

Inclusion compounds of plant growth regulators in cyclodextrins. Part VII. Study of the crystal structures of 2-Naphthylacetic acid encapsulated in β -cyclodextrin and heptakis(2,3,6-tri-O-methyl)- β -cyclodextrin complexes by X-ray crystallography

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Abstract

The crystal structures of the 2NAA/ β -CD and the 2NAA/TM β CD complexes are reported. The 2NAA/ β -CD complex crystallizes in the triclinic system forming a dimer inside the cavity of which two 2NAA molecules disordered over two sites are located. The dimers are stacked along the *c* axis according to the channel packing mode forming a nanotube which resembles a wireway as it contains guests molecules linked by π - π interactions inside each dimeric cavity and by H-bonds between the adjacent dimers. The 2NAA/TM β CD complex crystallizes in the orthorhombic space group P2₁2₁2₁. Its asymmetric unit contains one host, one guest distributed over two sites and one water molecule having a low occupancy factor. The complexes are packed in a head-to-tail mode forming a screw channel along the *b* axis. The carboxyl group of the guest protrudes towards the “free” space between the complexes and is H-bonded to the water molecule which in turn is H-bonded to the O5n atom of the host of the subsequent complex. The orientation of the guest molecule in the 2NAA/ β -CD complex has been found opposite to that of the guest in the 2NAA/TM β CD complex probably due to the formation of dimers and the π - π interactions between the naphthalene moieties of the encapsulated molecules inside the dimeric cavity.

Keywords: 2-naphthylacetic acid, β -Cyclodextrin, heptakis(2,3,6-tri-O-methyl)- β -Cyclodextrin, X-ray crystallography

Abbreviations: β -Cyclodextrin, β -CD; heptakis(2,3,6-tri-O-methyl)- β -Cyclodextrin, TM β CD

Introduction

The plant hormone auxins regulate cell elongation, division, differentiation and morphogenesis. Synthetic auxin analogues are also important selective herbicides [1]. Naturally occurring and synthetic derivatives of naphthalene have been shown that inhibit temporarily sprout growth. Depending on the situation, there is sample evidence that auxins can act in either an ethylene-independent or ethylene-dependent manner [2]. 2-Naphthylacetic acid (or β -Naphthylacetic acid; 2NAA; Scheme 1) is a synthetic auxin considered as an inactive analogue of α -Naphthylacetic acid (or 1-Naphthylacetic acid) and antagonist of the endogenous indole-3-acetic acid [3]. Increasing concentrations of 2NAA exert two opposing effects on the uptake of indole-3-acetic acid, depression and stimulation [4].

The use of β -Cyclodextrins (β -CD) and their permethylated derivatives, obtained by substitution of the hydrogen atoms of all their hydroxyls by methyl groups to obtain heptakis(2,3,6-tri-*O*-methyl)- β -CD (TM β CD), as hosts for the inclusion of a variety of substances with suitable size and shape, is well known [5]. This inclusion increases the solubility of sparingly soluble substances in water and protects the guests from loss by evaporation, attack by oxygen, visible and UV light, and from molecular reactions [6]. The flexibility and the elongation of the cavity of TM β CD, as a result of the absence of hydrogen bonds between their secondary methoxy groups, allows the inclusion of more bulky molecules [7].

As a part of an ongoing investigation of the crystal structures of inclusion compounds of plant growth regulators in either native or permethylated CDs we report here the crystal structures of the inclusion compounds of 2NAA in β -CD and TM β CD. Despite our efforts we were not able to obtain crystals of the inclusion compound of 2NAA in heptakis(2,6-di-*O*-methyl)- β -Cyclodextrin (DM β CD).

2. Experimental

2.1 Sample preparation

2NAA in powder form (obtained from Applichem) was added in aqueous solutions of β -CD and TM β CD (purchased from Fluka or Sigma) at a host:guest mole ratio 1:1. The mixture of 2NAA: β -CD was stirred for 30 min at 70°C until it

was limpid. Then it was gradually cooled to room temperature over a ten-day period in order to produce colourless crystals suitable for X-ray data collection. The mixture of 2NAA:TM β CD was stirred for 40 min at 38°C. The formed typical precipitate was maintained at 49°C until prismatic crystals of the complex suitable for X-ray data collection were formed.

2.2 X-ray data collection

High and low resolution X-ray data were collected using the synchrotron radiation light source at EMBL X11 beamline at the DORIS storage ring, DESY, Hamburg and a marCCD 165 detector. The data set of 2NAA/ β -CD was collected at cryogenic temperature: one crystal was picked with a cryo-loop and flash cooled under the N₂ stream to 100 K. The data set of 2NAA/TM β CD was collected at room temperature as the cryo-protecting oil was damaging the crystal. The processing and scaling of the data sets have been performed by using the programs *DENZO* and *SCALEPACK* [8].

