

Multiple Conformations of Benzil in Resorcinarene-Based Supramolecular Host Matrixes

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Six supramolecular complexes incorporating benzil as a guest, CMCR·bipy·benzil (α) **1** (CMCR = *C*-methylcalix[4]resorcinarene), CMCR·bipy·benzil (β) **2**, CMCR·2bpe·benzil·ethanol **3** (bpe = *trans*-1,4-bis(pyridyl)ethylene), CMCR·2bpe·benzil·2H₂O **4**, CMCR·2bpeh·benzil·ethanol **5** (bpeh = bis-(1-pyridin-4-yl-ethylidene)-hydrazine), and CECR·2bpe·benzil **6** (CECR = *C*-ethylcalix[4]resorcinarene), have been synthesized by hydrothermal and conventional methods and characterized by X-ray diffraction. Resorcinarene adopts a boat conformation in **1–4** and a bowl conformation in **5** and **6**. Compounds **1–4** show a brick-wall-like framework, in which two benzil molecules are incorporated. For **5**, bpeh spacers link CMCR molecules to give a one-dimensional wavelike polymer in which one benzil guest is embedded within the polymer cavity. Complex **6** forms a carcerand-like capsule in which two benzil guests are encapsulated. The O=C–C=O torsion angles vary from 91.8 to 139.3° and correlate with the length of the central C–C bond. The benzil concentration, which is ~6.2 mol/L in the neat crystals, varies between 1.01 and 1.51 mol/L in the structures studied, corresponding to a 6-fold dilution. The benzil molecules are disordered in the larger cavities of **4** and **5**. The two benzoyl fragments are almost perpendicular in **3**, which has the next largest cavity size when solvent volume is excluded, whereas a nearly *trans*-coplanar conformation occurs for the cavity with the smallest volume in **6**.

Introduction

Solid-state host–guest assembly has attracted intensive interest because of its application in fields as diverse as nonlinear optics, sensors, gas storage, and microreaction vessels.¹ Our interest lies in the use of supramolecular frameworks to explore the influence of the host environment on the geometry and other physicochemical properties of the guests.

In most solids, molecules are severely constrained by packing interactions with their neighbors.² Our time-resolved X-ray diffraction studies indicate that geometry changes on excitation are very much reduced in neat solids compared with those in isolated molecules.³ However, molecules embedded in supramolecular cavities have considerably more flexibility and accordingly show much larger variation in their geometry. Supramolecular solids thus can be exploited to study the effect of the environment, not only for the ground state of molecules but also for their excited states.

The physical properties and excited-state conformation of benzil have been widely investigated. Its excited triplet

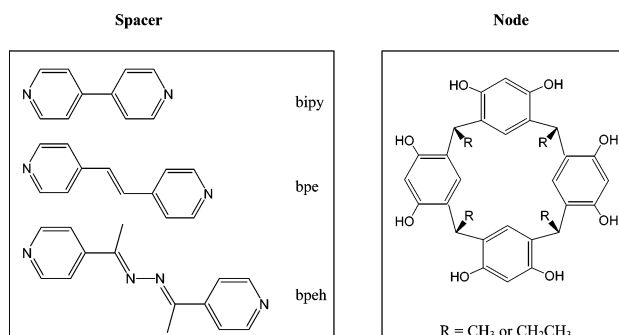
state has a millisecond lifetime at low temperature.¹¹ Spectroscopic experiments in solution,^{4–7} solution dipole moment measurements,⁸ and theoretical calculations⁹ indicate that the O=C–C=O group becomes *trans* planar in the T₁ lowest excited state of benzil, whereas spectroscopic studies in the crystalline state and in organic glasses indicate that the excited-state geometry and lifetime are affected by the constraining environment.^{10–17}

In contrast to the extensive spectroscopic investigations that have been conducted, only a few supramolecular

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SCHEME 1



complexes containing benzil as a guest have been reported. Furthermore, in the known structures either the benzil molecules are highly disordered as in the cholic acid channels¹⁸ and the β -cyclodextrin cavity¹⁹ or good quality crystals could not be obtained.²⁰ A drawback of single-molecule organic hosts such as cholic acid and cyclodextrin is that they cannot be chemically modified without destroying the basic crystal architecture. On the other hand, solids based on calix[4]resorcinarenes and bifunctional 4-pyridyl-type linkers can assemble into a diversity of frameworks,²¹ in which the sizes and shapes of cavities or channels can be tuned through variation of the spacer and thus can be used to embed a variety of guests including photoactive molecules such as decamethylruthenocene and benzophenone.²² Unlike in many other host–guest crystals such as cyclodextrins and cholic acids, in the resorcinarene-based solids the guests are frequently fully ordered, allowing detailed analysis of the guest geometry.^{18,19}

