

Weak Intermolecular Interactions in the (1:1) Pyridine Solvate of Dibenzotetraaza[14]annulene Copper(II) Complex. The Crystal Structure of [7,16-dibenzoyl-6,8,15,17-tetramethyl-5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato(2-)- κ^4 N]copper(II)·pyridine

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Abstract

Recrystallization of the title Cu(II) complex from pyridine afforded solid (1:1) pyridine inclusion compound. The crystal structure revealed a pleated-sheet-like arrangement of saddle-shaped molecules of the host, with molecules of pyridine enclathrated within intermolecular cavities. Careful analysis of intermolecular contacts showed that weak aromatic edge-to-face (C—H··· π) interactions occur between pyridine and host molecules. The crystal packing appeared to be also stabilized by the host–host C—H···O hydrogen bonds.

Introduction

Understanding host–guest interactions in supramolecular complexes has become crucial for further development of chemistry, biochemistry and materials science [1]. In particular, crystalline inclusion compounds (clathrates) have recently received a great deal of attention due to their potential applications as soft supramolecular materials [2]. Number of papers appeared evaluating non-covalent interactions in the crystalline inclusion complexes [3] and elaborating criteria allowing to precisely describe spatial relationships between interacting molecules [3b, c] [4].

Dibenzotetraaza[14]annulenes belong to synthetic macrocycles known since 1969 [5] and appreciated for their synthetic accessibility [6], rich chemistry [7] and similarity to the active sites of metalloenzymes. In recent years their potential to associate various guest molecules *via* supramolecular interactions has been recognized resulting in remarkable achievements [8]. It has been shown that the saddle-shaped molecules of dibenzotetraaza[14]annulene, possessing two concave surfaces defined by phenylene rings and diiminate fragments, can act as supramolecular receptors for complementary convex surfaces of fullerenes C₆₀ [9] and C₇₀ [10], as well as for o-carborane, S₈ and chalcogenides P₄S₃ and P₄Se₃ [11]. Inclusion properties of [6,17-dimethyl-8,15-diphenyldibenzo[b,i][1,4,8,11]tetraaza[14]annulenato]Ni(II) [6c], [12] have been studied by Ripmeester et al. [13]. The authors concluded that the molecule of host, although well suited

to large globular guests, appeared less appropriate for small molecules of various solvents. Among them, pyridine was mentioned to be indifferent to inclusion. Interestingly, we have recently observed that Cu(II) complex of *meso* substituted dibenzoyl derivative of dibenzotetraaza[14]annulene **1** (Figure 1) easily formed a 1:1 solvate with pyridine. The question has arisen therefore as to why the benzoyl substituents we introduced to the molecule of host affected its propensity to form a solvate with pyridine. Since pyridine is known to be often involved in effective aromatic π – π stacking [4a], it seemed reasonable to expect that this kind of supramolecular interactions would appear essential in the assembly processes leading to the solvate formation. In order to shed more light on this selectivity phenomenon we have carefully analyzed intermolecular close contacts and spatial relationships between molecules in the crystal lattice, using Malone's criteria and classification of X—H··· π and π – π interactions [4b].

Herein we report the crystal structure of the (1:1) pyridine solvate of [7,16-dibenzoyl-6,8,15,17-tetramethyl-5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato(2-)- κ^4 N]copper(II) (**1**) (Figure 1) and full analysis of intermolecular interactions.

Experimental

Materials and methods

Elemental analysis was performed with use of an EuroEA (Eurovector) microanalyser. Thermogravimetric measurements were made using a Mettler-Toledo

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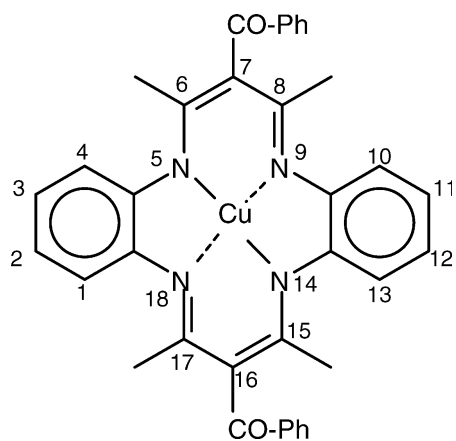


Figure 1. Chemical diagram of (1).

