in vivo electron transfer occurs between redox centers with small differences in redox potential, many of which are associated with membranes. Examples include NADH dehydrogenase, bc_1 complexes of mitochondria and photosynthetic bacteria, and the first reactions of mitochondrial cytochrome *c* oxidase.[2,3,42–45] Only the final reaction with molecular oxygen is decidely irreversible.

In this context then, we believe the electron transfer between the isopotential Mn porphyrin centers in our model systems to be highly relevant to in vivo systems. The background leak rates observed in our electron transfer assay are short circuits, possibly due to electron tunneling reactions as well as the effects of possible redox-active impurities in the lipid; the biological membranes also have many possible short circuiting reactions since they contain large amounts of unbound quinones and many other redox centers. In our models, we do not observe significant electron transfer above the background leak rate unless the incorporated PEI–porphyrins are capable of approaching one another to within 4 Å or less. These results suggest that distances separating biological redox components with small differences in electrochemical potential must be similarly small if rapid rates of directed electron transfer are to occur. A future extension of our model will involve synthesis of redox centers having small differences in midpoint potential (e.g., up to about 150 mV) for metalloporphyrins anchored on opposite sides of the bilayer.

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Solid-State Structural Characterization of 1,3-Cyclohexanedione and of a 6:1 Cyclohexanedione:Benzene Cyclamer, a Novel Host–Guest Species

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Abstract: 1,3-Cyclohexanedione (CHD) forms two stereoisomeric hydrogen-bonded supermolecules in the solid state. Both structures contain chains of enolized CHD molecules with very short hydrogen bonds (O···O < 2.58 Å) between the enolic OH and the carbonyl oxygen of a neighboring molecule. In the nonsolvated crystal form, I, CHD chains form with anti–anti hydrogen-bond stereochemistry. In crystals of II, composed of one guest molecule for every six CHD molecules, hexameric hydrogen-bonded rings of CHD with syn–anti hydrogen-bond stereochemistry form cyclic hosts, called cyclamers, which include a single ordered molecule of benzene. Monodeuteriobenzene and perdeuteriobenzene can also be included in CHD cyclamers. Structure II represents a new class of neutral guest complexes in which the host is a hydrogen-bonded analogue of a macrocyclic crown ether. CHD molecules behave functionally like macrocycles in their ability to trap small molecules in a highly selective manner. The X-ray crystal structures and solid-state ^{13}C CP/MAS NMR spectra of I and II are presented, and the criteria for designing other cyclamer structures with neutral guest molecules is discussed. Crystal data: I, $a = 8.193$ (5) Å, $b = 11.712$ (3) Å, $c = 6.128$ (3) Å, $\beta = 99.44$ (4)°, $P2_1/a$, $Z = 4$, 997 observed reflections; II, $a = b = 18.127$ (7) Å, $c = 10.542$ (3) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $R\bar{3}$, $Z = 18$, 764 observed reflections.

The importance of cryptands, cavitands, and chorands (crown ethers) as models for enzyme–substrate interactions has been the subject of intensive research during the last decade. Chemically diverse hosts have been designed, and a wide range of cavity sizes and types have been engineered.[1] The chemical and structural properties of the supermolecular host–guest species have been studied in detail, and these compounds have found many important applications based on their ability to selectively bind cations[2] and to serve as chiral recognition hosts for the separation of enantiomeric materials.[3] More recently efforts have been devoted to designing hosts that bind neutral small molecules.[4] All synthetic efforts in these areas have involved the design of σ-bonded macromolecules as the host species.

In this paper we describe a new approach to the design of crown ether type complexes based on construction of hydrogen-bonded host supermolecules. The host species, called a cylamer, is composed of small molecules which associate via hydrogen bonding into discrete ring-shaped aggregates. Similar kinds of cavities have been seen before in crystals of trimesic acid[5] and more recently in rigid bicyclic diol crystals,[6] but these structures contain infinite two-dimensional hydrogen-bonded networks rather than the discrete hydrogen-bonded aggregates that characterize cyclamers. While cyclamers could, in principle, exist in solution as analogues of σ-bonded crown ethers, trimesic acid and bicyclic diol hosts could not.

An example of a hydrogen-bonded host–guest species which can exist independently of its crystal structure is the water gas hydrate, one of the first structurally characterized clathrates.[7] The aqueous host in the gas hydrates differs from cyclamers primarily in that it is inorganic and it forms a spherical cavity rather than a ring. Organic hydrogen-bonded complexes are also known, for example, hydroquinone[8] and Dianin's compound,[9] both of which

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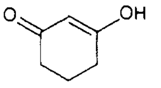
complex small molecules in the solid state. Their complexes are fundamentally different than those of cyclamers, however, since guest molecules pack between the hydrogen-bonded rings in hydroquinone and Dianin's complexes, rather *in* the rings as for cyclamers. In addition, the guest cavities in the clathrates are defined by hydrogen bonds only at two junctures, with van der Waals interactions occurring around the circumference of the cavities, so the cavity could not be retained in solution.