By using spacers of different lengths (Scheme 1) and both CMCR (CMCR = *C*-methylcalix[4]resorcinarene) and CECR (CECR = *C*-ethylcalix[4]resorcinarene), we have incorporated benzil in a series of resorcinarene-based supramolecular solids: CMCR·bipy·benzil (α) **1**, CMCR·bipy·benzil (β) **2**, CMCR·2bpe·benzil·ethanol **3**, CMCR·2bpe·benzil·2H₂O **4**, CMCR·2bpeh·benzil·ethanol **5** (bpeh = bis-(1-pyridin-4-yl-ethyldene)-hydrazine), and CECR·2bpe·benzil **6**. In all but two of these solids the benzil molecules are fully ordered within the supramolecular framework.

Results and Discussion

Compounds **1** and **2** appeared in the same reaction tube during the hydrothermal synthesis and were recognized by the difference in their crystal habits. They share the same basic framework but have space groups $P\bar{1}$ and $P2_1/c$, respectively. The polymorphism of complexes **1** and **2** is quite unusual in a supramolecular

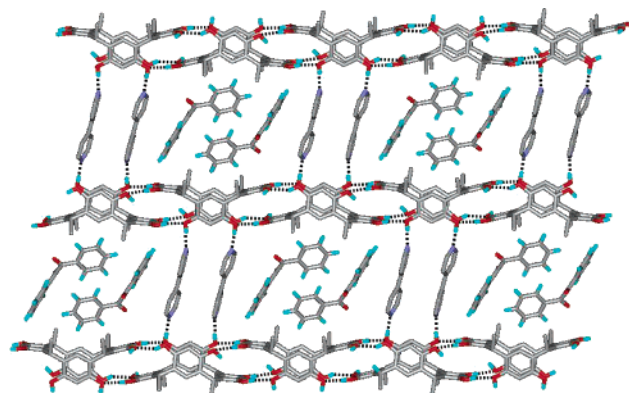


FIGURE 1. Brick-wall structure of **1**.

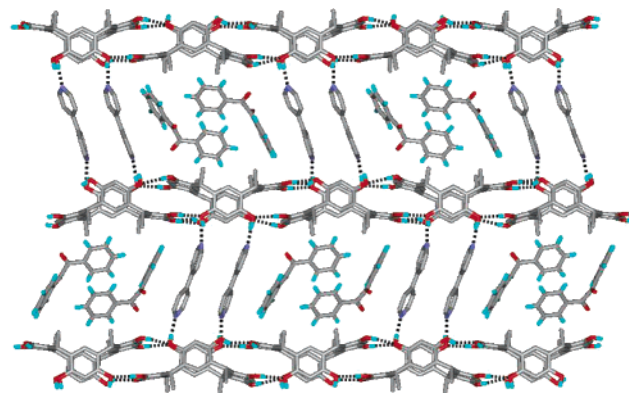


FIGURE 2. Brick-wall structure of **2**.

system, though it is a ubiquitous phenomenon for most organic compounds. The current study provides the first example of polymorphism among resorcinarene-based supramolecular solids. In both **1** and **2**, the CMCR molecules adopt a boat conformation and form one-dimensional (1D) infinite columns with neighboring CMCR molecules through intermolecular O–H···O hydrogen bonding. The columns in **1** are connected by two juxtaposed bipy monomer pillars through O–H···N hydrogen bonds to form skewed brick-wall sheets parallel to the (011) plane (Figure 1), similar to those found in CMCR·bipy·benzophenone·H₂O.²³ The bipy pillars are inclined to the CMCR columns by approximately 80°. Successive sheets are offset with respect to each other such that large cavities, rather than channels, are formed, which contain two benzil molecules related by an inversion center. A strong hydrogen bond from one of the hydroxyl groups of the CMCR molecule to a carbonyl group of benzil in the adjacent layer [O3···O9 = 2.890(2) Å, O3–H3···O9 = 164(2)°] stabilizes the structure.

