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Intermolecular Interaction Energies in Hydroquinone Clathrates at High Pressure

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Supporting Information

ABSTRACT: The energy landscape and its evolution with pressure have been studied for two hydroquinone clathrates in combination with the apohost β -hydroquinone structure. Pressure is used as a means for probing interatomic, or intermolecular, potentials. The forces in organic clathrates are generally dominated by strong intermolecular interactions in a host framework, with smaller contributions from subtle interactions between the guest molecules and the surrounding framework. Pairwise intermolecular interactions energies have been quantified for the hydroquinone–methanol and hydroquinone–acetonitrile clathrate up to pressures of 8.6(2) and 14.1(4) GPa, respectively. In both cases, reversible pressure induced phase transitions are observed, where the host framework tilts to form skewed cavity channels and break the 3-fold rotation symmetry. The compression of the hydroquinone–acetonitrile structure is found to be isotropic, whereas it is anisotropic for the hydroquinone–methanol compound, emphasizing the implication of different guest molecules. Host–host interactions especially through the O–H...O bonding network have an order of magnitude larger contribution to the lattice energy than the host–guest interactions, but these host–host interactions become increasingly less favorable with pressure ultimately leading the phase transitions. When small pressure is applied to the β -hydroquinone apohost, it transforms to the denser α -hydroquinone structure. However, when guest atoms are enclathrated, a templating effect is observed leading to new and different high-pressure host structures. Thus, even though the host–guest interactions are comparably modest in magnitude, the guest atoms direct the high-pressure structural rearrangements. The present study illustrates the complexity of the numerous superimposed interactions in even the simplest supramolecular aggregates, highlighting the need to reliably quantify intermolecular interaction energies before aspiring to predict the formation of more complex supramolecular structures.

INTRODUCTION

In recent years, advances in the fields of supramolecular chemistry and self-assembly have led to the discovery of new complex materials, e.g., self-assembling monolayers,¹ nanostructures,² helical polymers,³ and biomolecular⁴ and metal–organic framework materials.^{5–7} Despite this progress our ability to predict structural features and functionality is still limited. A lot of the knowledge obtained in the field of supramolecular chemistry comes in retrospect after the determination of a structure and its properties.⁸ This is in part due to the qualitative nature of designing structures using hydrogen bonding, π – π stacking, metal–ligand interactions, strong dipole–dipole association, hydrophobic forces, steric repulsion, etc. to direct the formation of complex end products. In order to progress in this regard, we consider it important to quantify all the superimposed intermolecular interactions through theoretical calculations, ensuring that no interactions are overlooked. To help in this endeavor Spackman et al. (inspired by Gavezzotti's PIXEL approach) recently developed an efficient computational approach for calculating accurate intermolecular energies.^{9–15} The method is used to calculate

intermolecular interactions energies between selected molecular pairs, expressed in four key energy terms: electrostatic, polarization, dispersion, and exchange-repulsion. The energies can then be graphically depicted as cylinders connecting molecules and forming *Energy Frameworks*.¹¹

Herein, we follow this scheme and quantify the intermolecular interaction energies for the two clathrates, hydroquinone–methanol (HQ/MeOH) and hydroquinone–acetonitrile (HQ/MeCN), as well as the apohost compound. We have subjected single crystals to high external pressures, forcing the molecules closer together, thereby enabling a comparison of how the different guest molecules influence the energy landscapes in the clathrates. The results are further compared to a similar study on the hydroquinone–formic acid clathrate.¹⁶ The simplicity of the HQ clathrates, together with their diverse structural chemistry, originating in part from the subtle interaction between the host HQ molecules and the enclosed

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Table 1. An Overview of the HP Experiments^a

	space group	<i>a</i> -axis/Å	<i>c</i> -axis/Å	<i>V</i> /Å ³	<i>P</i> _{max} /GPa	# HP points	# crystals	PTM
HQ/apohost	<i>R</i> $\bar{3}$	16.642(1)	5.483(1)	1315.0(2)	1.2(1)	3	2	Si oil
HQ/MeOH	<i>R</i> $\bar{3}$	16.6125(4)	5.5633(2)	1329.63(6)	8.6(2)	14	2	P/IP
HQ/MeCN	<i>P</i> $\bar{3}$	15.9884(5)	6.2467(3)	1382.91(9)	14.1(4)	15	3	P/IP

^aUnit cell parameters at ambient conditions are included.

Table 2. Crystallographic Information for the Studied Compounds at Ambient Conditions and at High Pressure

structure	HQ/apohost	HQ/MeOH	HQ/MeOH ^a	HQ/MeCN ^b	HQ/MeCN ^a
pressure/GPa	0.0001	0.0001	7.4(5)	0.0001	5.2(1)
<i>T</i> /K	295	295	295	295	295
formula	C ₆ H ₆ O ₂	3C ₆ H ₆ O ₂ ·0.9 CH ₃ OH	3C ₆ H ₆ O ₂ ·0.9 CH ₃ OH	3C ₆ H ₆ O ₂ ·CH ₃ CN	3C ₆ H ₆ O ₂ ·CH ₃ CN
space group	<i>R</i> $\bar{3}$	<i>R</i> $\bar{3}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{3}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	16.6420(13)	16.6125(4)	16.253(7)	15.9884(5)	16.8742(8)
<i>b</i> /Å	16.6421(13)	16.6125(4)	17.489(7)	15.9884(5)	17.705(4)
<i>c</i> /Å	5.4826(5)	5.5633(2)	4.258(5)	6.2467(3)	4.794(5)
α /°	90	90	84.53(6)	90	81.93(4)
β /°	90	90	95.17(8)	90	107.73(2)
γ /°	120	120	122.97(9)	120	127.21(2)
<i>V</i> /Å ³	1315.0(2)	1329.63(7)	1010(2)	1382.91(9)	1085(1)
<i>Z</i>	9	9	9	9	9
<i>P</i> _{calc} /(g/cm ³)	1.251	1.348	1.788	1.360	1.706
(<i>sin</i> θ / λ) _{max} /Å ⁻¹	0.624	0.712	0.555	0.714	0.554
completeness/%	100	100	35	100	38
<i>N</i> _{Tot,obs}	3448	4517	1633	9491	1560
<i>N</i> _{Uniq,obs}	596	894	344	938	399
<i>N</i> _{Obs} [<i>I</i> > 2σ(<i>I</i>)]	417	679	170	645	229
<i>N</i> _{Parameters}	38	34	50	56	44
<i>N</i> _{Restraints}	0	1	53	21	68
<i>R</i> _{int}	0.0519	0.025	0.1276	0.0502	0.1112
<i>R</i> ₁ , <i>R</i> ₁ [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0727, 0.0474	0.0802, 0.0654	0.1856, 0.1096	0.0810, 0.0497	0.2088, 0.1123
<i>wR</i> ₂ , <i>wR</i> ₂ [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.1243, 0.1096	0.1976, 0.1794	0.3255, 0.2638	0.1136, 0.1021	0.3381, 0.2332
GOF	1.179	1.071	1.113	1.098	1.125