851e Apparatus. Pyridine was dried and freshly distilled before use.

Preparation of the solvate (1·py)

Cu(II) complex 1 was synthesized according to previously reported procedure [14]. It was re-crystallized from small quantity of hot pyridine to give crystalline solvate in the form of black cubes with metallic sheen.

Elemental analysis

Found: 71.31% C, 5.00% H, 10.08% N. calculated for $C_{41}H_{35}N_5O_2Cu$: 71.03% C, 5.08% H, 10.10% N.

Thermogravimetry

TG curve of the product showed a mass loss of 11% in the 110–150 °C temperature range, corresponding to loss of pyridine (calculated for (1·py): 11.4%), and final decomposition of the product at 340 °C.

X-ray crystallography

The X-ray diffraction data were collected at room temperature on a Nonius KappaCCD single crystal diffractometer using graphite monochromatised MoK α radiation. Crystal data and a summary of data collection and structure refinement parameters are given in Table 1. The Denzo–Scalepack program package was used for unit cell parameters refinement and data reduction. The structure was solved by direct methods using SIR program and refined on F^2 using all data by full matrix least-squares procedures with SHELXL-97 [15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Except for pyridine for which hydrogen atoms were included in calculated positions, hydrogens were localized on difference Fourier maps and refined with isotropic displacement parameters. Despite high temperature factors, position of nitrogen atom in pyridine was determined unambiguously, on final Fourier map there are no peaks that could correspond to aromatic hydrogen atoms at proposed position of nitrogen. Crystallographic data for the structure reported in this paper

Table 1. Crystal data and structure refinement for (1·py)

Empirical formula	$C_{36}H_{30}N_4O_2Cu \cdot C_5H_5N$
Formula weight	693.28
Temperature (K)	293(1)
Wavelength (Å)	0.71070
Crystal system	Orthorhombic
Space group	Pnma
<i>a</i> (Å)	15.7430(2)
<i>b</i> (Å)	19.1350(3)
<i>c</i> (Å)	11.2450(5)
<i>V</i> (Å ³)	3387.47(17)
<i>Z</i>	2
<i>D_c</i> (g/cm ³)	1.359
μ (mm ⁻¹)	0.689
Reflections collected	7373
Independent reflections	3980
<i>R_{int}</i>	0.0206
Goodness of fit on F^2	1.053
<i>R</i> , <i>wR2</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0447, 0.1221
<i>R</i> , <i>wR2</i> (all data)	0.0606, 0.1347

have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 244336

Results and discussion

The compound 1 crystallizes in the orthorhombic Pnma space group with a half molecule in the independent part of the unit cell. Two halves of the molecule 1 are related by mirror plane that goes through the Cu²⁺ ion and both phenylene rings (Figure 2). The Cu²⁺ ion located on the crystallographic mirror plane is coordinated by four nitrogens with distances Cu–N equal 1.874 and 1.877 Å and exhibits square-planar coordination with the shift from nitrogens plane by 0.05 Å in direction of the phenylene rings. The molecule adopts typical saddle-like conformation, defining two concave surfaces on both sides of N₄ plane – the propanediimine-moieties-containing concave surface on one side of the N₄ plane and those including phenylenediamine rings on the opposite side (Figure 2). The cavities created in this way will be referred to as “deep” and “shallow”, respectively. The curvature of the concave surfaces is described by the angle between plane (N1, N2, C1, C3, C11) and related by mirror symmetry plane (N1', N2', C1', C3', C11') equal 52.1°, and the angle between (N1, N1', C16, C16') and (N2, N2', C13, C13') planes equal 48.0°. The benzoyl groups are almost perpendicular to tetraaza plane thus expanding the walls of the deep cavity, with the torsion angle (C5–C4–C3–C1) equal 84.4(3)°. This conformation minimizes steric interactions between phenyl rings and methyl groups C2 and C12 and is similar to that observed in the crystal structures of the *meso* derivatives, previously reported [16].