Compound **2** crystallizes with two CMCRs, four bipy molecules, and two benzil molecules in the asymmetric unit. Its topological architecture is essentially the same as that of **1**, the two compounds being polymorphs, but the brick-wall framework in **2** is somewhat more skewed with an angle of 75° between CMCR columns and bipy pillars (Figure 2). Each cavity contains two independent benzil guests, rather than the centrosymmetric dimer found in **1**.

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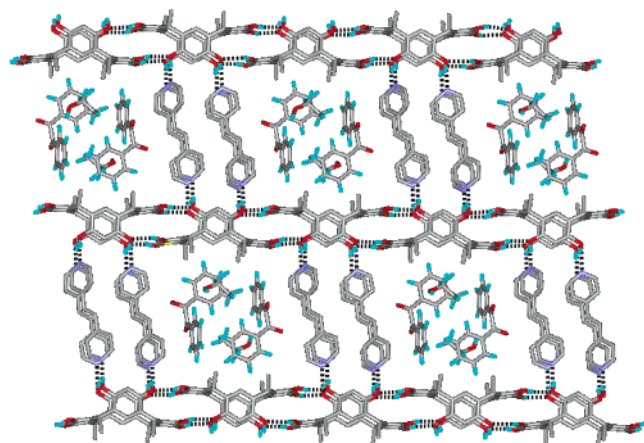


FIGURE 3. Brick-wall structure of **3**.

In **3**, the bpe linker replaces bipy, leading again to a brick-wall framework, here supported by two pairs of juxtaposed bpe dimers (Figure 3), similar to those observed in CMCR·2bipy·decamethylruthenocene·ethanol.²² There are significant π - π interactions between the bpe dimers, with center to center and interplanar separations of 3.964 and 3.226 Å, respectively. It is noteworthy that 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 is currently being explored by supramolecular methods.²⁴ As in **1** and **2**, the CMCR molecules are linked by hydrogen bonding into columns, which are connected by the linker bpe molecules to form a two-dimensional infinite-layered structure with large cavities. Each cavity contains a pair of fully ordered benzil molecules and two ethanol solvent molecules, related by a center of symmetry. The ethanol molecules are hydrogen bonded to CMCRs in adjacent sheets.

Hydrothermal synthesis with the same reactant ratio as was used in the preparation of **3** (but in water rather than ethanol) led to the formation of **4**, which is isomorphous with **3** but with an interlayer separation (parallel to the *b* axis) 1 Å larger than that in **3**, thus significantly increasing the cavity size. Compound **4** similarly has the four-pillar supported brick-wall framework (Figure 4) but in this case with an angle of 39.4° between the two proximal bpe molecules which are arranged antiparallel with a 4.45 Å separation between the centers of the double bonds. Two benzil guests, each disordered over two positions, and four water molecules, 2 by 2 related by a symmetry center, are accommodated within each cavity. The geometry of benzil in this complex could not be modeled accurately because of the disorder.

In **5** CMCR adopts a bowl-like conformation bisected by a mirror plane with four intramolecular hydrogen bonds along its upper rim. Four O-H...N hydrogen bonds between the hydroxyl groups and two stacked bpe dimers link the CMCR molecules into a 1D wavelike polymer. Adjacent polymers are arranged in a tongue-in-groove way, leaving a cavity between juxtaposed CMCRs in which one benzil and one ethanol molecule

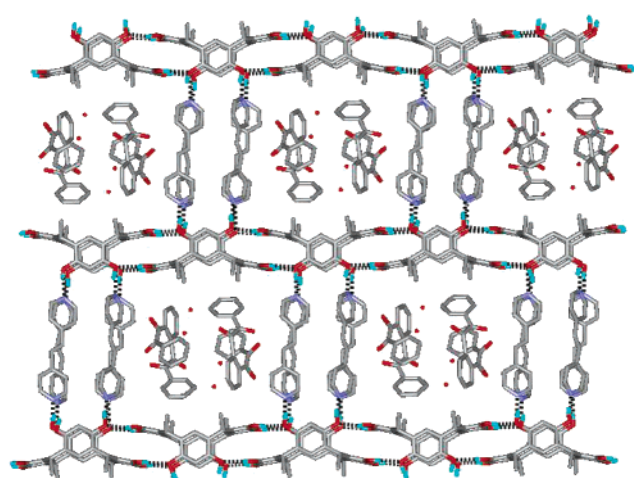


FIGURE 4. Brick-wall structure of **4**.