Naturally occurring examples of cyclamers include monensin and nigericin ionophores which form crown ether type rings via a single intramolecular hydrogen bond.[10] These antibiotics have been shown to have solution properties similar to their σ-bonded counterpart dianemycin,[11] demonstrating that solid-state hydrogen-bonded superstructures can be retained in solution and that *hydrogen bonds are realistic alternatives to σ bonds as the primary structural component of a host molecule.*

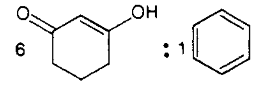
We have found that cyclic β-diketomethanes form strong intermolecular hydrogen bonds between their enol hydroxyl hydrogens and their carbonyl groups. These interactions lead to hydrogen-bonded chains of molecules which form cyclamers in the presence of suitable guest molecules. The preparation of 1,3-cyclohexanedione supermolecular structures, their characterization by X-ray crystallography and high-resolution solid-state NMR, and the role of hydrogen-bond interactions in controlling the formation of supermolecular species and novel host–guest complexes are described.

Experimental Section

Crystal Growth and Characterization. Flat, clear trapezoidal crystals (0.5 × 2 × 5 mm³) of 1,3-cyclohexanedione (Aldrich), I, were obtained by slow evaporation (room temperature) of tetrahydrofuran solutions.



I



II

The crystals showed no signs of decomposition upon removal from the mother liquor. The composition and purity of I was confirmed by ^{1}H NMR and by melting point determination (mp 103–104 °C, ΔH = 3.1 kcal/mol [lit. mp 103–105 °C]).

Large (10 mg) clear rhombohedral crystals of II, appearing as elongated crystals with hexagonal end faces, are the only crystal form of CHD obtained by slow evaporation of solvent from solutions of I and benzene, benzene-d_6, or monodeuteriobenzene. The crystals turn cloudy within minutes upon removal from the mother liquor, but they can be stabilized for X-ray structure analysis by coating freshly recrystallized crystals with epoxy glue. The coated crystals remain optically clear for several months and exhibit no loss in X-ray diffraction intensity during data collection. The cause of opacity in nonstabilized crystals is not completely understood. The behavior is suggestive of desolvation, but NMR measurements, reported below, show that there is no significant desolvation occurring under these conditions. The crystals can be desolvated by heating at 50 °C for 8 h or by placing the crystals under reduced pressure (20 mmHg) for 2 h.

Attempts have been made to incorporate other guest molecules into the cyclamer cavity by recrystallizations from a variety of organic solvents. The only other guest molecules which have been incorporated by this method are deuterated benzenes (in particular, hexadeuteriobenzene and monodeuteriobenzene). Fluorinated benzenes, alkyl-substituted benzenes, pyridine, chloroform, thiophene, and alcohols could not be complexed with cyclohexanedione by simple recrystallization procedures. The presence of deuterated benzene guest molecules was determined by deuterium NMR spectroscopy on solutions of the complex crystals dissolved in acetone (nondeuterated).

X-ray Structure Analyses of I and II. Crystal Data. The unit cell dimensions were obtained on a Nonius CAD-4 diffractometer (Mo Kα, λ = 0.7108 Å) by least-squares analysis of 25 reflections in the 2θ ranges 7–19° for I and 5–22° for II.

I: $C_6H_8O_2$, fw = 112.13, mp 103–104 °C, monoclinic, $P2_1/a$, a = 8.193 (5) Å, b = 11.712 (3) Å, c = 6.128 (3) Å, β = 99.44 (4)°, V = 580.1 (2) Å³, Z = 4, μ(Mo Kα) = 0.89 cm^{-1}, D_m = 1.300 g/cm³ (by flotation), D_c = 1.245 g/cm³, 2663 reflections measured for 0° < 2θ < 35°; 997 observed, $I > 3\sigma(I)$.