In the crystal, molecules of 1 are arranged into pleated layers parallel to (100) plane with pyridine molecules accommodated in cavities between them

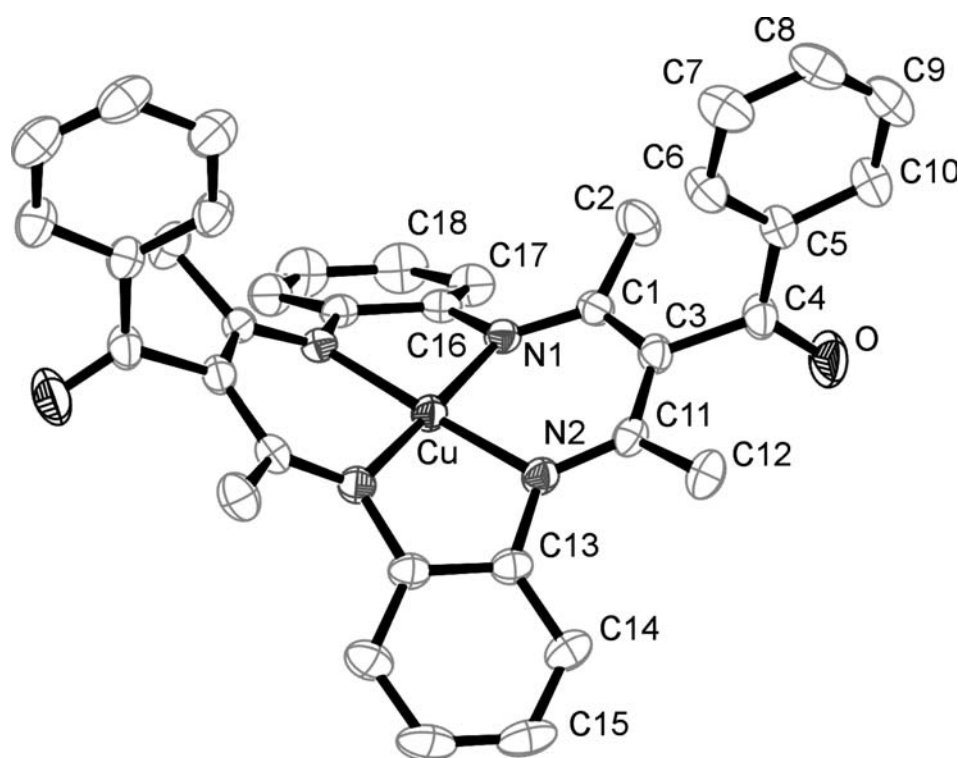


Figure 2. ORTEP drawing of (1) showing thermal ellipsoids at the 50% probability level. For clarity hydrogen atoms are omitted and symmetry related part of the molecule was not labeled.

(Figure 3). Each layer consists of rows of identically oriented molecules extending in z direction. The molecules in the row are tilted so their tetraaza planes make an angle of 18° in respect to the layer plane. The direction of tilt is opposite in succeeding layers. As a consequence of tilting, edge of the phenylene ring Q2 (C13–C14–C15–C15'–C14'–C13') points towards plane of the Q3 ring (C16–C17–C18–C18'–C17'–C16') of consecutive molecules like in an edge to face π – π stacking (Figure 4a). The angle between Q2 and Q3 ring planes is

equal 64.8° , the edge C15–C15' of the ring Q2 is 3.68 \AA from the plane of the ring Q3. The distance between H15 and center of the ring Q3 being equal 3.258 \AA is longer than sum of the van der Waals radii, this contact is also longer than 3.05 \AA listed as a limit for X–H... π interactions [4b].