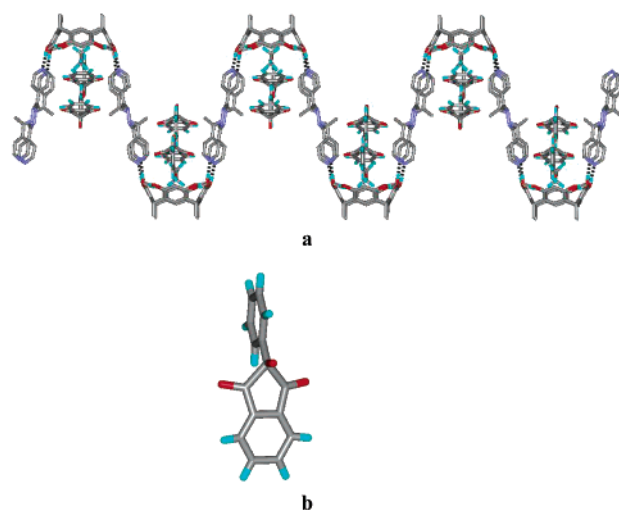


FIGURE 5. (a) Wavelike polymer in **5**. (b) Disordered benzil guest in polymer cavity.

are accommodated (Figure 5a). One of the phenyl rings and one carbonyl group of the benzil molecule are located on a mirror plane which bisects the second phenyl ring. As a result the two phenyl rings are perpendicular to each other and one of the carbonyl groups is disordered over two positions (Figure 5b).

In **6** bowl-shaped CECR is intramolecularly hydrogen bonded along the rim of the macrocycle. Two stacked bpe dimers act as pillars connecting two CMCR molecules to form a carcerand-like capsule containing two inversion-center-related benzil guests (Figure 6). The dihedral angles between the two pyridyl rings of the bpe linkers are 6.0 and 6.5°. The two molecules in each pair of bpe linkers are almost parallel with the angle between the best bpe planes equal to 4.6°.

A plethora of resorcinarene capsules bridged by water, halides, or alcohols have been reported.²⁵ Other pyridyl-spacer-sustained resorcinarene capsules similarly exhibit

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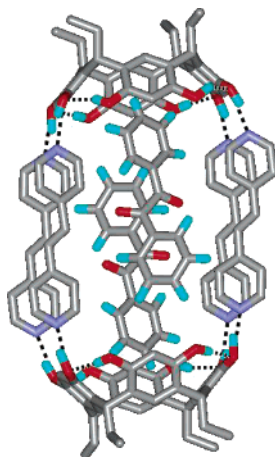


FIGURE 6. Carcerand-like capsule in **6**.

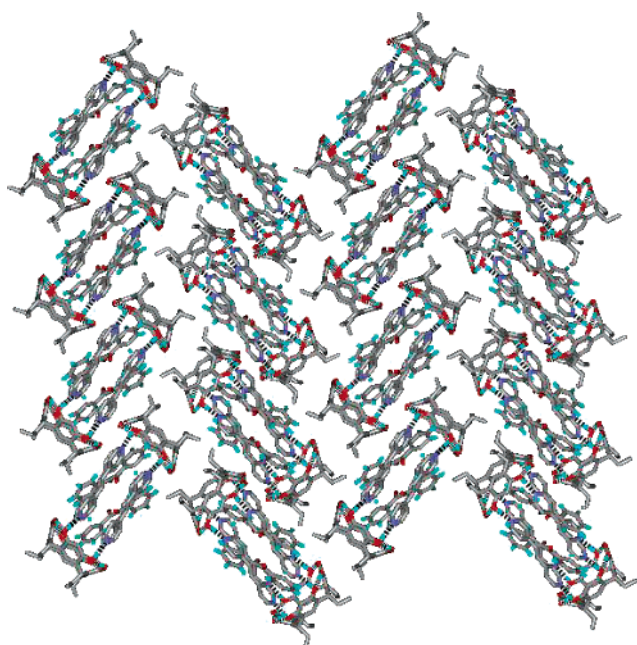


FIGURE 7. Herringbone arrangement of capsules in **6**.

large cavities capable of including multiple guests as in CMCR·2bipy·2nitrobenzene,²⁶ CMCR·2bipy·benzophenone,²³ and CMCR·2L·4toluene (L = 4'-(4-octyloxyphenyl)-4,2':6',4''-terpyridine).²⁷ The capsules in **6** are arranged in a herringbone fashion to produce a 2D sheet (Figure 7). The hydrogen-bonding geometry in **1–6** is summarized in Table S2 of the Supporting Information.

