Variable Conformation of Benzophenone in a Series of Resorcinarene-Based Supramolecular Frameworks

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ABSTRACT: Ten supramolecular complexes incorporating benzophenone (BZP) as a guest have been synthesized by hydrothermal and conventional methods and characterized by X-ray diffraction. They are CMCR·3bipy·2H$_2$O· BZP (CMCR = *C*-methylcalix[4]resorcinarene; bipy = 4,4′-bipyridine) **1**, CMCR·bipy·BZP·H$_2$O **2**, CMCR·2bpe·BZP (bpe = *trans*-1,4-bis(pyridyl)ethylene) **3**, CMCR·2bpmh·BZP (bpmh = bis-(1-pyridin-4-yl-methylidene)-hydrazine) **4**, CMCR·2bpeh·BZP·ethanol (bpeh = bis-(1-pyridin-4-yl-ethylidene)-hydrazine) **5**, CMCR·2bipy·BZP **6**, CECR·2bipy· BZP·0.5bipy (CECR = *C*-ethylcalix[4]resorcinarene) **7**, CECR·2bpe·0.5BZP·0.5ethanol **8**, CMCR·2bix·2BZP (bix = 1,4-bis(imidazol-1yl-methyl)benzene) **9**, and CECR·2bix·2BZP **10**. The resorcinarene molecule adopts a chair conformation in **1**, giving rise to a 3D stepped network. Compounds **2** and **3** have a brick-wall structure with boat-shaped CMCR but different spacer connectivity. A 3D 3-fold interpenetrating network exists in compound **4**, whereas a wavelike framework is found in **5**. Crystals of **6**, **7**, and **8** contain carcerand-like capsules. The use of a more rigid spacer generates **9** and **10**, which exhibit a double buckled framework with large channels. The 10 phases contain 12 independent benzophenone molecules (**9** and **10** each having two independent benzophenone molecules), eight of which are fully ordered within the supramolecular framework. Benzophenone occurs as a monomer in **1**, **5**, **8** and as a dimer in **2**, **3**, **4**, **6**, and **7**, while polymeric aggregates are found in **9** and **10**. The dihedral angles between the two phenyl rings of benzophenone vary from 42.0 to 67.9°, and correlate with the central C−C−C bond angles, which decrease with increasing dihedral angle. Quantum-mechanical calculations indicate the energy of the distortion imposed by the framework to range up to 32 kJ/mol, which is significant relative to the ∼85 kJ/mol lattice energy of the known neat benzophenone phases.

Introduction

In a supramolecular host/guest solid the properties of the guest molecules can vary with the framework in which they are embedded.[1] Thus, supramolecular solids offer a unique opportunity to study the conformation- and environment-dependence of molecules in a dilute, yet periodic, environment. In a preceding paper, we have described a series of supramolecular solids encapsulating the photoactive benzil molecule with a variety of molecular conformations.[2] The nature of the distortion from the isolated molecule's theoretical equilibrium geometry was found to depend on the size of the cavity in which the guest molecules are embedded, the benzil molecules being nearly trans-coplanar in the tightest cavities, and exhibiting a close to 90° dihedral angle between the phenyl planes when the molecule is least constrained.

We describe here a parallel study of the benzophenone molecule, captured in 10 different host frameworks with CMCR (CMCR = *C*-methylcalix[4]resorcinarene) and CECR (CECR = *C*-ethylcalix[4]resorcinarene) as basic node molecules. The host frameworks can be tuned by varying both the multifunctional linker molecules (Scheme 1), thus avoiding a drawback of single-molecule organic hosts such as cholic acid and cyclodextrin which cannot be chemically modified without large changes in the basic crystal architecture. The different frameworks provide a variety of different environments in which the guest molecule adopts a series of different conformations. We note that conformational isomers as observed in this study also occur in different polymorphs and in crystals with more than one molecule in the asymmetric unit, as elegantly demonstrated in the case of 4,4-diphenyl-2,5-cyclohexadienone.[3] However, the environmental variety that is attainable in multicomponent supramolecular systems is of course very much larger than that available in neat crystals.

Benzophenone (BZP) undergoes an S$_1$(n, π*) ← S$_0$ transition upon photoexcitation and subsequently relaxes into a strongly phosphorescing excited triplet state with a lifetime of 3.0 μs in benzene solution at room temperature,[4] and about 55 μs and 0.18−4.1 ms in neat crystals at room temperature[5] and 77 K, respectively.[6] Extensive studies on the luminescence behavior of benzophenone in solid phases have recently been reported by Vieira Ferreira and co-workers. In studies of *p-tert*-butylcalix[n]arene/benzophenone phases (n = 4, 6, 8), with samples prepared by solvent evaporation of mixtures with varying composition, benzophenone ketyl radical formation was observed for n = 6, 8 but not for n = 4, for which a triplet lifetime of about 80 μs was observed at room temperature.[7] The samples used were not structurally characterized, but a structure of *p-tert*-butylcalix[4]arene/benzophenone reported by Chowdhury et al. shows one of the phenyl rings to be pointing toward the center of the bowl-shaped *p-tert*-butylcalix-[4]arene molecule, with favorable *tert*-butyl-CH$_3$···π interactions judged to be of critical importance for the stability of the complex.[8] For a benzophenone/O-propyl-