Pleating of layers results from opposite orientation of deep and shallow cavities of molecules in neighboring rows. The contacts between rows are established by pairs of phenyl rings Q1A and Q1B

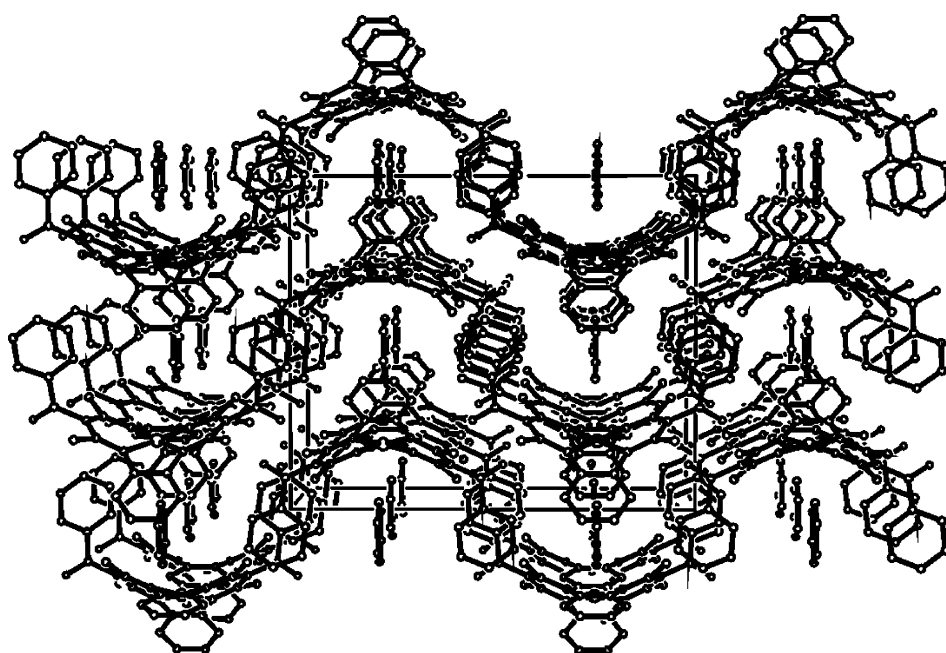


Figure 3. Packing diagram of (1 · py) showing pleated layers and pyridine molecules between layers.