2.3 Structure solution and Refinement

The structure of 2NAA/ β -CD has been solved by isomorphous replacement using the coordinates of the atoms of the macrocycle of the 3,5-dimethylbenzoic acid/ β -CD complex [9]. All the non-hydrogen atomic positions of the host β -CD and the guest 2NAA molecule have been located and refined by successive difference Fourier maps using *SHELXL97* [10]. The structure of 2NAA/TM β CD has been solved by a Patterson vector search method and Fourier recycling with the program *DIRDIF99* [11] using the coordinates of the atoms of the macrocycle of the ethyl laurate/TM β CD complex [12]. The solution has also been refined on a F^2 basis using *SHELXL97*. All the programs used for solving and refining the crystal structure were used under the interface and the graphical display support of the *WINGX* suite [13]. In both crystal structures, anisotropic thermal parameters were introduced only for selected non-hydrogen atoms due to the limited number of the observed data reflections. Hydrogen atom positions linked to primary, secondary or tertiary carbon atoms of the host molecules of both structures were calculated at C-H distances of 0.96, 0.97 or 0.98 Å respectively and their thermal parameters were set to 1.2 U_{iso} of the isotropic thermal parameter of the corresponding carbon atom. The naphthyl moieties of the guests of both complexes were considered

ideal. 20 (2NAA/ β -CD) and 30 (2NAA/TM β CD) reflections exhibiting poor agreement, were given zero weight during the final refinement cycles. Extinction correction has been performed in 2NAA/TM β CD. Final lattice parameters along with all the data collection parameters of the complexes are quoted in Table 1.

3. Results and discussion

3.1 The 2NAA/ β -CD complex

3.1.1 Description of the structure

The 2NAA/ β -CD complex crystallizes in the triclinic system (space group P1). The asymmetric unit of the complex consists of two β -CD molecules (HostA and HostB), two guest molecules (the host:guest stoichiometry being therefore 2:2) and 14.72 water molecules distributed over 38 sites. The two hosts form a head-to-head dimer via the O3nA ... O3(8-n)B hydrogen bonds where O3nA denotes the secondary 3-hydroxyls of the nth glucose unit of the HostA and O3(8-n)B the facing 3-hydroxyls of the (8-n)th glucose unit of the HostB. The angle between HostA and Host B O4n mean planes is about 1°. A guest molecule is found inside the cavity of HostA disordered over two sites GA1 and GA2 having occupation factors 0.65 and 0.35 respectively. The other guest molecule is located inside the cavity of HostB also disordered over two sites GB1 and GB2 having the same occupancies of 0.65 and 0.35 respectively. As it is indicated by the occupancy factors of the found sites and the measured distances between these sites the two guest molecules accommodated inside the dimeric cavity can co-exist occupying either the GA1-GB1 or the GA2-GB2 pair of sites (Fig. 1).

All the occupied sites of the guest molecules have a similar orientation: their naphthalene moieties are accommodated deeply inside the dimeric cavity while their carboxyl groups are located in the rim of their primary hydroxyl groups protruding from the host cavity. The naphthalene planes of GA1 and GB1 guest sites are stacked inside the dimeric cavity at a distance of 3.6 Å forming an angle of about 13° and shifted by 1.6 Å (measured shift between the centroids of the GA1 and GB1 naphthalene). These geometric features are indicative of a π - π interaction between the naphthalene moieties [14] of the guest molecules occupying this pair of sites. However, in the case of the other pair of occupied

sites which has been found having a lower occupancy (0.35), the measured angle, distance and shift between the GA2 and GB2 naphthalenes is 12° , 3.6 Å and 2 Å correspondingly, indicating only slight overlap and thus a reduced π - π interaction. The angles of the naphthalene of the guest sites GA1 and GA2 with the mean planes of O4nA or O4nB are about the same being 66° and 65° respectively. Guest sites GA2 and GB2 have the same geometry, the corresponding angles being 67° and 64° respectively. The carboxyl group of the molecule occupying the GA1 site forms a couple of hydrogen bonds with the carboxyl group of the one occupying the GB1 site of the adjacent dimer (Fig. 2; distances O1A1 ...O2B1 = 2.66 Å, O2A1 ...O1B1 = 2.66 Å). The carboxyl groups of the guests occupying GA2 and GB2 of the adjacent dimer are also hydrogen bonded (distance O2A2 ...O1B2 = 2.86 Å).