^aThe listed unit cell parameters are derived from using a pseudo hexagonal unit cell setting. ^bStructure solved in space group *R* $\bar{3}$.

guest molecules (e.g., MeOH, HCl, Ar), makes them attractive to study as model systems.^{17–20} Quantifying the numerous superimposed interactions in these clathrates, with pressure, will help advance our understanding of the formation of more complex aggregates.^{8,21–24}

EXPERIMENTAL SECTION

Synthesizing Single Crystals. Large single crystals (>1 mm) of the two hydroquinone clathrates were synthesized by slowly evaporating a solution of hydroquinone (0.550 g) dissolved in the desired solvent (MeOH or MeCN, 10 mL) at room temperature. The apohost (β -hydroquinone) crystals were prepared by dissolving hydroquinone (0.550 g) in propan-2-ol, and the solvent was allowed to slowly evaporate (>24 h) at room temperature. For the latter, the product formed was a mixture of two hydroquinone polymorphs, the α - and β -form. The difference in unit cell parameters was exploited to distinguish between the two polymorphs. All crystals were kept in the solution for as long as possible to limit desorption of guest molecules or absorption of gas molecules from the atmosphere.

High-Pressure Diffraction Experiments. High-pressure (HP) single crystal X-ray diffraction (SCXRD) experiments have been performed on the HQ apohost and HQ clathrates with the guest molecules MeOH and MeCN. Table 1 contains an overview of the experiments, including information about the maximum pressure achieved and the pressure-transmitting medium (PTM) employed for each experiment. All HP experiments were carried out using a plate-type diamond anvil cell (DAC) equipped with 600 μ m culet Boehler–Almax diamond anvils. Steel gaskets were used with holes of 0.3 mm

diameter, which were drilled after preindentation to a thickness of $\sim$ 0.1 mm. Consequently, the single crystal sample dimensions were restricted to $\sim$ 0.12 $\times$ 0.12 $\times$ 0.05 mm³ to limit scattering from the steel gasket. Two different PTM were used, silicone oil (Si oil) and a 1:1 pentane/isopentane mixture (P/IP), which are hydrostatic up to $\sim$ 1 GPa and $\sim$ 7 GPa, respectively.^{25,26} The PTM was chosen based on the proviso that the medium should not react with the clathrate or consist of species that are small enough to enter the clathrate cavities. The pressure was determined by the ruby fluorescence method prior to and after each diffraction experiment.²⁷ All single crystal HP experiments were performed on a SuperNova diffractometer from Agilent Technologies, using MoK α radiation (λ = 0.71073 Å). The diffracted intensities were collected on a CCD detector, and data were integrated and corrected for absorption using CrysAlisPro.²⁸ Diffraction peaks with bad intensity profiles, due to overlap with diamond reflections or powder rings, were rejected. The structure solution and refinement were carried out with SHELXT, using the Olex2 graphical user interface.^{29,30}

Because of the limited number of reflections collected in the HP experiments, certain constraints and restraints were applied to the structural models. The carbon atoms belonging to the HQ molecule were restrained to form a flat hexagon with the constraint of identical thermal displacement parameters. The same constraint was also used for the different guest molecules, further including a fixed occupancy constraint, and the hydrogen atoms were treated using a riding model. Selected crystallographic information from the resulting refinements is listed in Table 2. As the pressure is increased the general diffraction quality is decreased due to peak broadening, resulting in higher *R*₁ values. Care is therefore necessary when evaluating the resulting

structural information. In the present study, guest molecule geometries and host OH hydrogen positions have been optimized using density functional theory (DFT) calculations. After each geometry optimization, a frequency calculation was performed at the gamma point to check for instabilities (imaginary frequencies). This ensures that the resulting structures are stable with respect to the crystal energy despite some relatively high experimental R_1 values.

Theoretical Calculations. Owing to the inherent difficulty in determining accurate guest molecule geometries using SCXRD, DFT calculations have been carried out to optimize the guest molecule positions. In particular, the hydrogen positions cannot be determined reliably. For this reason, the hydrogen atoms belonging to the host OH groups were optimized as well. The different guest molecule geometries and host OH hydrogen positions have been optimized using CRYSTAL14³¹ and the B3LYP³²/pob_TZVP³³ level of theory including dispersion corrections as proposed by Grimme.³⁴ Unit cell parameters and host molecule coordinates have been fixed to the experimental values. The optimized atomic positions have been used in all the subsequent intermolecular interaction energy calculations. Model energies have been calculated between all unique nearest neighbor molecular pairs in the clathrate and apohost structures using CrystalExplorer and Gaussian09.^{27,28} The model (termed CE-B3LYP) uses B3LYP/6-31G(d,p) molecular wave functions calculated applying molecular geometries extracted from the crystal geometries, with X–H bond lengths constrained to standard neutron diffraction values.²⁹ This approach uses electron densities of unperturbed monomers to obtain four separate energy components: electrostatic, polarization, dispersion, and exchange-repulsion. Each energy term is scaled independently to fit a large training set of B3LYP-D2/6-31G(d,p) counterpoise-corrected energies from both organic and inorganic crystals. The CE-B3LYP energies reproduce the training set energies with a mean absolute deviation of ~ 1 kJ/mol.²⁶ Pairwise energies in the clathrates are depicted via *energy frameworks*, whereby cylinders with thickness proportional to the magnitude of the interaction energy link the center of mass of the molecules. For comparison with the CE-B3LYP energies, DFT interaction energies (based on dispersion- and counterpoise-corrected B3LYP/6-31G(d,p) calculations) using the same geometries have also been calculated.

RESULTS AND DISCUSSION

Structures of the Hydroquinone Clathrates at Ambient Conditions. At ambient conditions, hydroquinone itself forms two stable polymorphic structures, the α - and the β -HQ structures. The β -HQ structure is isostructural to the HQ clathrates, also called the HQ apohost structure. At ambient conditions the β -HQ structure has the space group symmetry $R\bar{3}$, with $a = b = 16.6420(13)$ Å, $c = 5.4826(5)$ Å, and $V = 1315.01(19)$ Å³. The α -HQ structure, which is the thermodynamically stable polymorph,³⁵ has the same $R\bar{3}$ space group symmetry, but forms a structure consisting of a H-bonded network of α -helices in addition to channels similar to the ones found in the β -form. The large unit cell volume amounts to 7165.9(13) Å³ at 293 K. Only the β -structure has been studied in the present work and will hereafter be termed the “HQ/apohost” structure (Figure 1a).