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Scheme 1

Spacers

Nodes

bipy

bpe

bpmh

bpeh

bix

R = CH₃ or CH₂CH₃
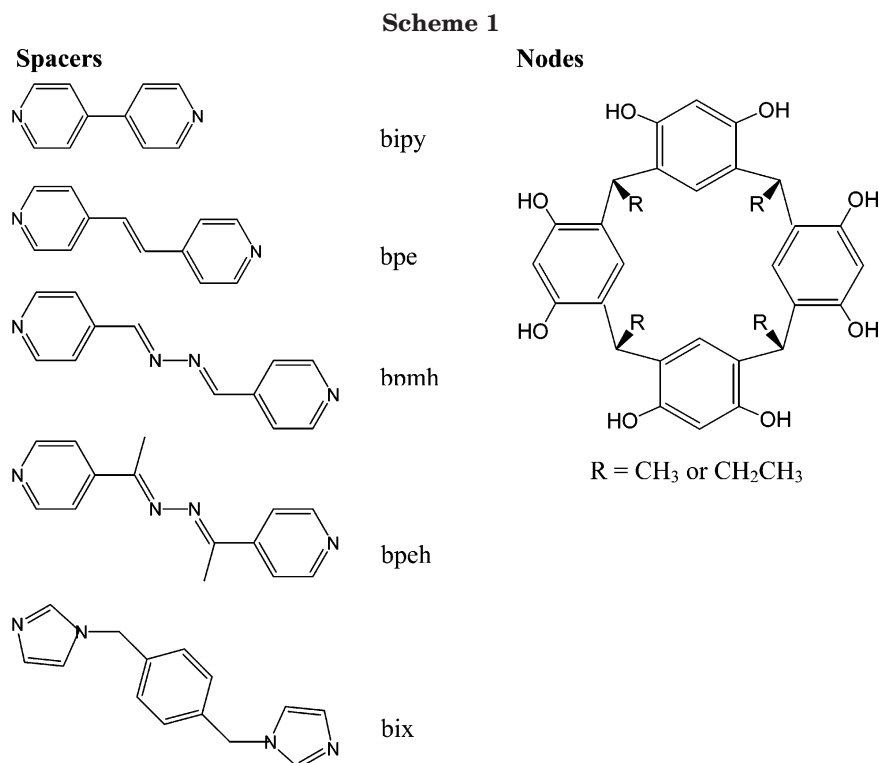
ated *p-tert*-butylcalix[4]arene mixture evidence for hydrogen abstraction from the propoxy substituents was obtained.[9]

Other spectroscopic investigations of benzophenone confined in host matrixes such as the cholic acid channels,[10] hexa-*tert*-butyl-37,38,39,40,41,42-hexaethoxycalix[6]arene (HBHEC) matrix[11] and the cyclodextrin cavities[12] have been reported. However, the correlation between spectroscopic information and full geometry of benzophenone cannot be established because of frequently occurring disorder or lack of suitable single crystals.[13,14] Although some frameworks containing benzophenone guests have been reported,[15–17] the structural information is still limited.

The phases included in this study are CMCR·3bipy·2H₂O·BZP (CMCR = *C*-methylcalix[4]resorcinarene; bipy = 4,4′-bipyridine) **1**, CMCR·bipy·BZP·H₂O **2**, CMCR·2bpe·BZP (bpe = 4,4′-bis-(pyridyl)ethylene) **3**, CMCR·2bpmh·BZP (bpmh = bis-(1-pyridin-4-yl-methylidene)-hydrazine) **4**, CMCR·2bpeh·BZP·ethanol (bpeh = bis-(1-pyridin-4-yl-ethylidene)-hydrazine) **5**, CMCR·2bipy·BZP **6**, CECR·2bipy·BZP·0.5bipy (CECR = *C*-ethylcalix[4]resorcinarene) **7**, CECR·2bpe·0.5BZP·0.5ethanol **8**, CMCR·2bix·2BZP (bix = 1,4-bis(imidazol-1yl-methyl)-benzene) **9** and CECR·2bix·2BZP **10**. The structures of **2**, **4**, and **6** have been briefly communicated before.[18] The 10 compounds surveyed contain 12 independent benzophenone molecules, of which eight are fully ordered within the supramolecular framework. As discussed below, they show a considerable variation in their molecular conformations.

Results and Discussions

All the complexes described were prepared either from ethanol solution or under hydrothermal conditions, which is an effective method for preparing resorcinarene-based supramolecular complexes. The two

methods generally lead to different frameworks. Full details are given in Experimental Section.

No binary resorcinarene/benzophenone complexes were obtained from any of the reaction mixtures, although given the potential for hydrogen bonding between the carbonyl group of benzophenone and the hydroxyl groups of the resorcinarenes, formation of such solids was anticipated. Several attempts to prepare resorcinarene/benzophenone binary complexes in the absence of linker molecules in the reaction mixture failed, only resorcinarene/solvent complexes were obtained. We note that in only one of the solids surveyed here, i.e., 5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxy-28-trifluoromethylsulfonylcalix[4] arene/benzophenone, in which benzophenone is located within the bowl-shaped cavity, hydrogen bonding occurs between benzophenone and a neighboring calixarene.[8]

One of characteristic features of the resorcinarene molecule is its flexibility. Four different conformations, described as bowl, boat, chair and saddle, have been identified by solution NMR methods.[19] While the first three have been observed in crystalline solids,[20] as has an intermediate "scoop" conformation,[21] the saddle conformation has so far not been found in the solid state. In general, the conformation adopted by the molecule is closely correlated with the nature of the framework. The chair conformation occurs in stepped networks with bifunctional pyridyl linkers, the boat conformation typically is found in brick-wall frameworks, whereas the bowl-shaped molecules form wavelike polymers or capsules.

Description of the Structures. The 3D stepped network of CMCR·3bipy·2H₂O·BZP (1). 2D stepped CMCR·2bipy sheets can pack compactly without voids that might accommodate guest molecules, but they can also be cross-linked into a 3D network by additional bipy linkers without guest inclusion, as in CMCR·3bipy.[22] In
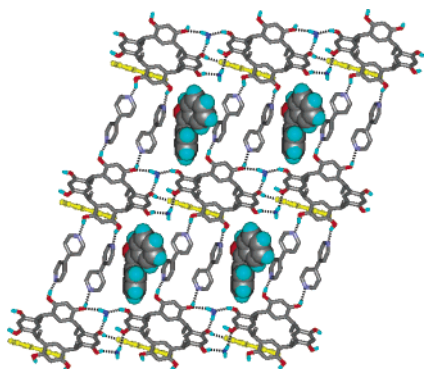
Figure 1. 3D stepped framework of **1**.

the presence of a suitable guest, water molecules interspersed between the CMCR's can effectively extend the cavity such that a molecule the size of benzophenone can be included while the 3D stepped framework is retained as is the case in solid **1** (Figure 1). Chair-shaped CMCR molecules are linked into columns by hydrogen-bonded water bridges to adjacent CMCR molecules. The four axial hydroxyl groups form O−H⋯N hydrogen bonds with bipyridine molecules, which link the columns into stepped sheets. These sheets are connected by additional bipyridines via O−H⋯N hydrogen bonds, giving rise to a three-dimensional network with cavities in each of which one benzophenone molecule is captured. Hydrogen bonding occurs between the benzophenone carbonyl group and the bridging water molecules (See Table S2).