3.1.2 *The molecular packing*

The 2NAA/ β -CD complex crystallises as a dimer in the space group *P1*, its cell dimensions are slightly greater than 15 Å and the observed crystal packing mode is that of a Channel. This crystal packing is in agreement with the one expected by the classification of the β -CD dimeric complexes packing modes according to their space group and cell dimensions [13]. The channels are formed by dimers stacked along the the *c* axis. The shifting between the dimers of the channel is 2.2 Å, considerably less than the usual shifting of about 3 Å characterizing this packing mode. The mean plane of the O4nB atoms of the dimers is inclined to the *ab* plane at an angle of 10° . The dimeric complexes of the same channel form a molecular tube containing guest molecules connected by the hydrogen bonds formed between the guests of adjacent dimers and by the π - π interactions between the guests of the same dimer (Figs. 2,3).

3.1.3 *Conformation of the host molecule*

Table 2 lists some parameters defining the conformation of the two host molecules HostA and HostB. All the glucose units of the hosts have the usual 4C_1 conformation as it is indicated by the Cremer-Pople puckering parameters *Q* and θ [15]. Apart from the differences concerning the disordered primary hydroxyl groups, the two host molecules have the same conformation In the case of the HostA three primary hydroxyl groups have been found disordered over two sites

and one over three sites whereas in the case of the HostB three primary hydroxyl groups have been found disordered over two sites. The occupied sites of the disordered primary hydroxyl groups are denoted as (a), (b) and (c) in Table 2 (column with header “t”). The majority of them have the *gauche-gauche* conformation pointing outwards the cavity and the rest have the *gauche-trans* configuration pointing inwards the cavity. The heptagons formed by the glucosidic O4n atoms are essentially planar and regular as indicated by the proximity of the values listed in columns with headers D_K , D , Φ and d of Table 2.

3.2 The 2NAA/TM β CD complex

3.2.1 Description of the structure. Molecular packing

The 2NAA/TM β CD complex crystallizes in the orthorhombic space group $P2_12_12_1$. Its asymmetric unit contains one host molecule, one 2NAA guest molecule distributed over two sites, A and B, having occupancy factors 0.78 and 0.22 respectively (Fig. 4), and one water molecule having an occupancy of only 0.33. The complexes related by the crystallographic symmetry of the twofold screw axis parallel to b , are packed in a head-to-tail mode (Fig. 5). The angle between the normal to the O4n mean plane of the TM β CD molecule and the b axis is about 4° . The molecular packing has the characteristics of a Screw Channel packing mode observed in the dimeric β -CD structures [16]. The mean planes of the glucosidic O4n atoms of two subsequent macrocycles of the same channel form an angle of 7.3 \AA and the projections of their centroids on the ac crystal plane are at a distance of 3.5 \AA from each other. The same molecular packing has been observed in the case of the 2,4,5-T/TM β CD complex which has been crystallized in the same space group and with similar unit cell dimensions (Triantafyllopoulou *et al*, unpublished data).

The water molecule is located at the “free” space existing between the subsequent hosts of the Screw Channel forming hydrogen bonds with the O57 atom of a vicinal host molecule (distance OW...O57 = 2.86 \AA) and the O1 of the carboxyl group of the guest (distance OW...O1 = 2.88 \AA) of the same asymmetric unit (Fig. 5).

The guest molecule occupying both sites (A and B) is encapsulated by the host with its naphthalene moiety accommodated at the secondary methoxy groups rim

and its carboxyl group protruded from the hydrophobic cavity towards the “free” space existing between the hosts of the channel (Figs. 4, 5). The naphthalene moieties of the two sites occupied by the guest molecule form angles of 63° (site A) or 62° (site B) with the mean plane of the O4 n atoms of the host.

3.2.2 Conformation of the host

All the glucose residues of the host molecule have the 4C_1 conformation as it is indicated by the Q and θ puckering parameters [15] (Table 3). Three methoxy groups have the *gauche-gauche* orientation (pointing outwards the cavity), three have the *gauche-trans* orientation (pointing inwards the cavity) and one is disordered over two sites (denoted as (a) and (b) in Table 3) having both orientations. The heptagon formed by the glucosidic O4 n atoms is not planar, the distances of these atoms from their mean plane ranging between -0.6Å and 0.5Å. Moreover, the distances of the O4 n atoms from their centroid (D_K) range between 4.7 Å and 5.2 Å and the O4($n-1$)...O4 n ...O4($n+1$) angles (Φ) between 121° and 137°. Therefore, the macrocycle is significantly puckered and its form deviates from that of a regular, planar heptagon (Fig. 6). These characteristics are common in all the permethylated β -CD crystal structures regardless of their crystal packing.