In the HQ/apohost structure, HQ molecules form a three-dimensional hydrogen bonded framework with infinitely long void channels running through the structure. The channels run along the c -axis and vary in thickness. The H-bonded framework forms hexagonal OH rings oriented in the ab -plane, which make up the narrow part of the void channels. When guest molecules are introduced into the structure they occupy the widest part of the void channels (which we will name cavities in the following), and the hexagonal OH rings can be seen as the top and bottom, separating adjacent cavities. The six HQ molecules enclosing each cavity (three tilting

Figure 1. (a) View of the HQ/apohost structure perpendicular to the c -axis, including the 0.0003 au procrystal electron density void surface. (b) The HQ/apohost structure oriented in the ab -plane. (c) The HQ/MeOH and (d) the HQ/MeCN structures at ambient conditions.

upward and three tilting downward) are related to each other by the 3-fold rotoinversion symmetry element at the center of the cavity, and form the walls around each cage. Each HQ molecule connects two adjacent void channels, as can be seen in Figure 1b. Introducing methanol into the structure has very limited influence on the HQ framework, evident from the comparable unit cell parameters for the apohost and the HQ/MeOH compound; $a = b = 16.6420(13)$ and $16.6125(4)$ Å, $c = 5.4826(5)$ and $5.5633(2)$ Å, respectively. The space group symmetry is also the same ($R\bar{3}$) with the implication that the MeOH guest molecule complies with the symmetry of the host framework resulting in symmetry related disorder about the mentioned $\bar{3}$ symmetry axis. In addition, a previous molecular dynamics simulation study of the HQ/MeOH clathrate has shown that the methanol molecule is dynamically disordered and can rotate freely in the structure, while having a molecular reorientation energy of 5.4 kJ/mol needed for flipping the molecule.¹⁹ Despite this, a sound guest molecule geometry was obtained from the single crystal X-ray diffraction data at 100 K and ambient pressure conditions. A guest molecule occupancy of 92% was estimated from the 100 K data compared with the known maximal guest occupancy of 97%.³⁶ In light of the high degree of disorder suggested from the molecular dynamics study, the guest molecule geometry was also optimized by DFT as explained in the methods section. In contrast to the experimental guest position, the DFT optimized guest position is slightly shifted toward the cavity walls in the ab -plane, Figure 1c. The optimized geometries are used to quantify the host–guest interaction energies using *Energy Frameworks* in the following section.

Inclusion of the larger acetonitrile guest molecule results in a significant change in the host framework, namely, a shorter a -axis (15.9884(5) Å) and a longer c -axis (6.2467(3) Å) stretching the cavities along this direction. The guest molecules lie on the 3-fold rotation axis. In 1956 Wallwork and Powell discovered weak diffraction spots breaking the rhombohedral

host centering of the HQ/MeCN structure ($h - k + l \neq 3n$),³⁷ while the full structure and space group symmetry, $P3$, was established almost 60 years later by Clausen et al.³⁸ In the latter crystallographic study, the collection of high quality data at both synchrotron and neutron facilities was used in combination with theoretical calculations to model the guest ordering.³⁸ The study revealed that in any cavity channel all acetonitrile molecules are oriented in the same direction. However, there are three crystallographically different MeCN molecules, and thus cavity channels in the crystal structure and the orientation of MeCN are reversed in one of these three. The resulting “superstructure” reflections are very weak as they reflect the tiny difference in electron density between the average structure and the superstructure. In the experiments presented here the weak reflections breaking the host symmetry are observed, but they are not strong enough (significant σ/I ratio) to be included in the refinement of the structural model. The structural refinement at 100 K and ambient pressure resulted in fully occupied guest positions in correspondence with previous chemical analysis.²⁰ In all the following structural models, the guest occupancy is therefore constrained to this value.

Compression and Pressure Induced Phase Transitions. An overview of the high-pressure experiments for HQ/apohost, HQ/MeOH, and HQ/MeCN is given in Table 1, with selected crystallographic information listed in Table 2. Data were measured on the HQ/apohost structure up to 1.2(1) GPa using two different single crystals and silicone oil (Si oil) as PTM. The structure was found to be metastable as soon as pressure was applied in the DAC. Both when using Si oil and also pentane/isopentane (P/IP) as PTM the sample turns polycrystalline within 1–2 days. The result is especially evident from the data collected at 0.32(5) GPa, where the sample turns polycrystalline in the middle of the diffraction experiment, i.e., 10 h into the data collection. A complete data set was collected at 0.18(1) GPa on the previous day, with the same sample. For the second crystal only a single data set at 1.2(1) GPa was successfully collected before the crystal turned polycrystalline. A high-pressure Raman study has shown that applying a pressure of 0.24 GPa partially transforms a β -HQ powder into the α -form.³⁹ Subsequent pressure increase to 0.4 GPa completes the transformation. It is likely that if the authors of the Raman study had waited a sufficient amount of time they would have observed a complete conversion already at 0.24 GPa. The transformation to the α -phase cannot be confirmed from the measured diffraction data, but it is most likely the same transition as observed in the Raman study. The fact that a β -HQ powder is used in the Raman study without any PTM probably lowers the kinetic barrier for the $\beta \rightarrow \alpha$ transformation, compared to this study.

The complete data set collected at 1.2(1) GPa shows that the c -axis is compressed by 8.5(1)%, while the a -axis is only compressed by <1%, Figure 2a. The compression along the c -axis resulted in a 0.469(3) Å reduction in the HQ stacking distance, where the stacking distance is equivalent to the length of the c -axis and the cavity height. In the ab -plane the oxygen donor...acceptor distance decreased by only 0.083(3) Å.

Diffraction data on the HQ/MeOH compound have been collected up to a pressure of 8.6(3) GPa on two different crystals compressed using P/IP as the PTM, and the unit cell parameters are plotted in Figure 2b. As for the apohost structure, the compression is highly anisotropic. At 6.2(1) GPa the c -axis is compressed by 19.1(1)%, while the a -axis is

Figure 2. Normalized unit cell parameters as a function of pressure for (a) HQ/apohost, (b) HQ/MeOH, and (c) HQ/MeCN. Unit cell parameters at ambient conditions are listed in Table 1. Sphere, circle, and pentagon symbols indicate measurements performed on different single crystal. For HQ/MeOH and HQ/MeCN the vertical line indicates the onset of a phase transition. After the transformation a pseudo hexagonal unit cell setting is used, and as a result $a \neq b$, $\alpha \neq \beta \neq 90^\circ$ and $\gamma \neq 120^\circ$. Insets show the evolution of the unit cell angles from the LP the HP phase. Notice that the chosen pressure intervals are different for the three figures.

reduced by only 2.1(1)%. At 3.1(3) GPa a small kink in the compressibility is observed where a subsequent pressure increase results in a slightly longer a -axis. The kink is only based on a single pressure point, and no structural changes on the atomic level were found to indicate the discovery of a phase transition. It is most likely that the 3.1 GPa kink is an outlier. For both crystals a reversible phase transition is observed above

Figure 3. (a) The HQ/apohost structure at ambient conditions, (b) the HP structure of HQ/MeOH at 7.4(5) GPa, and (c) the HP structure of HQ/MeCN at 5.2(1) GPa with corresponding energy frameworks in the same orientation. The electrostatic, dispersion, and total energies are colored red, green, and blue, respectively, with cylinder thickness proportional to the magnitude of the interaction energy. Only energies of absolute magnitude >10 kJ/mol are included in the figures. The three distinct host energies (1–3) are indicated for the apohost structure, with interaction 1 having a magnitude of -33 kJ/mol at ambient conditions.