The Brick-Wall Structures of CMCR·bipy·BZP· H₂O (2) and CMCR·2bpe·BZP (3). Compounds **2** and **3** are examples of the quite common[23] brick-wall framework structures. In both each CMCR adopts a boat conformation and connects with the neighboring CMCR molecules through intermolecular O−H⋯O hydrogen bonds to form one-dimensional infinite column, but the connectivity mode of the linkers differs. In **2**, CMCR columns are connected by two juxtaposed bipy monomer linkers to give a BW2a-type brick wall[22] and two benzophenone and two water molecules are included as guests within each cavity (Figure 2a). Replacement of bipy linker by the longer spacer bpe gives compound **3**, in which the CMCR columns are connected by two pairs of juxtaposed bpe dimers through O−H⋯N hydrogen bonds to form BW4-type brick wall[22] sheets as shown in Figure 2b. There are significant π−π interactions within the bpe dimers (the center-to-center and interplanar separations being 4.18 and 3.94 Å, respectively). The two olefin groups are parallel and separated by less than 4.2 Å, thus meeting the geometric criteria for solid-state photochemical [2+2] dimerization, which are being explored by supramolecular methods.[24] A pair of benzophenone molecules, related by an inversion center, with one phenyl ring of each benzophenone disordered over two positions, is included in each cavity. The disorder of the guest molecules appears related to the larger size of the cavities in the brick-wall framework of **3** relative to that in **2**.

The 3-Fold Interpenetrating Network of CMCR· 2bpmh·BZP (4). A much larger cavity was constructed with the much longer linker bpmh, resulting in **4**. However, as often encountered in crystal engineering,[25]
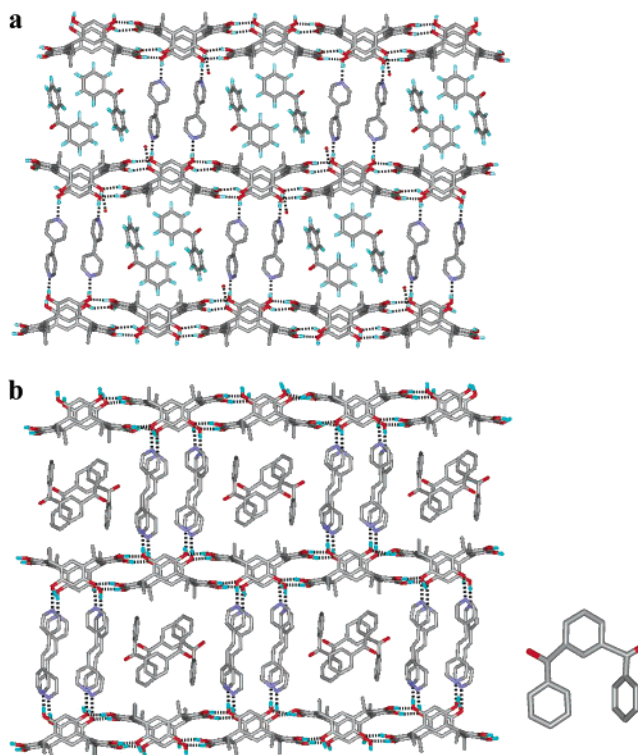
Figure 2. Brick-wall frameworks of **2** (a) and **3** (b). The disordered benzophenone in **3** is shown in the right side of **b**.
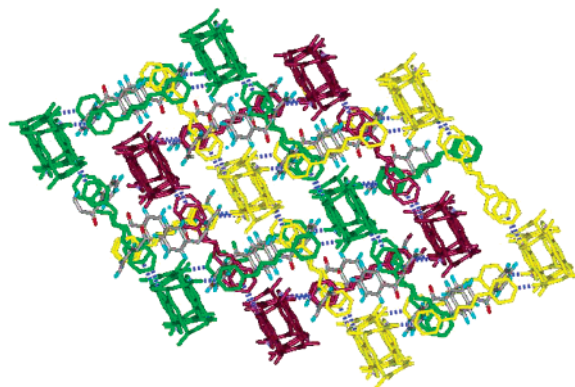

Figure 3. 3D triple interpenetrating networks of **4**. Each color corresponds to the node and linker molecules of a different network. The rectangular boxes in the projection are the CMCR molecules connected by the bpeh linkers of the same color.

the large void leads to self-inclusion of several three-dimensional frameworks, in the case of **4** to triple interpenetration. But even in the triply interpenetrated structure a large cavity in which two benzophenone molecules are encapsulated is retained.

The bpmh spacers in **4** link the CMCR columns into a BW2a-type brick-wall, which is further connected by additional bpmh's into a three-dimensional network. The 3-fold penetration is achieved by bpmh linker pairs threading through the voids of two successive brick-walls (Figure 3).