4. Concluding remarks

The macrocycles of the dimeric hosts of the 2NAA/ β -CD complex form a nanotube, developed along the c axis, inside of which are located the guest molecules. The guests found inside the dimeric cavity are linked by π - π interactions, while those of the adjacent dimers are hydrogen bonded. Therefore, the nanotube resembles a wireway (Fig. 2).

In the case of the 2NAA/TM β CD, the complexes are stacked along the b axis forming a screw channel in the following way: The guest molecule of a complex protruding from the macrocycle cavity is hydrogen bonded to a water molecule located at the “free” space between the complexes which in turn is hydrogen bonded to the O5 n of the host of the subsequent complex in the Screw Channel (Fig. 5).

The naphthalene moiety of the guest molecule is located at the rim of the secondary hydroxyls (in the case of the 2NAA/ β -CD) or the secondary methoxy groups (in the case of the 2NAA/TM β CD). The depth of immersion of the

naphthalene is about the same in both cases as the distance between the naphthalene centroid and the mean plane of the O4n atoms of the host varies from 1.8 to 1.9 Å in 2NAA/ β -CD and from 1.6 to 2.6 Å in 2NAA/TM β CD. In addition, the slope of the naphthalene plane relative to the mean plane of the host's O4n atoms is quite similar in both cases varying from 64° to 67° in 2NAA/ β -CD and from 62° to 63° in 2NAA/TM β CD. However, the orientation of the guest molecule in the 2NAA/ β -CD complex is opposite to that of the guest in the 2NAA/TM β CD complex. The carboxyl of the 2NAA in the 2NAA/ β -CD is found located at the primary hydroxyls rim of the host (Fig. 2) whereas in the case of the 2NAA/TM β CD complex the guest's carboxyl protrudes from the hydrophobic cavity towards the opposite direction (Fig. 5). In the case of the 2NAA/ β -CD crystal structure, it is probably the formation of the dimeric cavity and the π - π interactions between the encapsulated naphthalenes that drive the complexation to this particular mode.

Supplementary data

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 846763 and 846764. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

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Table 1. Crystal data and structure refinement for the 2NAA/ β -CD and 2NAA/TM β CD complexes

	2NAA/ β -CD	2NAA/TM β CD
Empirical formula	C ₁₀₈ H ₈₀ O _{88.72}	C ₇₅ H ₁₂₂ O ₃₇
Formula weight	2797.24	1615.73
Temperature, K	100 (2)	293 (2)
Wavelength, Å	0.81480	0.81600
Crystal system, space group	Triclinic, <i>P</i> 1	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å), α (°)	15.546(5), 101.546(5)	15.059(2), 90
<i>b</i> (Å), β (°)	15.549(5), 101.544(5)	21.657(5), 90
<i>c</i> (Å), γ (°)	15.814(5), 103.924(5)	27.768(6), 90
Volume, Å ³	3509.1(19)	9056(3)
Z, Calculated density Mg/m ³	1, 1.324	4, 1.185
Absorption coefficient, mm ⁻¹	0.119	0.095
F(000)	1438	3472
Theta range for data collection	2.46 to 28.29°	1.89 to 21.98
Limiting indices	0 ≤ <i>h</i> ≤ 18, -17 ≤ <i>k</i> ≤ 16, -18 ≤ <i>l</i> ≤ 17	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 19, 0 ≤ <i>l</i> ≤ 25
No of unique reflections	10160	3769
Completeness to theta	28.29 87.8 %	21.98 92.6 %
Refinement method	Full-matrix-block least- squares on F ²	Full-matrix-block least- squares on F ²
Data / restraints / parameters	10160 / 81 / 1317	3769 / 25 / 552
Goodness-of-fit on F ²	1.003	1.083
Final R indices [I > 2σ(I)]	R ₁ = 0.1009, wR ₂ = 0.2713	R ₁ = 0.1014, wR ₂ = 0.2599
R indices (all data)	R ₁ = 0.1032, wR ₂ = 0.2750	R ₁ = 0.1062, wR ₂ = 0.2663
Largest diff. peak and hole, e·Å ⁻³	0.05 and -0.03	0.42 and -0.37
(Δ/σ) _{max}	0.048	0.077

Table 2. Conformational characteristics of the host molecules of the 2NAA/ β -CD complex