6.2(1) GPa. For the first crystal, the phase transition resulted in the formation of a single large crystal domain and multiple smaller twin domains. The first pressure point measured after the phase transition was at 7.4(5) GPa. During the measurement the pressure inside the DAC dropped significantly, resulting in a large difference between the pressure measured before and after the experiment, which is the cause of the large pressure deviation at this pressure. The pressure was then allowed to stabilize before more data were collected. When the pressure had stabilized, the pressure was found to have dropped to 6.7(1) GPa. Data were then measured at this pressure and subsequently at 8.6(3) GPa. At 8.6(3) GPa, substantial peak broadening had emerged, which greatly lowered the data quality and the experiment was stopped. For the second crystal, the phase transition resulted in the formation of three large twin domains, and the experiment was discontinued. The structure could be solved, however, by integrating data from a single twin domain, and the structure is depicted in Figure 3b. The biggest structural change is a tilting of the six-membered OH-ring breaking the 3-fold rotoinversion symmetry and reducing the space group symmetry to $P\bar{1}$. The methanol guest molecule lies in the middle of the cavity, still enclosed by three upward and three downward pointing host molecules. By using a pseudohexagonal triclinic unit cell setting ($a \neq b$, $\alpha \neq \beta \neq 90^\circ$ and $\gamma \neq 120^\circ$) for the HP structure it is possible to directly relate the new unit cell parameters to the LP structure and quantify the deviation from trigonal symmetry. The transformation is not evident from the tiny volume decrease across the phase transition. The length of the unit cell parameters on the other hand changes significantly with the c -axis increasing

($\sim 3\%$) and the a -axis decreasing ($\sim 3\%$) significantly more than the almost unchanged b -axis ($<0.4\%$). Increasing the pressure further led to a subsequent shortening of the c -axis while the a - and b -axis increased. The length of the c -axis still corresponds to the cavity height. The unit cell angles also start to diverge more and more from 90° and 120° as the pressure is increased further.

Diffraction data on the HQ/MeCN compound have been collected up to a pressure of 14.1(4) GPa on three different crystals using P/IP as PTM. The compression of the unit cell parameters is plotted in Figure 2c. Compared to the HQ/MeOH it is apparent that the compression is much more isotropic, with the a - and c -axes being compressed at almost identical rates. At 4.0(1) GPa the a - and c -axes are compressed 5.56(2)% and 6.88(1)%, respectively. This is in contrast to the HQ/MeOH structure at 4.3(1) GPa in which the a - and c -axes are reduced by 1.85(7)% and 16.0(1)%, respectively. We attribute the difference in compressibility to the acetonitrile guest molecule stretching the cavities and thereby hindering the compression of the c -axis. Above 4.0(1) GPa a reversible phase transition is observed, although only one out of the three measured samples remained a single crystal. The new high-pressure structure could be solved in the triclinic $P\bar{1}$ space group (Figure 3c). The HP phase resembles the one for HQ/MeOH, although this phase transition is much more abrupt leading to large changes in the unit cell parameters. During the transformation, the acetonitrile guest molecules flip away from the 3-fold rotation axis, enabling the compression of the c -axis, which is then reduced by more than 17%. As for the HP HQ/MeOH phase, the six-membered OH-rings are tilted with the

cavity height at 5.2 GPa being squeezed down to 4.794(1) Å. The *a*- and *b*-axis in turn expands approximately 12% and 17%, respectively, before starting to decrease, while the unit cell angles in the HP phase remain quite constant at $\alpha \approx 82^\circ$, $\beta \approx 107^\circ$, and $\gamma \approx 128^\circ$. The changes in unit cell parameters resemble the changes observed in the pressure induced phase transition in the hydroquinone–formic acid (HQ/HCOOH) clathrate, where the reversible isosymmetric transformation ($R\bar{3}$) causes an immense reduction of the *c*-axis of 27%, compensated by an increase of the *a*-axis by 14.4%.¹⁶ Above 14.1(4) GPa the collected diffraction data could no longer be used to extract structural information. This is most likely the result of the non-hydrostatic environment above 7 GPa, resulting in increasing strain with pressure, causing severe peak broadening. It should be noted that since broad peaks were observed the sample remains crystalline above 14.1(4) GPa.

Intermolecular Interaction Energies. *Energy Framework* representations of the intermolecular interactions in the HQ/apohost structure at ambient conditions are presented in Figure 3a. The electrostatic, dispersion, and total interaction energies between molecular pairs are colored red, green, and blue, respectively, with the thickness of each cylinder connecting molecules proportional to the magnitude of the energy. Each HQ molecule in the apohost structure has 10 nearest neighbors, although only three distinct interactions, enumerated 1–3 in Figure 3a. The strongest interaction is between immediate neighbors in the six-membered OH rings. The HQ molecules have four neighbors of this kind, each with a total interaction energy of -33 kJ/mol (1). The interaction energy is dominated by a large electrostatic contribution. The HQ molecules stack along the *c*-axis with a single neighbor above and below. This interaction is comprised of attractive dispersion forces, and repulsive electrostatic and exchange-repulsion energy terms, which cancel one another out, resulting in a small total interaction energy of -3 kJ/mol (2). Each HQ molecule has four remaining equivalent neighbors, where the benzene rings are oriented perpendicular to each other, resulting in $C-H\cdots\pi$ interactions. This interaction energy mainly consists of dispersion forces to give a total interaction energy of -12 kJ/mol (3).

The host-framework interaction energies in the HQ/MeOH structure are very similar to the HQ/apohost with total interaction energies of -33 , -2 , and -12 kJ/mol for interactions 1–3. Since the methanol guest molecule is heavily disordered at ambient conditions, the guest geometry has been optimized using DFT calculations for 12 pressure points in the pressure range of 0.0001–7.4(5) GPa. The position of the H atom in the host six-membered OH ring is found to influence the intermolecular interaction energies in the host framework.¹⁶ The position of the hydroxyl H atom has therefore also been optimized in the DFT calculations. The methanol guest molecule is surrounded by 12 neighboring host molecules with the individual total host–guest interaction energies ranging from -9 to 1 kJ/mol. Adding the 12 individual host–guest total interaction energies amounts to -56 kJ/mol, in the following termed the host–guest *cluster* energy.