Wavelike CMCR·2bpeh·BZP·ethanol (5). In **5** bowl-like CMCR is located on a 2-fold axis with four intramolecular hydrogen bonds along its upper rim. Four intermolecular O−H⋯N hydrogen bonds between the hydroxyl groups and two stacked bpeh dimers link
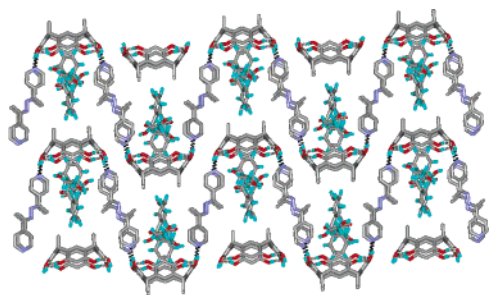
Figure 4. Wavelike framework of **5**.
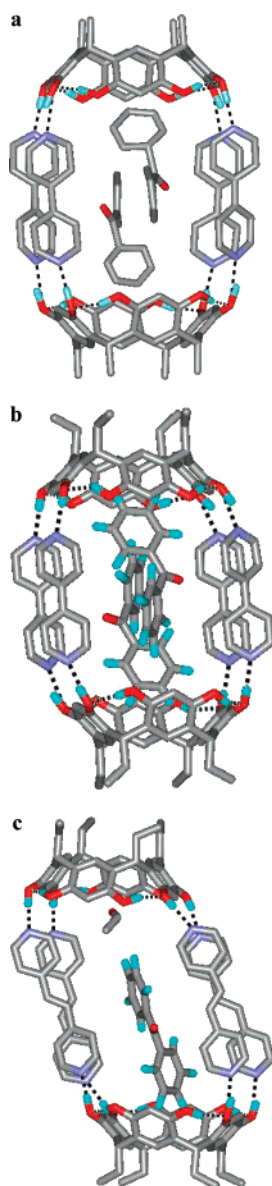
Figure 5. Capsules in compounds **6** (a), **7** (b), and **8** (c).

the molecules into a 1D wavelike polymer. Adjacent polymer chains arrange in a tongue-in-groove way with an ethanol- and benzophenone-containing cavity located between juxtaposed CMCRs (Figure 4). The two phenyl rings of the benzophenone molecule are bisected by a 2-fold axis, leading to 2-fold disorder. Strong hydrogen bonds are found between the carbonyl oxygen and ethanol molecules.
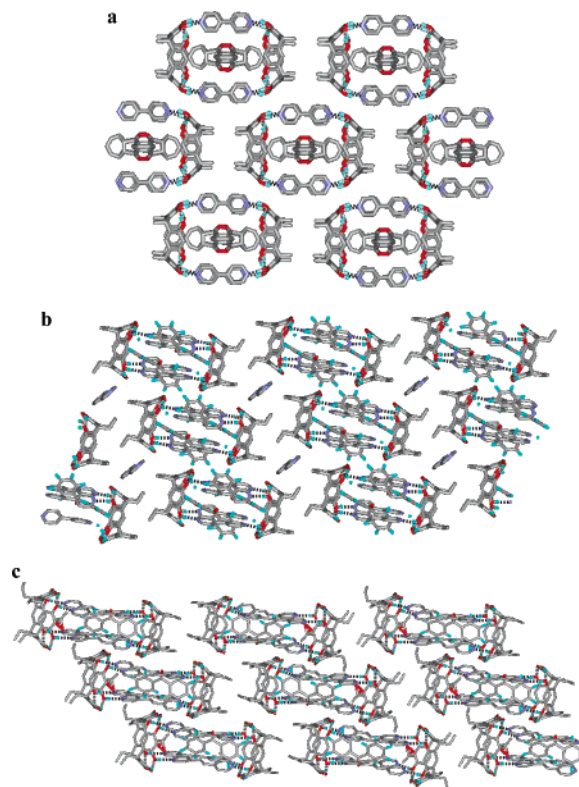

Figure 6. Capsule packing diagram in **6** (a), **7** (b), and **8** (c).

Capsule Frameworks of CMCR·2bipy·BZP (6), CECR·2bipy·BZP·0.5bipy (7), and CECR·2bpe·0.5BZP·0.5ethanol (8). A plethora of carcerand-like CMCR capsules, in which two bowl-shaped CMCR molecules are bridged by water, halides, or alcohols, have been reported.[26] When bifunctional pyridyl linkers bridge the CMCR molecules the cavity is enlarged and multiple guests can be included, as in CMCR·2bipy·2nitrobenzene,[27] CECR·2bpe·2pyrene,[28] CECR·2bpe·benzil,[2] and CMCR·2L·4toluene (L = 4′-(4-octyloxyphenyl)-4,2′:6′,4″-terpyridine).[29]

In **6** this arrangement occurs with stacked bipy dimers as pillars (Figure 5a). One of the pyridyl rings of the bipy is disordered over two positions. The cavity contains two disordered benzophenone molecules with one phenyl ring of each protruding out of capsule. Replacement of CMCR by CECR generates the similar capsule structure of **7** (Figure 5b), in which the twist angles of the bipy linkers are 33.0 and 44.1°, respectively. The cavity contains two inversion-center related benzophenone guests with as in **6** one phenyl ring of each protruding out of the capsule.

In compound **8**, the CECR molecules are linked by two stacked bpe dimers (Figure 5c), which have twist angles in the 5.1−26.3° range. The double bonds in adjacent bpe's are crossed, precluding [2+2] photoaddition.[24] Although the bpe spacer is longer than bipy, the size of the cavity in the capsule is not larger as the cavity is skewed, and only one benzophenone and one disordered ethanol molecule are included. Unlike in **6** and **7** the single benzophenone molecule in **8** is completely enclosed in the interior cavity of the capsule.