Residue	D_K (Å)	D (Å)	Φ_h (°)	d (Å)	τ (°)	t (°)	C
HostA							
I ($n=1$)	5.0	4.4	130	0.01	11	-57 (a) 43 (b)	<i>gg</i> <i>gt</i>
II ($n=2$)	5.1	4.3	126	-0.03	13	-66	<i>gg</i>
III ($n=3$)	5.0	4.5	129	0.03	9	-58	<i>gg</i>
IV ($n=4$)	4.9	4.3	131	0.00	15	-64 (a) 64 (b)	<i>gg</i> <i>gt</i>
V ($n=5$)	5.1	4.4	127	-0.02	13	-53 (a) 49 (b)	<i>gg</i> <i>gt</i>
VI ($n=6$)	5.1	4.3	128	0.01	11	-43 (a) -51 (b) 81 (c)	<i>gg</i> <i>gg</i> <i>gt</i>
VII ($n=7$)	5.0	4.4	129	0.00	7	-69	<i>gg</i>
HostB							
I ($n=1$)	5.0	4.4	130	-0.01	11	-57 (a) 36 (b)	<i>gg</i> <i>gt</i>
II ($n=2$)	5.1	4.3	126	0.03	13	-66	<i>gg</i>
III ($n=3$)	5.0	4.5	129	-0.03	9	-58	<i>gg</i>
IV ($n=4$)	4.9	4.3	131	-0.00	14	-65 (a) 69 (b)	<i>gg</i> <i>gt</i>
V ($n=5$)	5.1	4.4	127	0.02	14	-51 (a) 53 (b)	<i>gg</i> <i>gt</i>
VI ($n=6$)	5.1	4.3	128	0.01	11	-98 (a) -47 (b)	<i>gg</i> <i>gg</i>
VII ($n=7$)	5.0	4.4	130	-0.01	7	-68	<i>gg</i>

$D_K = K...O4n$, where K is the centroid of the $O4n$ heptagon; $D = O4n...O4(n+1)$ distances; $\Phi_h = O4(n-1)...O4n...O4(n+1)$ angles; d = deviations of the $O4n$ atoms from their least-squares plane; τ = tilt angles between the optimum $O4n$ plane and the mean plane of the $O4(n-1)$, $C1n$, $C4n$, $O4n$ atoms; torsion angles $t = O5n-C5n-C6n-O6n$ where (a), (b) and (c) denote the occupied sites of the disordered primary hydroxyl groups; C = conformation of the hydroxyl groups

Table 3. Conformational characteristics of the host molecules of the 2NAA/TM β CD complex

Residue	Q (Å)	θ (°)	D_K (Å)	D (Å)	Φ_h (°)	d (Å)	τ (°)	t (°)	C
I ($n=1$)	0.56	8	4.7	4.5	137	0.1	9	-66.6	<i>gg</i>
II ($n=2$)	0.56	7	5.0	4.3	125	0.5	14	-55 (<i>a</i>) 76 (<i>b</i>)	<i>gg</i> <i>gt</i>
III ($n=3$)	0.58	2	5.2	4.5	123	-0.2	14	-74	<i>gg</i>
IV ($n=4$)	0.56	5	4.9	4.3	129	-0.4	21	77	<i>gt</i>
V ($n=5$)	0.56	2	4.8	4.4	132	0.4	15	-83	<i>gg</i>
VI ($n=6$)	0.55	5	5.1	4.4	124	0.3	13	-73	<i>gg</i>
VII ($n=7$)	0.52	5	5.2	4.2	121	-0.6	26	78	<i>gt</i>

Q and θ = Cremer-Pople parameters; $D_K = K...O4n$ distances, where K is the centroid of the $O4n$ heptagon; $D = O4n...O4(n+1)$ distances; $\Phi_h = O4(n-1)...O4n...O4(n+1)$ angles; d = deviations of the $O4n$ atoms from their least-squares plane; τ = tilt angles between the optimum $O4n$ plane and the mean plane of the $O4(n-1)$, $C1n$, $C4n$, $O4n$ atoms; torsion angles $t = O5n-C5n-C6n-O6n$ where (*a*) and (*b*) denote the occupied sites of the disordered primary hydroxyl groups; C = conformation of the hydroxyl groups

Figures Legends

Figure 1 The asymmetric unit of the 2NAA/ β -CD crystal structure. Two guest molecules are accommodated inside the formed head-to-head dimer occupying either the GA1-GB1 or the GA2-GB2 pair of sites

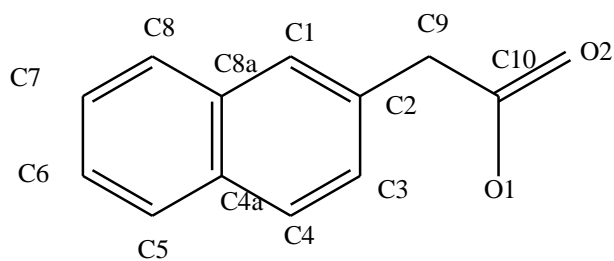
Figure 2 The type of the molecular packing of the 2NAA/ β -CD crystal structure is that of a Channel formed by dimers along the c axis. The guests found inside these nanotubes are linked by π - π interactions inside the dimeric cavities and by H-bonds between adjacent dimers.