As mentioned the HQ/MeCN structure has a significantly elongated *c*-axis (14%) and shortened *a*-axis (4%) compared with the apohost. The difference must be a direct consequence of interactions between the acetonitrile guest molecule and the surrounding host molecules. Considering the shape and position of the guest molecule, it is clear that the host structure

can be perturbed along the *c*-axis. The MeCN molecule is also the longest known guest molecule to form HQ clathrates. Although the host framework is slightly different in the HQ/MeCN clathrate compared to the apohost structure, only small differences are found between the host energy frameworks. The host–framework interaction energies for the HQ/MeCN structure are -32 , -2 , and -13 kJ/mol for interactions 1–3, respectively, all within 1 kJ/mol of the corresponding host framework energies in the HQ/apohost and HQ/MeOH structures. For the HQ/MeCN structure the host–guest *cluster* energy amounts to -71 kJ/mol, which is a significantly more attractive interaction energy compared with the HQ/MeOH clathrate. In addition, the total interaction energy between guest molecules in adjacent cavities along the *c*-axis was found to be -10 kJ/mol. This attractive guest–guest interaction is believed to be important for the compound's isotropic compression with pressure, compared with the other two clathrates.

If we imagine that two acetonitrile molecules in adjacent unit cells along the *c*-axis are oriented antiparallel to one another (with the cyano groups oriented head-to-head) this would result in a large repulsive total interaction energy of 31 kJ/mol. Energy considerations therefore indicate that neighboring MeCN molecules in the channels are oriented parallel to each other (head-to-tail). Ordering of acetonitrile molecules in adjacent channels on the other hand cannot be explained by these energy considerations. In a molecular dynamics study of the HQ/MeCN compound a reorientation energy of 46 kJ/mol was calculated for flipping the acetonitrile molecule 180° about the *ab*-plane.¹⁹ The rotation about the *c*-axis on the other hand was not studied. To determine whether the acetonitrile molecule can freely rotate inside the cavity, host–guest *cluster* energies were calculated as a function of the rotation angle. Owing to the 3-fold rotation axis present in the structure, a rotation range of only 120° is needed. The results are plotted in Figure 4 which shows very small changes. The differences in the maxima and minima of the total host–guest interaction energy amount to just 3 kJ/mol, indicating that the acetonitrile can rotate without relaxing the host framework. The biggest change is observed in the repulsion energy term when the guest molecule is rotated 90° counterclockwise with respect to Figure

Figure 4. Host–guest *cluster* energies (CE-B3LYP) for HQ/MeCN at ambient conditions as a function of rotation about the *c*-axis (counterclockwise). The total interaction energy is the sum of the four individual energy components. 0° corresponds to the orientation depicted in Figure 1d.

Figure 5. (a–h) Electrostatic, polarization, dispersion, repulsion, and total interaction energies of selected intermolecular interactions in HQ/MeOH and HQ/MeCN calculated using CE-B3LYP model energies from CrystalExplorer, along with DFT interaction energies from Gaussian 09. The interactions are labeled 1–3 and for the different host–host interactions (see Figure 3) and H-G *cluster* for the host–guest *cluster* interaction energies, respectively. Notice that the energy axes are different for each figure. Only a limited number of pressure points are included for clarity, thus including 0.001, 1.9(1), 4.3(1), and 7.4(5) GPa for HQ/MeOH and 0.0001, 2.14(2), 4.0(1), 8.07(6), 11.0(3), and 14.1(4) GPa for the HQ/MeCN structure.

1d, leading to a reduction of 6 kJ/mol in the summed repulsion energy term.

The evolution of the interaction energies 1–3 and the host–guest *cluster* interaction energies with pressure for HQ/MeOH and HQ/MeCN is depicted in Figure 5. The plot includes the electrostatic, polarization, dispersion, repulsion, and total interaction energy terms calculated using CE-B3LYP model energies from CrystalExplorer, along with DFT interaction energies calculated using Gaussian09 software. The HP structures are sufficiently similar to compare interaction energies directly with the LP structures. The only difference

is that, since the HP structures are triclinic, they contain three slightly different host molecule geometries, and an energy average is thus included in the figure. The changes in intermolecular interaction energies for the host framework are very similar for the HQ/MeOH and HQ/MeCN clathrates, although for clarity a detailed description of the interactions in HQ/MeOH will be followed by a comparison with the energies calculated for HQ/MeCN.

The strongest host–host interaction energy (1) for HQ/MeOH is the interaction between neighboring ring members, Figure 5a. The interaction is mainly stabilized by a large

attractive electrostatic energy term (-49 kJ/mol) compensated in part by an exchange-repulsion energy (35 kJ/mol) resulting in a total interaction energy of -33 kJ/mol at ambient conditions. As the pressure increases and the molecules are forced closer together, the magnitude of both the electrostatic and repulsion energy terms increases significantly. The hydrogen donor–acceptor distance, $O\cdots O$, decreases $0.19(1)$ Å up to $6.2(1)$ GPa. The trend continues into the HP phase, with the different energy terms having values similar to those of the LP phase. The variation in individual interaction energies for the three different host molecules in the triclinic HP phase is also very small. At $7.4(5)$ GPa the electrostatic energy and repulsion terms reach values of -91 and 88 kJ/mol, respectively. The total CE-B3LYP interaction energy at the same pressure is -34 kJ/mol compared to a value of -25 kJ/mol derived from the DFT calculation. This difference in total energies from the CE-B3LYP and DFT energies are almost nonexistent at ambient conditions but becomes increasingly more significant with pressure. This tendency is evident in all the HP data containing large exchange-repulsion energy terms and is also described in the previous paper concerning intermolecular interaction energies in HQ/HCOOH.¹⁶ When more crystallographic high-pressure data becomes available, a correction to the exchange-repulsion energy term could possibly account for the discrepancy.

At ambient conditions, interaction 2 between the stacked hydroquinone molecules is made up of an attractive dispersion energy term of -9 kJ/mol, and smaller repulsive electrostatic and exchange-repulsion energy terms of 5 and 2 kJ/mol, respectively, resulting in a total interaction energy of only -2 kJ/mol. As the pressure is increased the dispersion and repulsion energy terms increase in magnitude, while the electrostatic interaction energy changes sign to give a small attractive contribution to the total energy at $4.3(1)$ GPa. Across the phase transition, the total interaction energy gets surprisingly more attractive according to both the CE-B3LYP and DFT energies. For the three distinct molecules in the HP phase a slight variation is found in the interaction energy between the stacked host molecules. For all three interactions the dispersion energy is the same, but one interaction has significantly lower electrostatic and repulsion energy terms ($E_{\text{ele}} = -1$ kJ/mol and $E_{\text{rep}} = 25$ kJ/mol), and another has significantly higher energy terms ($E_{\text{ele}} = -14$ kJ/mol and $E_{\text{rep}} = 38$ kJ/mol). When looking at the total interaction energy, the energy differences cancel out and result in the same total energy for the three distinct $\pi\cdots\pi$ interactions.