Geometry Changes. Two polymorphic modifications of neat benzil are known with the O=C–C=O torsion angle (φ) ranging from 103.1 to 113.8° among the four independent molecules in the two polymorphs.^{28–30} As the benzil molecules are constrained within the host framework of the supramolecular crystals, the planar benzoyl fragments are rotated around the central C–C bond such as to fit the environment of the host, leading to a variation of the O=C–C=O torsion angle from 91.8 to

139.3° (Table 1, Figure 8). The benzil guest in **1** adopts a conformation close to its optimal isolated-molecule geometry as calculated theoretically (123.4°), whereas the dihedral angles between the two carbonyl groups in **2** are similar to those of neat benzil structures. However, significant deviations from the optimal and neat geometries are found in **3** and **6**, demonstrating the defining influence of the host environment on the guest arrangement. Spectroscopic results have been interpreted as showing that the benzil phosphorescence can occur from both skewed and trans-planar excited triplet states,^{11,13} though evidence from other physical techniques is still lacking. The crystalline environment of **6**, in which the benzil torsion angle equals 139.3°, would most easily accommodate a change to a trans-planar conformation. It is clear that the inclusion of benzil in calixarene cavities does not in general promote deviations from planarity as sometimes stated but may in fact lead to a more nearly trans-planar conformation.

The central C–C bond length decreases significantly when the O=C–C=O torsion angle increases beyond 90° toward the planar trans configuration (Table 1, Figure 9),³¹ as may be expected because of increasing conjugation. It is consistent with the spectroscopic data which suggest that the central C–C bond order of the dicarbonyl fragment of benzil increases on going from the skewed ground-state conformation to the trans-planar excited state ($\varphi = 180^\circ$). The average carbonyl bond length is almost constant in the neat HT benzil phase and **1–3**, but its value in **6** is more than 0.01 Å longer, again in agreement with the observed decrease in the CO bond order upon excitation. The lengths of the C–C bonds between the carbonyl and phenyl rings, which are much shorter than the central C–C bond, are not affected.

Nature of Dimers. With the exception of compound **5**, all benzil guests occur in the host framework cavity as dimers, but the nature of the dimers varies considerably (Figure 10). In **1** and **2** the centrosymmetric dimers interact with each other by formation of π – π interactions between two phenyl rings. In **3**, the phenyl rings of two center-of-symmetry-related benzil molecules are almost perpendicular to each other with a dihedral angle of 84.3°, the benzil dimer being stabilized by C–H··· π interactions. The two benzil molecules in **6** are held together by C–H···O hydrogen-bonding interactions between the phenyl rings and carbonyl groups.

Cavity Size. The concentration of the benzil guests and the solvent-accessible volume of the host frameworks as calculated by PLATON³² are listed in Table 1. The dilution of benzil in the host–guest crystal relative to that in the neat solids is of advantage in studies of photoinduced molecular change in crystals, as fewer photons are required to achieve a large conversion percentage of the photochemically active molecules. Two