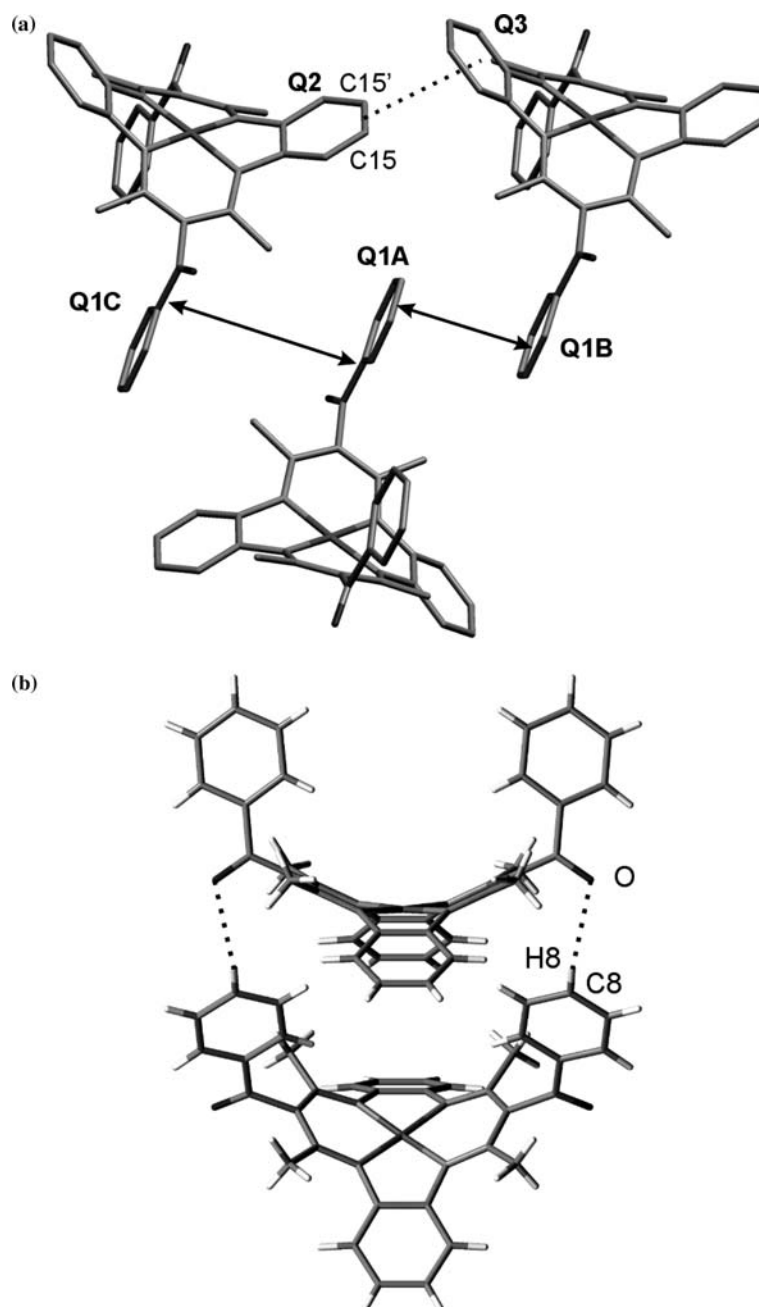


Figure 4. (a) Interactions between molecules of **1** involving aromatic rings; and (b) C—H···O hydrogen bonds.

arranged in a face-to-face π - π stacking fashion (Figure 4a). The distance between centers of rings is equal 4.43 Å while the offset is equal 1.2 Å. The separation between rings equal 4.26 Å is significantly larger than typically observed distance 3.3–3.8 Å [4b] thus this interaction is very weak and should not be classified as a π - π stacking. The distance between another pair of phenyl rings Q1A and Q1C is even longer (about 5.97 Å) and does not contribute to stabilization of molecular packing.

The only strong polar group in the molecule of **1** is a carbonyl group. As shown on Figure 4b, this group acts as an acceptor of the C8—H8···O hydrogen bond to the molecule in the next layer. The carbonyl oxygen is in the distance 2.669 Å from the phenyl ring hydrogen H8 and

3.494 Å from the C8 atom, the angle C8—H8···O is equal 152.8°. These values are typical for the geometry of C—H···O interactions [17] and indicate presence of weak hydrogen bonds between molecules.

As the distances between molecules of **1** are relatively long and does not indicate presence of strong attractive interactions except for a weak C—H···O hydrogen bond, important role in stabilization of the structure plays the pyridine. The molecule of pyridine is located on the crystallographic mirror plane, in the cage defined by the molecules of **1** belonging to two adjacent layers (Figure 3). Thus it resides in fact in both cavities – in a deep cavity of the host molecule from one layer and in a shallow cavity from the other.

The walls of the cage accommodating pyridine are formed by two pairs of parallel phenyl rings (Figure 5a) that make edge to face contacts with the pyridine. The angle between pyridine and phenyl ring plane is equal 82.6° . The geometry of interaction resembles type IV according to the classification of $X-H \cdots \pi$ interactions by Malone *et al.* [4b], however all distances between phenyl ring hydrogens and center of pyridine ring are longer than 3.5 \AA significantly exceeding limit 3.05 \AA for this type of interaction.