Figure 3 The molecular packing of the 2NAA/ β -CD crystal structure (ab plane). The nanotubes formed along the c axis contain linked guest molecules.

Figure 4 The 2NAA/TM β CD crystal structure. The guest molecule is distributed over two sites, A and B, having occupancy factors 0.78 and 0.22 respectively.

Figure 5 The molecular packing of the 2NAA/TM β CD crystal structure. The complexes are packed in a head-to-tail mode along the b axis forming a Screw Channel.

Figure 6 The host molecule of the 2NAA/TM β CD complex is puckered and the sevenfold symmetry is not maintained.



Scheme 1

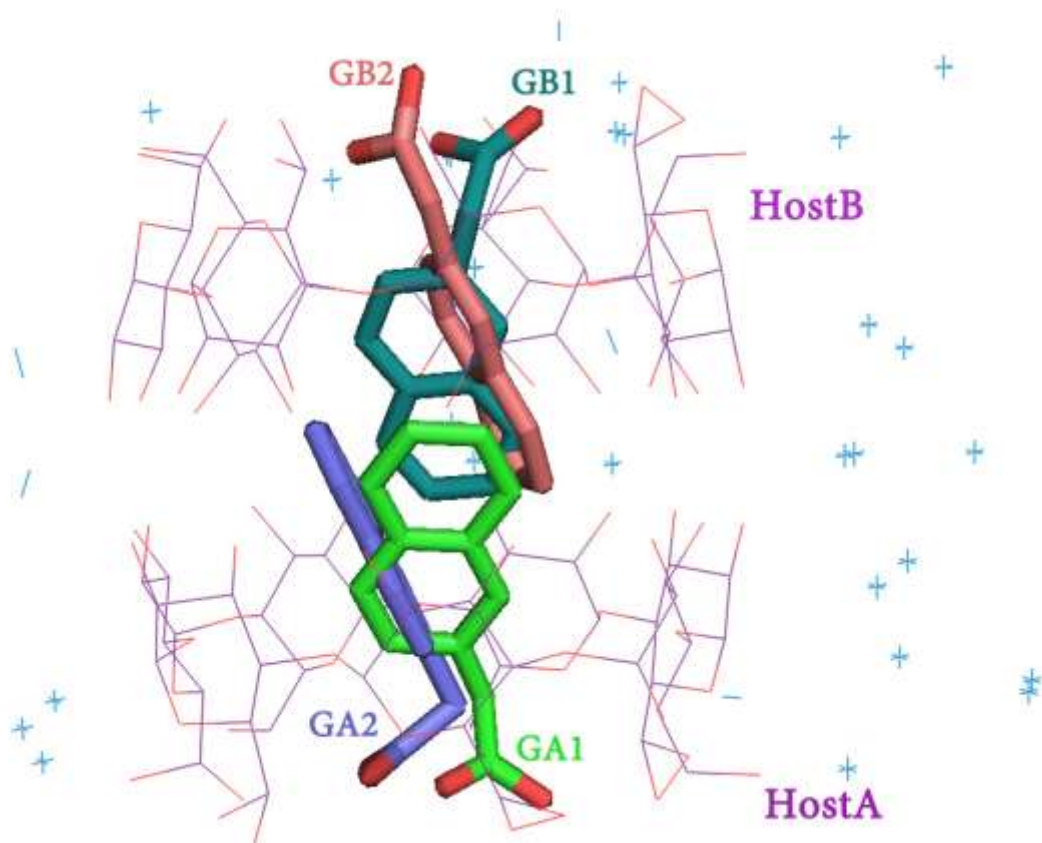


Figure 1 The asymmetric unit of the 2NAA/ β -CD crystal structure. Two guest molecules are accommodated inside the formed head-to-head dimer occupying either the GA1-GB1 or the GA2-GB2 pair of sites