In all three solids the capsules are linked into frameworks. The capsule structure of **6** crystallizes in the space group *Fddd*, with a structure reminiscent of
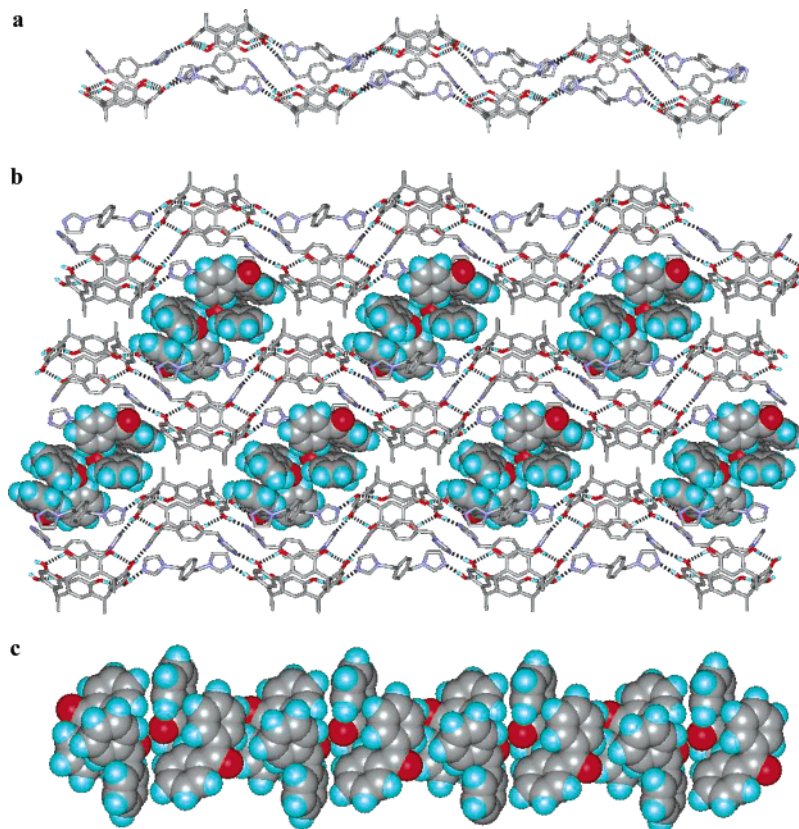
Figure 7. (a) Double bucked polymer of **9** (b) layer structural motif of **9**, showing the four benzophenone molecules included within each cavity. (c) 1D benzophenone polymeric aggregate.

that of simple face-centered cubic metals with supramolecular capsules rather than metal atoms (Figure 6a). Compounds **7** and **8** pack in a similar, although less symmetric manner with the ethyl groups of adjacent CECRs interleaved (Figure 6b,c). In **7** four capsules enclose a large cavity containing a bipyridine molecule. Its orientation is almost perpendicular to the plane of the capsules. The enclosure is different from that found in CMCR·2bipy·2nitrobenzene[27] and CECR·2bpe·2pyrene[28] in which two nitrobenzene resp. pyrene molecules are enclosed by the hydrocarbon tails of two adjacent capsules.

While the use of CMCR frequently gives rise to the brick-wall structure, we have not found similar structures with CECR. Apparently, the bulkiness of the ethylene group of CECR reduces the cavity volume sufficiently to preclude inclusion of guests of the size of benzophenone. A similar limitation does not apply to the capsule structure, since the ethylene groups point to the outside of the cavity.

The Double Buckled Frameworks of CMCR· 2bix·2BZP (9) and CECR·2bix·2BZP (10). Following a different approach, we have matched the flexibility of the resorcinarenes by using a flexible linker. 1,4-bis-(imidazol-1yl-methyl)benzene) or bis-imidazole xylene (bix) can exist in cis, trans, and gauche conformations. Two new benzophenone inclusion compounds **9** and **10** with buckled-polymer structures were synthesized. In **9** adjacent bowl-shaped CMCRs are connected into a 1D buckled polymer chain along the [001] direction by two bix linkers, through O—H···N hydrogen bonding, (Figure 7a). The CMCR molecules in one chain are all oriented in the same direction perpendicular to the chain, and
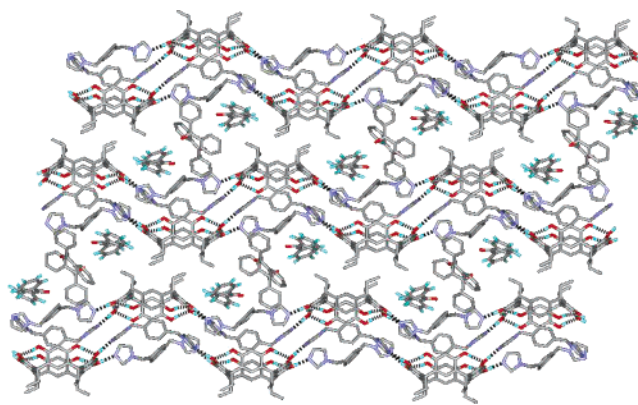
Figure 8. Double buckled chain framework of **10**.

have four intramolecular hydrogen bonds along their upper rim. This arrangement is distinct from the commonly observed wavelike polymer formed by CMCR and rigid pyridyl spacers, in which the CMCRs are directed in an up-and-down fashion, but shows similarity with the rodlike polymer CMCR·2bipy·4-bromobiphenyl.[30] The two bridging bix linkers adopt the trans and gauche conformations. Two adjacent chains are closely packed, such that the central phenyl ring of the gauche-conformational bix is located within the bowl cavity of the CMCR belonging to an adjacent chain, generating a double buckled chain (Figure 7a).

Neighboring double-buckled chains are arranged with the CMCRs oriented in opposite directions and form a layer in the (011) plane, with large voids, occupied by four benzophenone guests, two by two related by an inversion center, as illustrated in Figure 7b. Successive

Table 1. Relation between the Dihedral Angle between Two Phenyl Rings of Benzophenone and Other Structural Parameters in Compounds 1−10 and Benzophenone Inclusion Compounds in the Literature

	host framework	conc (mol/L)	cavity size/ one BZP ($Å^3$)	Ph−C twist angle (°)	Ph−Ph dihedral angle (°)	C=O bond length (Å)	$C_{ph}-C_{car}-C_{ph}$ (°)	ref
theoretical optimization				28.9, 28.9	52.5			
neat BZP ($P2_12_12_1$)		6.64	296		54.4	1.225(3)	121.4(2)	31
neat BZP ($C2/c$)		6.66	300	29.3, 43.5	64.5	1.223(2)	118.9(1)	32
1	step	1.07	305	16.7, 29.3	42.0	1.236(5)	122.9(5)	
2	brick-wall	1.54	275	18.5, 37.8	52.4	1.222(2)	120.4(2)	
3	brick-wall	1.10	474					
4	3D interpenetrating network	1.16	308	23.9, 43.3	62.7	1.217(4)	119.5(3)	
5	wavelike	1.04	310					
6	capsule	1.24	310					
7	capsule	1.09	316	25.6, 37.4	58.7	1.217(5)	120.5(3)	
8	capsule	0.60	282	14.7, 37.3	49.6	1.254(5)	123.3(4)	
9	buckled chain	1.86	318 (A)	29.3, 33.4	56.2	1.221(3)	119.9(2)	
			312 (B)	21.1, 34.0	48.0	1.233(3)	120.9(2)	
10	buckled chain	1.75	322 (A)	23.8, 27.1	46.1	1.224(3)	122.4(3)	
			341 (B)					
H1/2BZP[a]			286	16.1, 39.7	52.8			15
H2/BZP[a]			334	29.7, 44.7	67.9			8
H3/BZP[a]			307	22.6, 38.1	55.3			16
H4/BZP[a]			305 (A)	28.8, 35.5	57.5			17
			318 (B)	31.4, 31.4	57.7			
2-cholic acid/BZP	bilayer							13
β-CD/BZP	cavity							14