The nitrogen atom of pyridine faces towards the copper ion in the shallow cavity, however the distance from N3 to Cu is equal 3.199 \AA . This distance is much longer than expected for nitrogen coordinated to copper atom, thus position of pyridine is stabilized by other interactions.

In the plane of symmetry the pyridine molecule is surrounded by three molecules of **1** and makes contacts with their phenylene moieties (Figure 5b). The shortest contact is observed in the shallow cavity between phenylene ring Q3A (C16–C17–C18–C18'–C17'C16') and C23–H23. The distance between H23 and center of ring Q3A is equal 2.794 \AA , the angle $\alpha(\text{C23-H23} \cdots \text{Q3A})$ is equal 174.6° , the angle Θ between H23 \cdots Q3A direction and phenylene ring plane is equal 75.8° and the offset, horizontal distance of H from center of a ring, is equal 0.685 \AA . According to classification of $X-H \cdots \pi$ interactions [4b], this is interaction of Type II. Another short interaction is observed between H19 and phenylene ring Q2A (C13–C14–C15–C15'–C14'–C13'). The distance H19 \cdots Q2 is equal 2.877 \AA , $\alpha(\text{C19-H19} \cdots \text{Q2})$ is equal 135.9° , the angle Θ

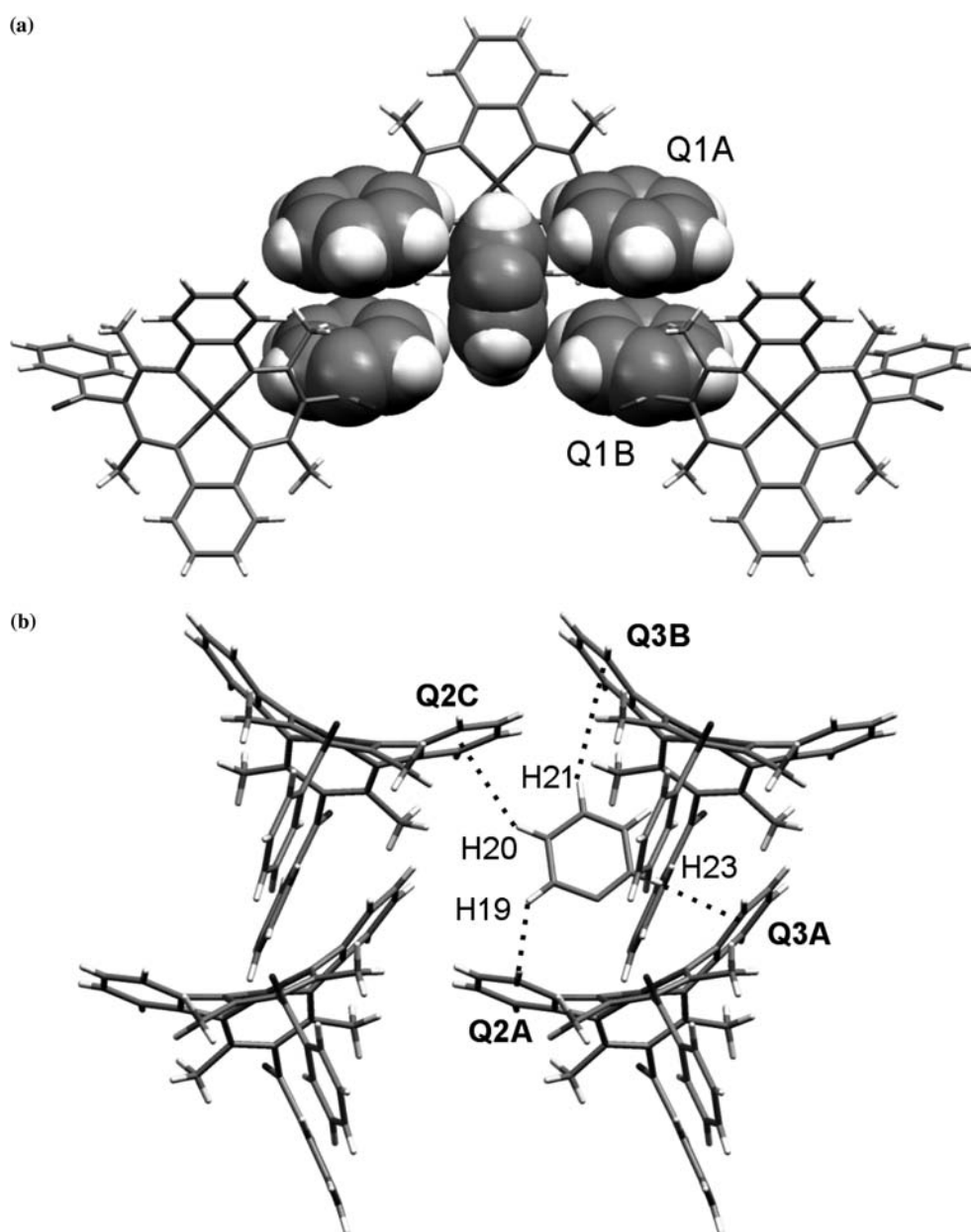


Figure 5. (a) Interactions between molecules of (**1**) and pyridine. Aromatic rings on both sides of pyridine and pyridine shown with van der Waals radii; and (b) $C-H \cdots \pi$ interactions in the plane of pyridine molecule.

is equal 82.3° and the offset is 0.386 Å. These values are in the range expected for interaction of Type III.

The packing of molecules shows also potential interactions between C20–H20 and Q2C ring of molecule C and between C21–H21 and ring Q3B of molecule B (Figure 5b). The distances between hydrogen and center of a ring are however equal 3.255 and 3.618 Å, longer than expected for interactions of Type I to IV. The offset parameter of these interactions equal 0.943 and 2.135 Å respectively is also out of the range expected for interactions of Type V.