The remaining host–host interaction, 3, between the perpendicularly oriented neighbors, has contributions from both the dispersion and electrostatic energy terms, $E_{\text{disp}} = -10$ kJ/mol and $E_{\text{ele}} = -4$ kJ/mol, amounting to a total interaction energy of -12 kJ/mol. At elevated pressures the magnitude of these two energy terms becomes larger and is not compensated for by the change in the repulsion energy term. As a result, the total interaction energy is lowered by 2 kJ/mol from ambient to $4.3(1)$ GPa, resulting in a total interaction energy of -13 kJ/mol (CE-B3LYP) or -15 kJ/mol (DFT). Of particular note here is the acceptable agreement between the CE-B3LYP and DFT energies that is generally observed when the exchange-repulsion energy component is relatively small.¹⁶ In the HP phase the repulsion energy term increases more than the electrostatic and dispersion energy terms, and the total interaction energy is therefore slightly lowered. The different

energy terms for this interaction are comparable for the three distinct host molecules in the triclinic HP phase.

The MeOH guest geometry has been optimized using DFT calculations for 12 pressure points in the pressure range of 0.0001 – $7.4(5)$ GPa. At ambient conditions, the methanol guest molecule is positioned in the middle of the cavity along c and slightly shifted off-center in the ab -plane. Already at the first pressure point ($0.8(1)$ GPa) the cavity compression results in the MeOH molecule becoming located in the middle of the cavity. At ambient pressure, the H atom in the OH group points directly toward the closest host molecule, which is pointing upward with respect to the guest atom C–O bond. At $4.3(1)$ and $5.26(4)$ GPa, the MeOH is rotated 60° about the c -axis with the C–OH group now directed toward a downward pointing host molecule. The H atom from the –OH group generally points toward the nearest host molecule. The variation in MeOH geometries (found in the [Supporting Information](#)) at the different pressure points indicates that several guest geometries exist with similar cohesive energies. Following this logic, it makes sense to evaluate the evolution of the host–guest interaction energies with pressure, where a summation of the 12 individual host–guest interactions is compiled for each pressure. The host–guest cluster interaction energies are shown in [Figure 5g](#). The host–guest interactions consist mainly of dispersion forces, $E_{\text{disp}} = -54$ kJ/mol, and smaller electrostatic and repulsion energy terms, $E_{\text{ele}} = -23$ kJ/mol and $E_{\text{rep}} = 29$ kJ/mol. As the pressure is elevated the magnitude of all four individual energy terms increases, resulting in only small changes in the total interaction energies. The same tendency is evident across the phase transformation resulting in total interaction energies of -68 kJ/mol (CE-B3LYP) or -57 kJ/mol (DFT) at $7.4(5)$ GPa.

For HQ/MeCN the guest molecule geometry and the host hydroxyl H atom have been optimized at 15 pressure points in the pressure range from 0.0001 to $14.1(4)$ GPa. As anticipated, the intermolecular host–host interactions as a function of pressure resemble the host interaction in the HQ/MeOH structure, although in this case data are measured to significantly higher pressure. The interaction, 1, between adjacent host molecules in the OH ring consists of a large contribution from the electrostatic and repulsion energy terms, $E_{\text{ele}} = -42$ kJ/mol and $E_{\text{rep}} = 27$ kJ/mol, at ambient conditions. Again for this clathrate both of these energy terms increase in magnitude from ambient pressure up to $4.0(1)$ GPa with $E_{\text{ele}} = -64$ kJ/mol and $E_{\text{rep}} = 58$ kJ/mol at $4.0(1)$ GPa. Interestingly, at a similar pressure of $4.3(1)$ GPa, the same interaction in the HQ/MeOH clathrate structure has much larger electrostatic and repulsion energy terms, $E_{\text{ele}} = -83$ kJ/mol and $E_{\text{rep}} = 80$ kJ/mol, even though it has a significantly longer a -axis. The reason may be that the larger MeCN guest molecules do not allow for the OH ring to shrink. The same tendency is evident in the HP phase comparing the energy terms for HQ/MeCN at $8.07(6)$ GPa and HQ/MeOH at $7.4(5)$ GPa. Further increase of the pressure results in values of $E_{\text{ele}} = -103$ kJ/mol and $E_{\text{rep}} = 113$ kJ/mol, for the HQ/MeCN compound at $14.1(4)$ GPa giving total interaction energies of -23 kJ/mol (CE-B3LYP) and -7 kJ/mol (DFT).

At ambient conditions, interaction 2, between the adjacent stacked HQ molecules, is made up of small contributions from the dispersion, electrostatic, and repulsion energy terms, $E_{\text{disp}} = -6$ kJ/mol, $E_{\text{ele}} = 4$ kJ/mol, and $E_{\text{rep}} = 1$ kJ/mol. Up to $4.0(1)$ GPa the dispersion and repulsion energy terms increase to -12 and 11 kJ/mol, respectively. The same interaction for HQ/

Figure 6. Host–host and host–guest *cluster* interaction energies *cluster* per host/guest molecule for (a) HQ/MeOH and (b) HQ/MeCN with pressure, based on DFT calculations. LP phase host–host energies (black), LP host–guest energies (blue), HP phase host–host energies (red/pink), and HP host–guest energies (green).

MeOH at 4.3(1) GPa has much larger absolute energy terms, $E_{\text{disp}} = -23$ kJ/mol and $E_{\text{rep}} = 25$ kJ/mol, which one would anticipate since this structure has a significantly shorter *c*-axis. In the HP phase the electrostatic, dispersion, and repulsion energy terms all increase with increasing pressure, with the electrostatic interaction now being attractive, resulting in a total interaction energy of -4 kJ/mol (CE-B3LYP) or 6 kJ/mol (DFT) at 14.1(4) GPa. As was the case with these interactions in the HQ/MeOH compound, the three distinct interactions of this kind in the HQ/MeCN compound have quite different electrostatic and repulsion energies. One of the interactions can be distinguished by having larger electrostatic and repulsion energy terms ($E_{\text{ele}} = -24$ kJ/mol and $E_{\text{rep}} = 53$ kJ/mol at 14.1(4) GPa) in comparison to the other two ($E_{\text{ele}} = -14$ kJ/mol and $E_{\text{rep}} = 39$ kJ/mol at 14.1(4) GPa).