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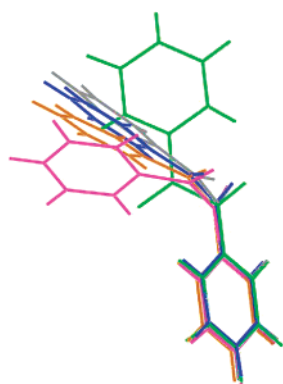
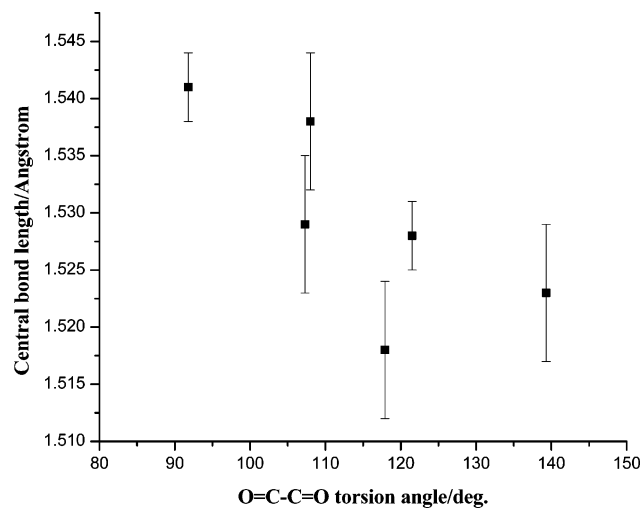
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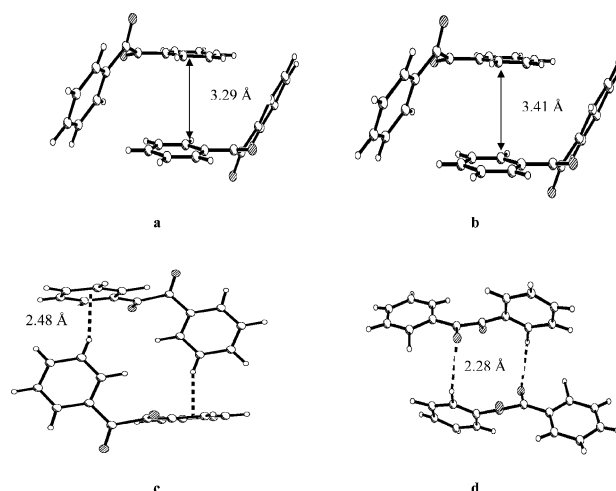
TABLE 1. Relation between the O=C–C=O Torsion Angle and Other Structural Parameters

	O=C–C=O torsion angle (deg)	concn (mol/L)	cavity size/ two benzil (Å ³)	central C–C bond length (Å)	C=O bond length (Å)	C–C _{ben} bond length (Å)	C _{ben} –C _{ben} bond length (Å)
theoretical optimization	124.3			1.535	1.221	1.488	1.397
neat benzil (HT phase, <i>P</i> ₃₁₂₁) ^a	107.3	6.16	616.6	1.529(6)	1.217(5)	1.467(6)	1.388(7)
neat benzil (LT phase, <i>P</i> ₂₁) ^b	103.1	6.20	602.9	1.532(14)	1.225(11)	1.479(13)	1.393(14)
	107.8		602.6	1.549(16)	1.216(12)	1.476(13)	1.400(14)
	113.8		589.4	1.526(13)	1.223(11)	1.474(13)	1.396(14)
1	121.5	1.51	630.0	1.528(3)	1.219(2)	1.477(2)	1.388(3)
2	108.0	1.51	654.1	1.538(6)	1.218(5)	1.475(6)	1.388(6)
	117.9			1.518(6)	1.212(5)	1.482(6)	1.384(6)
3	91.8	1.13	838.8 ^c 660.5 ^d	1.541(3)	1.216(2)	1.478(3)	1.388(3)
4		1.06	1045.5 ^c 927.9 ^d				
5	~98.0	1.01	940.0 ^c 715.7 ^d				
6	139.3	1.12	610.6	1.523(6)	1.231(5)	1.470(6)	1.384(6)

^a Data collected at 100 K. ^b Data collected at 70 K. ^c Solvent molecules included in the calculation of the cavity volume. ^d Solvent molecules excluded in the calculation of the cavity volume.

**FIGURE 9.** Diagram of superposed benzil molecules in **1** (gray), **2a** (brown), **2b** (blue), **3** (pink), and **6** (green).**FIGURE 9.** Dependence of the central C–C bond distance on the O=C–C=O torsion angle for the benzil molecule.

benzil molecules fit well in the smaller cavities of the brick-wall frameworks of **1** and **2**, resulting in fully ordered guests and the absence of solvent molecules. With benzophenone instead of benzil as the guest within the same CMCR·bipy framework, two water molecules are incorporated within the cavity to fill the gap left by

**FIGURE 10.** Benzil dimers in compounds **1** (a), **2** (b), **3** (c), and **6** (d).

the smaller guests.²³ The replacement of bipy with the longer bpe spacer leads to a larger cavity, which can accommodate additional ethanol solvent molecules. Because of the nonparallel arrangement of the two proximal bpe spacers in **4**, the solvent-accessible volume in this solid is significantly larger than in **3**, though the frameworks are constructed with the same building blocks and are similar.