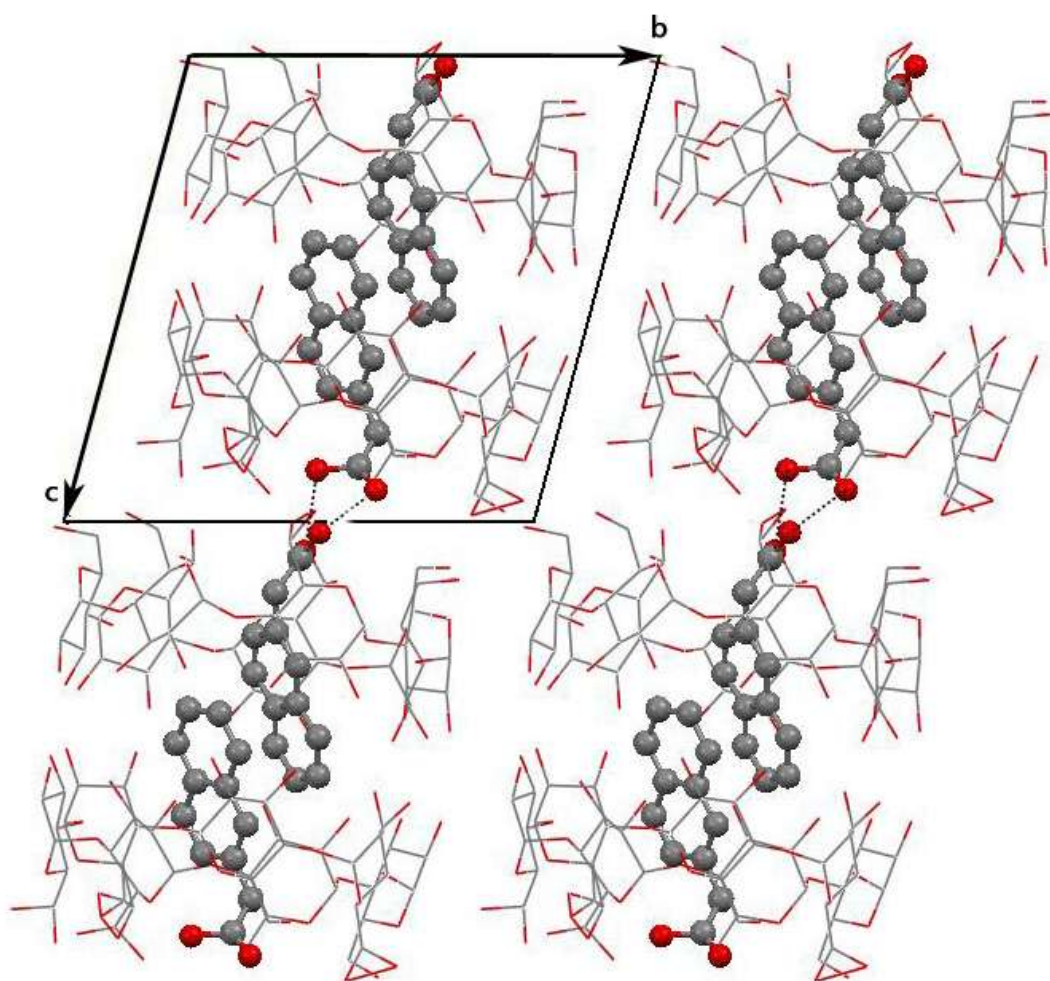


Figure 2

The type of the molecular packing of the 2NAA/ β -CD crystal structure is that of a Channel formed by dimers along the c axis. The guests found inside these nanotubes are linked by π - π interactions inside the dimeric cavities and by H-bonds between adjacent dimers.