For interaction 3, the interaction energies are almost identical to the same interaction in the HQ/MeOH compound up to 4.3(1) GPa. After the phase transition the magnitude of the electrostatic, dispersion, and repulsion energy terms increase in magnitude resulting in a total interaction energy of -6 kJ/mol (CE-B3LYP) or -2 kJ/mol (DFT) at 14.1(4) GPa. Also, one of the three distinct interactions of this kind in the HP structure has quite different energy terms compared to the other two. At 14.1(4) GPa one interaction has energies of $E_{\text{ele}} = -10$ kJ/mol, $E_{\text{disp}} = -14$ kJ/mol, and $E_{\text{rep}} = 15$ kJ/mol, while the other two have the following energies, $E_{\text{ele}} = -21$ kJ/mol, $E_{\text{disp}} = -24$ kJ/mol, and $E_{\text{rep}} = 42$ kJ/mol. Host–guest *cluster* interaction energies between the acetonitrile guest molecule and the surrounding 12 host molecules are plotted in Figure 5h. As is the case for the HQ/MeOH structure the host–guest interaction energies consist mainly of dispersion forces and smaller contributions from the electrostatic and repulsion energy terms. The magnitude of the host–guest interaction energy terms is larger for the HQ/MeCN structure, owing to the MeCN molecule being bigger than the MeOH guest. During the phase transition the acetonitrile molecule flips, resulting in completely different host surroundings. From 8.07(6) to 14.1(4) GPa there is a steep increase in the magnitude of the electrostatic and repulsion energy terms compared to the dispersion energy. This results in similar electrostatic and dispersion energy terms of -134 kJ/mol and -132 kJ/mol, respectively. The large accumulated repulsion

energy term determined from the summed host–guest interaction energies results in a large difference between the total host–guest interaction energies calculated using CE-B3LYP, -22 kJ/mol, and DFT, 49 kJ/mol.

To explain this very large discrepancy between the two calculation methods, we have already touched upon how the magnitude of the exchange–repulsion energies from the CE-B3LYP is systematically too small for short intermolecular distances. Furthermore, it may be that at these high pressures and short intermolecular distances the Basis Set Superposition Error is not accurately accounted for in the DFT interaction energy calculations.

Host–Host and Host–Guest Cluster Energies from DFT. As established previously, the strength of host–guest interaction energies in the clathrates can be quantified by adding together the 12 nearest neighbor host–guest interaction energies. These can then be compared to the strength of the host framework by summing the individual interaction energies between a host molecule and the 10 nearest host neighbors, giving us the host–host *cluster* interaction energy. In Figure 6 these energies are plotted for HQ/MeOH and HQ/MeCN at the different measured pressure points. Since the DFT energies are deemed most reliable,¹⁶ only these energy calculations are included. When comparing total host–guest interaction energies with the host framework, it is important to take into account that there are three host molecules per cavity in the studied clathrates; additionally the guest occupancy could be lower than 1. Thus, in Figure 6 the *cluster* energy per host/guest molecule is plotted.

For both clathrates the host–host *cluster* energies are similar up until the phase transition pressures: at ambient pressure, they amount to -182 kJ/mol for the HQ/MeCN structure, and -185 kJ/mol for the HQ/MeOH structure. This is reduced to approximately -150 kJ/mol for both clathrates at a pressure of 4 GPa. In contrast, the host–guest *cluster* interactions are much more constant in the LP phases. A likely explanation is that the large cavity clathrates can be significantly compressed without overlap between the valence shells of the guest molecules and the host structure, resulting in less repulsive interactions. In the HQ/MeCN structure the host–guest *cluster* interaction energy lies around -75 kJ/mol, while for the smaller guest molecule in HQ/MeOH results in a constant host–guest *cluster* energy of

Figure 7. Pressure dependence of the volume of the unit cell as well as of the two isosurface volumes for (a) HQ/MeOH and (b) HQ/MeCN. Solid lines show the BM EoS fits to the volumes in the LP regions, except for the 0.0003 au iso-ED surface in (a) where no acceptable BM EoS fit could be achieved. Dashed lines show the HP phase. Unit-cell volume (red diamonds); 0.0020 au isosurface (blue circles) and 0.0003 au iso-ED surface (green triangles). The red, blue, and green filled circles correspond to the volumes of the unit cell, the 0.0020 au isosurface, and 0.0003 au isosurface, respectively, for the apohost structure at 1.2(2) GPa. The shapes of different surfaces are displayed next to the respective plots with HQ/MeOH at 7.4(5) GPa, and HQ/MeCN at 5.2(1) GPa. The 0.0020 au isosurface is orange and the 0.0003 au surfaces are green, with the displayed reduced primitive unit cells each enclosing a single cavity. The guest molecules are artificially removed from the structures prior to calculating the iso-ED surfaces.

about -60 kJ/mol up until the phase transition. In the different HP phases, the host–guest interactions all become more repulsive toward higher pressure. In the last pressure point for the HP HQ/MeOH structure both the host–guest *cluster* interaction energy and the host–host *cluster* energy are lowered compared to the LP phase. This observation does not seem credible and should be explored further.

After the phase transition in the HQ/MeCN structure, there is a steep decrease in the magnitude of both the total host–guest and the total framework energies. At the highest pressure achieved (i.e., 14.1(4) GPa) the total host–guest interaction energy becomes repulsive, reaching 49 kJ/mol. The total host framework energy at the same pressure is -22 kJ/mol, although it varies significantly for the three different host molecules. In the whole LP HQ/MeCN region, the total interaction energy between adjacent guest molecules remains constant between 10 and 11 kJ/mol.

Cavity Compression Analysis and Equation of State.

When external pressure is applied to a molecular compound the molecules will be forced together. Most often this leads to an elimination of the low-electron density (low-ED) regions in the structure before any structural rearrangements. In clathrates (when empty), the low-ED regions are found inside the cavities, and thus it can be informative to look at how cavity volumes change as a function of pressure and how the compression behavior is affected by the presence of different guest molecules. The method was introduced recently for the

HQ/HCOOH clathrate.¹⁶ The two iso-ED surface values employed here are 0.0020 au ($0.0136 \text{ e } \text{\AA}^{-3}$) and 0.0003 au ($0.00204 \text{ e } \text{\AA}^{-3}$), probing the space outside the van der Waals radii of the atoms and the cavity volumes, respectively. The shapes of the iso-ED surfaces for the two clathrate compounds are depicted in Figure 7.

The evolution of the calculated volumes in the measured pressure ranges for the HQ/MeOH and HQ/MeCN is also shown in Figure 7. At ambient conditions in the apohost structure the 0.0020 au and 0.0003 au surfaces comprise 17.1% and 6.6% of the total crystal volume, respectively. For both HQ/MeOH and HQ/MeCN the 0.0020 au volume decreases faster compared to the 0.0003 au volume. This is because the 0.0020 au surface, below approximately 2 GPa, also includes low-ED regions between host molecules which do not constitute part of the cavity volume region. Both volumes decrease steeply up to around 4 GPa where the volume changes flatten out. At 4 GPa the cavity volumes have been halved.

