 Crystallography

X-ray measurements for crystals **3**, **4** and **5** were taken on SuperNova diffractometer (Oxford Diffraction) (*10*), equipped with Dual Cu at zero Atlas diffractometer and CryoJet low temperature device using MoKα radiation ($\lambda = 0.71073$ Å); data collection, CrysAlisPRO (*10*); cell refinement, CrysAlisPRO (*10*); data reduction, CrysAlisPRO (*10*); absorption correction, multi-scan (*10*); program used to solve structure, SIR92 (*11*); program used to refine structure, SHELXL97 (*12*); molecular graphics, ORTEP-3 (*13*); software used to prepare material for publication, SHELXL97 (*12*) and WinGX (*14*).

The structures were solved by direct methods and refined by full matrix least squares using anisotropic displacement parameters for non-H-atoms. The H-atoms of aromatic C—H, methyl and methylene groups were found on Fourier difference maps and included in the refinement in the positions calculated from geometrical conditions. The H-atoms at N and O-atoms were localised on Fourier difference maps and refined with restrained N—H and O—H distances (DFIX procedure in SHELX97) in riding model with $U_{iso} = U_{Equation}$ (parent atom).

Crystal data: **3** $C_{50}H_{46}N_4O_4{\cdot}0.90\ CHCl_3$: $T = 110(2)$ K, monoclinic, space group $P2_1/c$, $a = 13.8790(8)$, $b = 15.7021(10)$, $c = 20.6126(12)$Å, $\beta = 105.886(6)$, $V = 4320.5(4)$Å^3, $Z = 4$, $Dx = 1.344$ Mg m^{-3}. Intensity data: $\theta_{max} = 25.00°$, completeness 0.998, $R = 0.1001$ for 5056 reflections with $I > \sigma(I)$, $wR^2 = 0.2603$ for all 7597 unique reflections; relatively high *R*-factors are due to disordered solvent molecules (site occupancy factors for chlorine atoms of chloroform molecules with different orientations are as follows: 0.30 at positions Cl1—Cl2—Cl4, 0.30 at positions Cl3—Cl5—Cl6, 0.20 at positions Cl5—Cl6—Cl7 and 0.10 at positions Cl2—Cl4—Cl8), goodness-of-fit parameters $S = 1.024$. CCDC N. 898799.

Crystal data: **4** $C_{48}H_{42}Br_2N_4O_4$: $T = 110(2)$ K, monoclinic, space group $P2_1/n$, $a = 15.8211(3)$, $b = 7.9364(1)$, $c = 16.0007(3)$ Å, $\beta = 90.832(2)°$, $V = 2008.88(6)$ Å^3, $Z = 2$ ($Z' = 0.5$), $Dx = 1.486$ Mg m^{-3}. Intensity data: $\theta_{max} = 30.00°$, completeness 0.997, $R = 0.0403$ for 3859 reflections with $I > \sigma(I)$, $wR^2 = 0.1124$ for all 5835 unique reflections, goodness-of-fit parameters $S = 0.954$. CCDC N. 898800.

Crystal data: **5** $C_{58}H_{52}N_6O_4^{2+}2Br^-$ 2 CH_3OH: $T = 113(2)$ K, triclinic, space group $P\bar{1}$, $a = 9.0889(2)$, $b = 9.3100(2)$, $c = 15.4082(4)$ Å, $\alpha = 82.966(2)$, $\beta = 79.175(2)$, $\gamma = 87.680(2)°$, $V = 1270.76(5)$ Å^3, $Z = 1$ ($Z' = 0.5$), $Dx = 1.465$ Mg m^{-3}. Intensity data: $\theta_{max} = 30.00°$, completeness 0.999, $R = 0.0331$ for 6565 reflections with $I > \sigma(I)$, $wR^2 = 0.0874$ for all 7398 unique reflections, goodness-of-fit parameters $S = 1.060$. CCDC N. 898801.

4. Conclusions

A new bis(2-hydroxybenzoyl) derivative of the DNTAA macrocycle **1** was obtained as a fairly insoluble product of a reaction between 2,3-diaminonaphthalene and 3-formylchromone. The alkylation of both phenolic OH groups of **1** successfully led to new derivatives with open-chain pendant substituents and an *O*,*O*-bis-alkylated bridging superstructure. Crystallographic studies of the products **3**–**5** were carried out, revealing numerous non-covalent interactions. Among the interactions, those involving naphthylene moieties, in both π–π and CH–π modes, seem to have a crucial role in stabilising the crystal structures. Thus, the presence of naphthylene fragments in the structures of DNTAA derivatives provides additional opportunities for non-covalent interactions of the molecules.

In summary, the new macrocyclic ligand **1**, incorporating naphthylene moieties crucial for generating non-covalent interactions and carrying reactive phenolic OH substituents, represents a valuable building block that is suitable for use in the preparation of various supramolecular receptors.

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