[a] H1 = 9,10-bis(3,5-dihydroxy-1-phenyl) anthracene; H2 = 5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxy-28-trifluoromethylsulfonyl-calix[4]arene; H3 = 1,1,6,6 tetraphenylhexa-2,4-diyne-1,6-diol; H4 = octakis(μ_3-hydroxo)-octadecacarbonyl-hepta-manganese.

layers pack in the [100] direction such as to link the voids into continuous channels occupying 35% of the crystal space and containing columns of benzophenone molecules (Figure 7c).

Replacement of CMCR by CECR gives **10**, with a structure similar to **9** (Figure 8). The relatively larger ethyl tail of CECR leads to a larger cavity between the double buckled polymers and to disorder of one of benzophenone guest molecules.

Discussion

Hydrogen Bond Competition. The supramolecular frameworks provide a variety of local environments for benzophenone. Although the carbonyl group of benzophenone can be a good hydrogen bond acceptor as in the benzophenone complexes with 9,10-bis(3,5-dihydroxy-1-phenyl)anthracene,[15] 5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxy-28-trifluoromethylsulfonylcalix[4]-arene[8] and 1,1,6,6 tetraphenylhexa-2,4-diyne-1,6-diol[16] (O(N)-H⋯O=C hydrogen bonds), and the resorcinarenes provide numerous hydroxyl groups, no significant hydrogen bond interactions between carbonyl and resorcinarene host were found in any of our benzophenone inclusion complexes. The nitrogen acceptor atoms of the pyridyl and imidazol-based spacers evidently compete effectively for the hydrogen donor atoms. The weakness of the interaction between the carbonyl group of benzophenone and the OH groups of the resorcinarenes is also evident from the absence of binary resorcinarene−benzophenone phases in our reaction mixtures. In **1** and **5**, the benzophenone carbonyl groups are involved in hydrogen-bond interactions with water and organic solvent molecules.

Geometry Changes. A summary of host-frameworks and benzophenone geometries from this study and from host/guest complexes reported in the literature is given in Table 1. Neat benzophenone exists in two polymor-
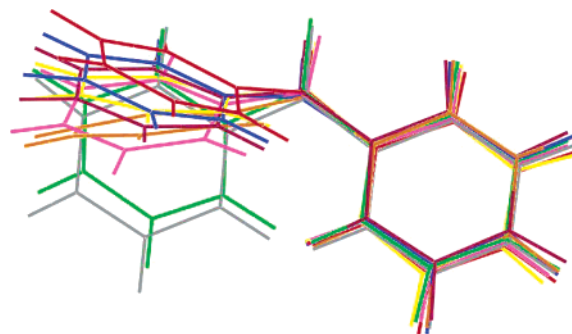

Figure 9. Superposition of the benzophenone conformations occurring in the supramolecular frameworks studied. Numerical details on the molecular conformations are given in Table 1.

phic forms, the stable α-form[31] and a metastable β-form,[32] in which the dihedral angles between the two phenyl rings are 64.5 and 54.4°, respectively, compared with a value of 52.5° calculated for the isolated molecule. In the host frameworks the dihedral angles vary within a range of 42.0 to 67.9° (Table 1), which is similar to the 46.3−68.7° range found for the derivatives of benzophenone retrieved from Cambridge Structural Database.[33] The conformations of the benzophenone molecules found in the supramolecular frameworks reported here are illustrated in Figure 9. Unlike in our previous study of benzil,[2] the phenyl-group dihedral angles and the cavity size as calculated by PLATON[34] show no direct correlation, although the smallest cis-C−C−C−O torsion angles tend to occur for the smallest cavity volumes (in **1** and **8**).

The central C−C−C bond angle of the carbonyl group varies from 118.9(1)° to 123.3(4)° (Table 3, only low temperature data sets are included). This angle decreases gradually as the dihedral angle changes toward 90° (Figure 10). The correlation can be attributed to steric hindrance, which is maximal in the planar
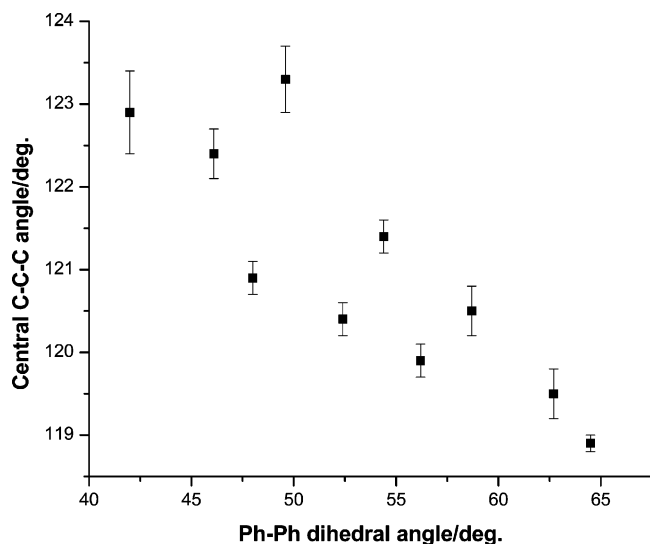
Figure 10. The dependence of central C−C−C bond angle on phenyl dihedral angle for benzophenone molecules.
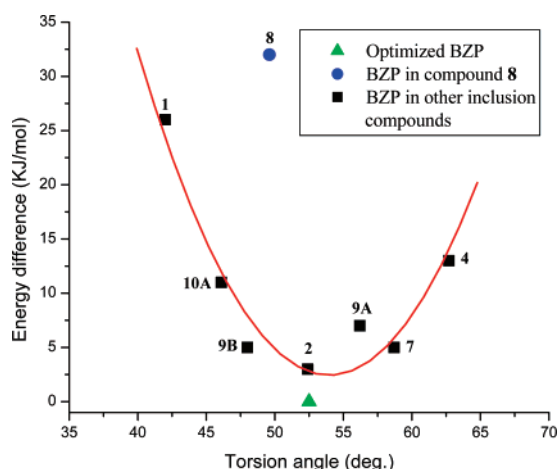
Figure 11. The dependence of energy of the benzophenone molecules with the experimentally determined conformations on the dihedral angle between the phenyl groups. The curve fit excludes the conformation found in compound **8**, in which the C=O bond is lengthened by about 0.03.