To simplify this comparison and mathematically describe the cavity changes as a result of the compression of the two low-density regions, they were fitted using a Birch–Murnaghan (BM) equation of state (EoS). While fitting EoS to low-ED regions of a structure does not make sense from a thermodynamic standpoint, the values can be compared internally when exchanging guest molecules to see the effect on the cavity compression. Uncertainties of the low-ED compressions were estimated by using the standard deviation

from the unit cell volumes and evaluating how adding or subtracting a standard deviation affected the calculated low-density volumes. The resulting low-ED volume EoS fits, together with normal BM EoS fits to the unit cell volume, are shown in Figure 7, and the extracted parameters are tabulated in Table 3.

Table 3. Birch–Murnaghan Equation of State Parameters for HQ/MeOH and HQ/MeCN

HQ/MeOH	χ^2	$V_0/\text{\AA}^3$	K_0/GPa	K'
V_{unitcell} (BM3)	2.79	1329.6(1)	8.3(12)	9.7(20)
$V_{0.0020}$ (BM2)	4.13	235.7(2)	1.25(3)	4.00 ^a
HQ/MeCN	χ^2	$V_0/\text{\AA}^3$	K_0/GPa	K'
V_{unitcell} (BM3)	0.97	1382.92(9)	8.5(3)	11.4(6)
$V_{0.0020}$ (BM2)	0.99	289.7(2)	1.59(1)	4.00 ^a
$V_{0.0003}$ (BM3)	0.88	99.42(9)	2.65(9)	3.17(9)
HP V_{unitcell} (BM2) ^b	1.08	1087.5(16)	42.2(12)	4.00 ^a

^a K' has an implied value for the second-order Birch–Murnaghan EoS.

^bFor the HP phases the volume and compressibility at the onset pressure point are used and not V_0 and K_0 . (V_p and K_p).

Comparing the unit cell volume compression first, the hardness of both clathrates is very similar with bulk moduli, K_0 , of approximately 8 GPa. This value is the same as for HQ/HCOOH ($K_0 = 9.0(11)$ GPa, BM3) although high compared with other molecular compounds, e.g., $\text{C}[\text{Si}(\text{CH}_3)_3]_4$ with $K_0 = 5.5(13)$ GPa, most likely owing to the H-bonded host framework in the clathrate.⁴⁰ For the HQ/MeCN data, the EoS fits for the compression of the low-density regions result in small K_0 values of ~ 1.6 GPa and ~ 2.5 GPa for the 0.0020 au and 0.0003 au surface data, respectively. For the HQ/MeOH structure, having an even smaller guest molecule, the K_0 value of 1.25(3) GPa is even lower. A EoS fit of the 0.0003 au surface data for the HQ/MeOH structure could not be applied successfully. These low K_0 values illustrate how easy the cavity volumes are reduced as a function of pressure, even with the guest molecule present. The compressibility of the HQ/apohost at a single pressure point, 1.2(1) GPa, is inserted into Figure 7 (filled circles). As expected, the apohost is more compressed at 1.2 GPa than the filled HQ structures, suggesting that the guest molecules resist cavity compression.

For the HQ/MeCN structures a sufficient number of HP data points have been measured to fit an EoS. Since V_0 values are not known for the HP structures, the unit cell volumes at the onset pressure of the phase transition have been used, thereby obtaining the hardness of the compound at the onset pressure, K_p . Since the onset pressure point for the phase transitions in HQ/HCOOH and HQ/MeCN are at similar pressures, we can compare their K_p values, 38(2) and 42(1) GPa for the HP structure of HQ/HCOOH and HQ/MeCN, respectively. The K_p values indicate that the HP phases have similar hardness, which are expected owing to their structural similarities.

CONCLUSION

Reversible pressure-induced phase transitions were observed for all studied structures at moderate pressures, and new high-pressure crystal structures were determined for HQ/MeOH and HQ/MeCN. For the HQ/MeCN system, having the largest guest molecules, the phase transition takes place at around 4 GPa. For the HQ/MeOH structure, which has the smallest guest molecule, the onset pressure is above 6.2(1)

GPa. The HP phases of these two clathrates are similar, with the host framework tilting to form skewed cavity channels and in the process breaking the 3-fold rotation symmetry.

The pressure dependence of the interaction energies in the hydroquinone clathrates as well as the apohost structure have been studied. Comparing the host framework energies in the LP structures, we see very similar interaction energies for both HP clathrate structures. Looking at the host–guest cluster interaction energies we see that the interaction energies are almost constant as the pressure is increased, until the onset of the phase transition. The magnitude of the host–guest cluster interaction energies is lower for the MeOH structure as the guest species. Even though the compression of the HQ/MeCN is isotropic compared with the anisotropic compression of HQ/MeOH, the cavity volumes are compressed at the same rate for both compounds.

The major contribution to the crystal lattice energies comes from host–host interactions especially through the O–H...O hydrogen bonding network. Even though the O–H...O hydrogen bond forming the neck of the clathrate cavities is changed from a normal electrostatic hydrogen bond ($\text{O} \cdots \text{O} \sim 2.72$ Å) at ambient conditions to a more energetic partly covalent hydrogen bond at high pressure ($\text{O} \cdots \text{O} \sim 2.55$ Å), these host–host intermolecular interactions become increasingly less favorable at increased pressure. The reduced host–host interaction energies appear to ultimately lead to the structural rearrangements in the phase transitions. It is, however, notable that when the empty apohost β -hydroquinone structure is subjected to pressure, a phase transition to the denser α -hydroquinone apohost structure is observed. Yet when the hydroquinone host structure enclathrates guest molecules, a structure directing effect is observed leading to new high pressure host structure motifs.

Comparison between intermolecular energies calculated at high pressure using CE-B3LYP and DFT shows that the CE-B3LYP model provides reliable electrostatic, dispersion, and polarization energies, but it appears to underestimate the repulsion energies. When more crystallographic high-pressure data become available, a correction to the scale factor used to calculate the CE-B3LYP repulsion energies may give more accurate and reliable results for high-pressure geometries of molecular compounds.¹⁶ Altogether, the present work illustrates the complexity of relatively simple self-assembled systems and highlights the need for quantitative and reliable intermolecular energies when analyzing supramolecular aggregates. Quantitative description of the nature and strengths of intermolecular interactions in simple systems can help rationalize the highly complex structures studied in crystal engineering and supramolecular chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00408.

All the presented intermolecular interaction energies, geometries and information on the theoretical calculations (PDF)

Accession Codes

CCDC 1539394–1539433 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The

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Notes

The authors declare no competing financial interest.

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