Relation between Cavity Size and Geometry. It is noteworthy that the solids with the largest cavity size after subtraction of solvent volume (**4** and **5**) contain disordered benzil molecules. In the remaining four solids the largest O=C–C=O torsion angle occurs for the smallest cavity volume (**6**), whereas an ~90° torsion angle is observed for **3** which has the larger cavity, after taking into account the volume occupied by the solvent molecules (Table 1). As the isolated molecule has, according to theory, a torsion angle of ~124°, it appears that the tighter cavity induces a tendency for a nearly trans-planar geometry of the benzil guest molecules.

Conclusions

Six new supramolecular frameworks consisting of resorcinarene nodes and 4-pyridyl-based spacers and

encapsulating benzil guest molecule have been synthesized. To our knowledge this is the first time that the variation of molecular conformation has been studied in a series of related supramolecular solids. The large variation of the O=C–C=O torsion angles from 91.8 to 139.3° illustrates the pronounced effect of the supramolecular environment on molecular conformation. The benzil concentration in the solids, which is ~6.2 mol/L in the neat crystals, varies between 1.01 and 1.51 mol/L, corresponding to a 4- to 6-fold dilution. The O=C–C=O torsion angle correlates with the central C–C bond length which decreases significantly with the gradual change of benzil conformation from almost perpendicular toward trans-coplanar geometry. We conclude that supramolecular solids offer the possibility of studying a single molecule in well-defined but different conformations.

Experimental Section

Preparation of CMCR·bipy·benzil (α) (1) and CMCR·bipy·benzil (β) (2). CMCR (0.05 mmol, 27.2 mg), bipy (0.1 mmol, 15.6 mg), benzil (0.1 mmol, 21 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 and then cooled to room temperature over 4 days. Prismatic and blocklike yellow crystals were found and identified as **1** and **2**, respectively.

Preparation of CMCR·2bpe·benzil·ethanol (3). CMCR (0.05 mmol, 27.2 mg), bpe (0.1 mmol, 18.9 mg), and benzil (0.1 mmol, 21 mg) in 3 mL of ethanol were heated until a clear solution was obtained. Yellow needle crystals appeared when the solution was cooled to room temperature during 1 day. The crystals were kept in their mother liquor to avoid possible loss of solvent molecules before data collection.

Preparation of CMCR·2bpe·benzil·2H₂O (4). CMCR (0.05 mmol, 27.2 mg), bpe (0.10 mmol, 18.9 mg), benzil (0.1 mmol, 21 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 and then cooled to room temperature during 4 days. Yellow prismatic crystals were collected.

Preparation of CMCR·2bpeh·benzil·ethanol (5). CMCR (0.05 mmol, 27.2 mg), bpeh (0.1 mmol, 24 mg), and benzil (0.1

mmol, 21 mg) in 5 mL of ethanol were heated until the solution became clear. Light-orange crystals were obtained after 1 week by slow evaporation at room temperature.

Preparation of CECR·2bpe·benzil (6). CECR (0.05 mmol, 30 mg), bpe (0.10 mmol, 18.9 mg), and benzil (0.1 mmol, 21 mg) in 5 mL of ethanol were heated until a clear solution appeared. Orange crystals were obtained after 2 weeks through slow evaporation at room temperature.

Crystallography. X-ray data were collected with the SMART program on a Bruker SMART1000 charge-coupled device (CCD) diffractometer installed at a rotating anode (Mo K α radiation $\lambda = 0.71073\text{\AA}$) source and equipped with an LN₂ Oxford Cryostream cooler. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.³³ Crystallographic information is summarized in Table S1 of the Supporting Information. Hydrogen atoms were taken from difference electronic Fourier maps and refined isotropically. For compound **3**, disordered benzil and water molecules are refined isotropically.

Theoretical Calculation. The geometry optimization of the benzil molecule was performed with the Gaussian 98 package using density-functional theory (DFT) without any symmetry restriction. The B3LYP functional with a 6-311++G** basis set was used for the C, H, and O atoms.

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Supporting Information Available: Tables of crystallographic information and hydrogen-bonding geometry; X-ray crystallographic files in CIF format for the structures of **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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