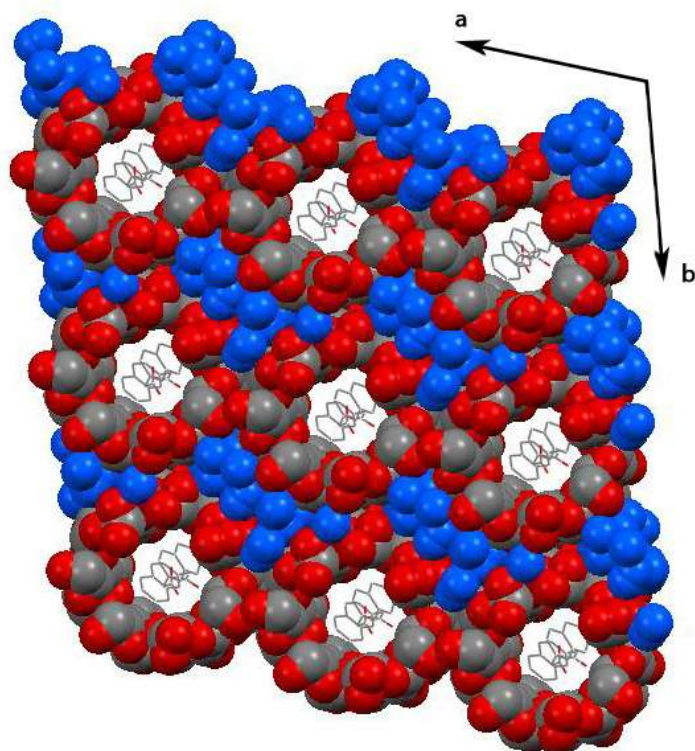


Figure 3

The molecular packing of the 2NAA/ β -CD crystal structure (ab plane). The nanotubes formed along the c axis contain linked guest molecules.

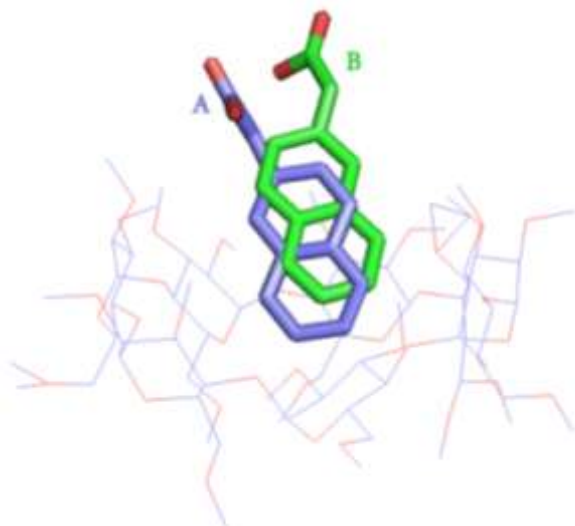


Figure 4

The 2NAA/TM β CD crystal structure. The guest molecule is distributed over two sites, A and B, having occupancy factors 0.78 and 0.22 respectively.

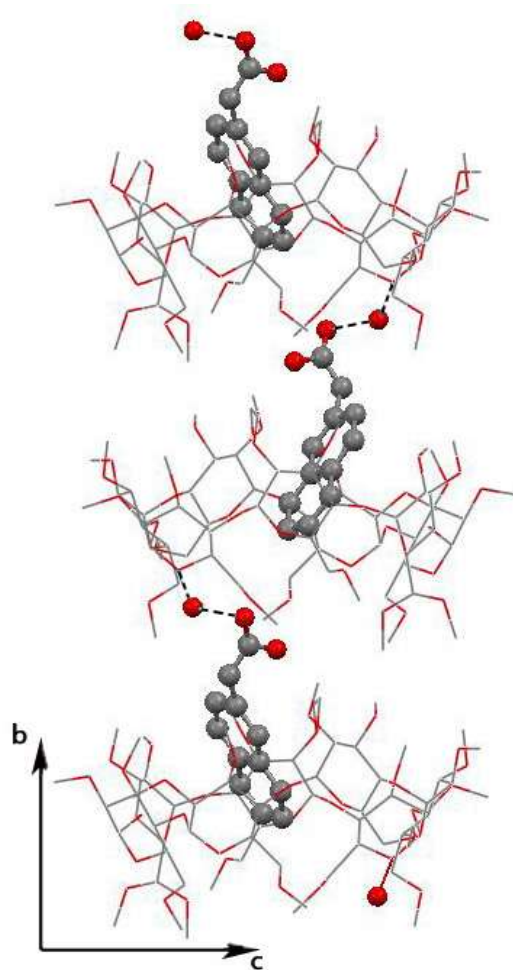


Figure 5

The molecular packing of the 2NAA/TM β CD crystal structure. The complexes are packed in a head-to-tail mode along the *b* axis forming a Screw Channel.

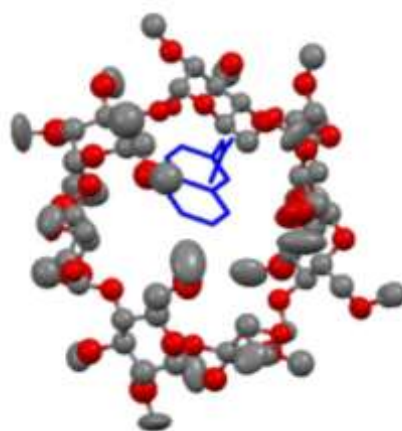


Figure 6

The host molecule of the 2NAA/TM β CD complex is puckered and the sevenfold symmetry is not maintained.