conformation, but eliminated to a large extent as the dihedral angle approaches 90°. The C=O bond length remains unaffected with the exception of **8**, which shows an increase of about 0.03 Å from the average value. Further examination of surrounding environment of this carbonyl group reveals that three short contacts occur between the carbonyl and hydrogen atoms from CECR and the bpe linker molecule, while at most two C⋯H contacts occur in any of the other structures, thus providing a plausible explanation for lengthening.

For each of the observed conformations and for the optimized isolated molecule the energy was calculated as described in Experimental Section. As shown in Figure 11, with the exception of **8**, which exhibits an unusually long C=O distance, a parabolic relation is found between the energy and the dihedral angle. The sacrifice in guest energy is as large as 32 kJ/mol for **1**, which may be compared with the lattice energy of the stable and metastable forms of benzophenone, which have been calculated as −85.90 and −83.01 kJ/mol, respectively, by Kutzke et al.[32] The considerable loss in
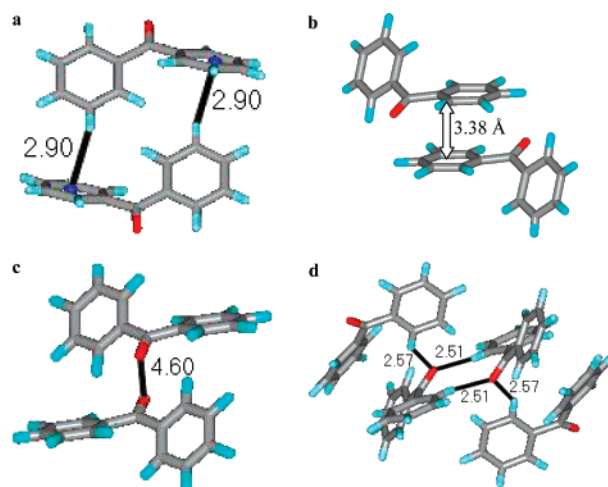
Figure 12. Benzophenone dimers found in the supramolecular complexes **2** (a), **4** (b), **7** (c), and a tetramer in **9** (d).

energy must be compensated by the stability of the stepped framework. The conformation in **2**, in which two benzophenones are located in cavities in a brick wall framework, is remarkably close to that of the isolated molecule.

Types of Benzophenone Aggregates. Benzophenone occurs as a monomer in **1**, **5**, and **8**, and as a dimer in **2**, **3**, **4**, **6**, and **7**. A dimer was also found in 9,10-bis-(3,5-dihydroxy-1-phenyl)anthracene·2benzophenone.[15] Although the molecules in the dimers are all related by inversion centers, they are arranged in considerably different manners (Figure 12). In **2**, two benzophenone molecules are oriented in an antiparallel fashion with the two carbonyl groups well separated. The adjacent phenyl rings of the two benzophenones show C−H⋯π contacts (2.90 Å) (Figure 12a). The dimer in **4** is held together by strong π−π interactions between two phenyl rings of proximal benzophenones (the interplanar and center-to-center distances are 3.381 and 3.675 Å, respectively) (Figure 12b). The two carbonyl groups show an O−O contact of 4.6 Å in **7** (Figure 12c) compared with 3.87 Å in 9,10-bis(3,5-dihydroxy-1-phenyl)anthracene·2benzophenone.[15] Two symmetry related benzophenone molecules in **9** form a dimer through C−H⋯O hydrogen bond interactions (2.51 Å); the dimer is further extended into a tetramer through C−H⋯O hydrogen-bond interactions (of length 2.57 Å) with two adjacent benzophenones (Figure 12d). The disorder interferes with detailed analysis of the dimer or tetramer arrangements in **3**, **6**, and **10**.

Conclusions

Ten supramolecular frameworks consisting of resorcinarene nodes and different linker molecules encapsulate benzophenone guest molecule with varying conformations in differently shaped cavities. The dihedral angle between the phenyl planes of the guest molecules varies from 42.0 to 67.9° demonstrating the effect of the supramolecular environment on molecular conformation. Theoretical calculations indicate the energy of the distortion of the guest molecules imposed by the framework to range up to 32 kJ/mol, which is not negligible relative to the ∼85 kJ/mol lattice energy of the known neat benzophenone phases.

The variety that can be achieved even with a restricted choice of node and linker molecules illustrates the remarkable versatility of the supramolecular solid state, which is capable of providing different, but well-defined, environments for a single chemical species. The effect of this nanoscale diversity on molecular properties is an important subject for further study.

The prediction of the type of crystal structure that will be obtained with given reactants and well-defined crystal growth conditions remains an elusive goal that will require further insight into the kinetic processes and thermodynamic relations during the self-assembly process.