Conclusions

In contrast to *meso* unsubstituted dibenzotetraaza[14]annulenes studied earlier [13], *meso* dibenzoyl derivative **1** [(7,16-dibenzoyl-6,8,15,17-tetramethyl-5,14-dihydrodibenzo[b,i] [1,4,8,11]tetraazacyclotetradecinato(2-)-κ⁴N)copper(II)] was found to form a crystalline (1:1) inclusion complex with pyridine. It has been confirmed by means of elemental analysis, thermogravimetry and single crystal X-Ray diffraction. The crystal packing appeared to be typical for clathrates, with the pyridine molecules entrapped within intermolecular cages built up of saddle shaped host molecules. Benzoyl substituents introduced at the *meso* positions are involved in formation of the deep concave surface of the host molecule, thus increasing the dimensions of the intermolecular cavities, as compared with those found in crystals of *meso* unsubstituted host [12, 13]. Careful analysis of intermolecular close contacts and geometric arrangement of the molecules in the crystal lattice, using Malone's criteria [4b], revealed C–H···π interactions of the Type II and III [4b] between pyridine and phenylene moieties of the host molecule. The *meso* benzoyl substituents were found to contribute also significantly in stabilization of the crystal lattice *via* host–host C–H···O hydrogen bonds. Although pyridine is considered to be well suited for effective aromatic π–π stacking [4a], here no significant face-to-face interactions have been found.

The results presented here well agree with Nishio's *et al.* conclusions [3d–f], inferred from their database study of crystal structures deposited in Cambridge Structural Database (CSD). According to their work, intermolecular C–H···π interactions involving hosts and guests have been found to play an important role in controlling the crystal packing in majority of inclusion complexes studied.

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