Experimental Section

General. *C*-methylcalix[4]resorcinarene (CMCR), 4,4′-bipyridine (bipy), 4,4′-bis-(pyridyl)ethylene (bpe), and benzophenone (BZP) were obtained from commercial sources. Bis(4-pyridylmethylidyne)hydrazine (bpmh),[35] bis(4-pyridylethylidyne)hydrazine (bpeh),[35] 1,4-bis(imidazol-1yl-methyl)benzene (bix),[36] and C-ethylcalix[4]resorcinarene (CECR)[37] were prepared according to literature methods.

Preparation of CMCR·3bipy·2H$_2$O·BZP (1) and CMCR·bipy·BZP·H$_2$O (2). CMCR (0.05 mmol, 27.2 mg), bipy (0.1 mmol, 15.6 mg), benzophenone (0.1 mmol, 18.2 mg), and 4 mL of water were sealed in a 6-mL Pyrex glass tube. The tube was allowed to stay at 140 °C for 24 h, followed by cooling to room temperature over 4 days. Two kinds of crystals, colorless plates and yellowish blocks, were separated and identified as **1** and **2**, respectively.

Preparation of CMCR·2bpe·BZP (3). CMCR (0.05 mmol, 27.2 mg), bpe (0.10 mmol, 18.9 mg), and benzophenone (0.1 mmol, 18.2 mg) in 3 mL of ethanol were heated until the solution became clear. Yellow crystals were obtained after 2 h when solution was cooled at room temperature.

Preparation of CMCR·2bpmh·BZP (4). CMCR (0.05 mmol, 27.2 mg), bpmh (0.1 mmol, 20.8 mg), and benzophenone (0.1 mmol, 18.2 mg) were mixed in 5 mL of ethanol solution and heated until the solution became clear. The solution was cooled and some orange precipitate (identified as CMCR·2bpmh·ethanol) was filtered off. Yellow prismatic crystals of **4** were obtained from the filtrate at room temperature after 5 days.

Preparation of CMCR·2bpeh·BZP·ethanol (5). CMCR (0.05 mmol, 27.2 mg), bpeh (0.1 mmol, 23.6 mg), and benzophenone (0.1 mmol, 18.2 mg) were mixed in 5 mL of ethanol solution and heated until the solution became clear. Light orange crystals were obtained after one week by slow evaporation at room temperature.

Preparation of CMCR·2bipy·BZP (6). CMCR (0.05 mmol, 27.2 mg), bipy (0.1 mmol, 15.6 mg), benzophenone (0.1 mmol, 18.2 mg), and 4 mL of water were sealed in a 6-mL Pyrex glass tube under an argon atmosphere. The tube was allowed to stay at 140 °C for 24 h, followed by cooling to room temperature over 4 days. Light yellow block-shaped crystals were identified as **6**. Crystals of **1** and **2** were also harvested from the same tube.

Compound **6** can also be readily prepared from ethanol solution. CMCR (0.05 mmol, 27.2 mg), bipy (0.10 mmol, 15.6 mg), and benzophenone (0.1 mmol, 18.2 mg) in 3 mL of ethanol were heated until the solution became clear. Yellow crystals were obtained after 2 days through slow evaporation at room temperature.

Preparation of CECR·2bipy·BZP·0.5bipy (7). CECR (0.05 mmol, 30 mg), bipy (0.10 mmol, 15.6 mg), and benzophenone (0.1 mmol, 18.2 mg) in 5 mL of ethanol were heated until the solution became clear. Orange crystals were obtained after two weeks through slow evaporation at room temperature.

Preparation of CECR·2bpe·0.5BZP·0.5ethanol (8). CECR (0.05 mmol, 30 mg), bpe (0.10 mmol, 18.9 mg), and benzophenone (0.1 mmol, 18.2 mg) in 5 mL of ethanol were heated until the solution became clear. Orange crystals were obtained after two weeks through slow evaporation at room temperature.

Preparation of CMCR·2bix·2BZP (9). CMCR (0.05 mmol, 27.2 mg), bix (0.10 mmol, 23.8 mg), and benzophenone (0.1 mmol, 18.2 mg) in 5 mL of ethanol were heated until the solution became clear. Light orange crystals were obtained after one week through slow evaporation at room temperature.

Preparation of CECR·2bix·2BZP (10). CECR (0.05 mmol, 30 mg), bix (0.10 mmol, 23.8 mg), and benzophenone (0.1 mmol, 18.2 mg) in 5 mL of ethanol were heated until the solution became clear. Light orange crystals were obtained after two weeks through slow evaporation at room temperature.

Crystallography

X-ray data for compounds **1**−**10** were collected with the SMART program on a Bruker SMART 1000 CCD at 90 K. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.[38] All non-hydrogen atoms are refined anisotropically and hydrogen atoms, except those of disordered benzophenone and solvent molecules, were taken from difference electronic Fourier maps and refined isotropically. One phenyl ring of the benzophenone guest in **3** is disordered over two positions with a ratio of 0.619(7)/0.381. A 2-fold axis passes through the two phenyl rings of benzophenone in compound **5**, implying the molecules to be disordered over two positions with equal occupancy. One of the two independent benzophenone guests in compound **10** is disordered over two positions with a ratio of 0.529(3)/0.471. Two methylene groups of gauche conformational bix in **10** are also disordered. Crystallographic information on the complexes **1**−**10** is summarized in Table S1 and hydrogen bond parameters for compounds **1**−**10** are given in Table S2 of the Supporting Information.

Theoretical Calculations

The geometry optimization and energy calculations of the benzophenone molecules were performed with the GAUSSIAN 98 package[39] using density functional theory (DFT) without any symmetry restrictions. The B3LYP functional with a 6-311++G** basis set was used for the C, H, and O atoms.

Supporting Information Available: Tables of crystallographic information and hydrogen bonding geometry for complexes **1**−**10**. X-ray crystallographic files in CIF format for the structure of **1**−**10**: CCDC-158838 (**1**), 168091 (**2**), 224415 (**3**), 195326 (**4**), 224416 (**5**), 168092 (**6**), 224417 (**7**), 224418 (**8**), 224419 (**9**), 224420 (**10**). This material is available free of charge via the Internet at http://pubs.acs.org.

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