Table I. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for Compounds I and II (Esd's in Parentheses)[a]

atom	x/a	y/b	z/c	B, Å²
		(a) Compound I		
O(1)	0.5834 (2)	0.2951 (1)	0.3928 (2)	6.35 (4)
O(2)	0.9197 (2)	0.3183 (1)	1.0722 (2)	5.93 (4)
C(1)	0.6658 (3)	0.2454 (2)	0.5533 (3)	4.50 (4)
C(2)	0.7526 (3)	0.3073 (2)	0.7328 (3)	4.52 (4)
C(3)	0.8395 (2)	0.2551 (2)	0.9103 (3)	4.18 (4)
C(4)	0.8498 (3)	0.1290 (2)	0.9308 (3)	5.18 (5)
C(5)	0.7194 (6)	0.0679 (3)	0.7751 (8)	5.3 (1)
C(5A)	0.8113 (6)	0.0677 (3)	0.7163 (7)	5.2 (1)
C(6)	0.6734 (3)	0.1184 (2)	0.5613 (4)	6.25 (6)
H(C(2))	0.747 (2)	0.389 (1)	0.727 (3)	4.2 (4)*
H(O(2))	0.969 (3)	0.272 (2)	0.191 (4)	9.0 (7)*
		(b) Compound II		
C(1)	0.38643 (8)	0.01781 (8)	0.1626 (2)	3.99 (4)
C(2)	0.46662 (8)	0.02270 (8)	0.1559 (2)	4.08 (4)
C(3)	0.54011 (8)	0.09806 (8)	0.1608 (2)	4.00 (4)
C(4)	0.54194 (9)	0.18096 (9)	0.1703 (2)	5.17 (4)
C(5)	0.46160 (9)	0.17474 (9)	0.1172 (2)	5.85 (5)
C(6)	0.38279 (8)	0.09835 (9)	0.1702 (2)	4.65 (4)
O(1)	0.31878 (6)	−0.05256 (6)	0.1661 (1)	5.68 (3)
O(2)	0.61602 (5)	0.10515 (6)	0.1606 (1)	5.56 (3)
C(11)	0.3983 (2)	−0.2508 (1)	0.1667 (0)	6.99 (6)
H(C(11))	0.440 (1)	−0.194 (1)	0.164 (2)	9.5 (6)*
H(O(2))	0.613 (1)	0.048 (1)	0.158 (2)	8.8 (5)*
H(C(2))	0.4661 (8)	−0.0293 (8)	0.150 (1)	4.6 (3)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

II: $C_7H_9O_2$, fw = 125.12, mp 77–90 °C, hexagonal, $R\bar{3}$, a = b = 18.127 Å, c = 10.542 (3) Å, α = β = 90°, γ = 120°, Z = 18, μ(Mo Kα) = 0.85 cm^{-1}, D_m = 1.25 g/cm³ (by flotation), D_c = 1.28 g/cm³, 3690 reflections measured for 0° < 2θ < 26°; 1169 independent reflections (R_{int} = 0.024); 764 observed, $I > 1\sigma(I)$.

Structure Solution. Intensities were corrected for Lorentz and polarization factors; absorption corrections were not applied. The structures were solved by direct methods and Fourier synthesis by using the SDP package[12] implemented on a PDP11/34 computer (atomic scattering factors were taken from the *International Tables*). All hydrogen atoms of I were located on difference electron density maps and refined with isotropic thermal parameters. Only benzene, hydroxyl, and C(2) hydrogen atoms were found experimentally and refined for compound II. Other idealized proton positions were introduced to the structure factor calculation with fixed isotropic temperature factors. The structures were refined with anisotropic temperature factors for all non-hydrogen atoms by using full-matrix least-squares procedures with unit weights applied to the structure factors of I and a weighting scheme with $w = 4F^2/\sigma^2(F^2)$ applied to the structure factors of II. The refinements converged to R = 0.052 and R_w = 0.043 for I (shift/error max = 0.25) and R = 0.037, R_w = 0.041 (shift/error max = 0.04) for II. No significant electron density peaks were found below 0.2 e/Å³ (I) and 0.17 e/Å³ (II). Positional parameters for both structures are given in Table I, and selected bond lengths and angles are given in Table II. Thermal parameters, structure factor tables, and tables of intra and intermolecular bond lengths and angles have been submitted as supplementary material.

^{13}C CP/MAS NMR. The ^{13}C CP/MAS NMR spectra were obtained on a Nicolet NT-150 spectrometer at a carbon frequency of 37.735 MHz with a home-built cross-polarization/magic angle spinning (CP/MAS) unit and probe. The decoupling field used was 55 kHz. The spinner system is a modified version of Wind's,[13] with a sample volume of 0.3 cm³. The samples were spun at a 3.8-kHz frequency (100 rpm). The CP contact time was 4 ms, and the pulse sequence repetition time was 2 s; 8K data points were collected with a spectrum width of 16 kHz and an acquisition time of 64 ms. Chemical shifts are given relative to an external Me_4Si standard, with hexamethylbenzene as a secondary

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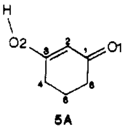
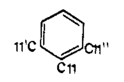
Table II. Selected Intramolecular Bond Lengths (Å) and Bond Angles (deg) for Compounds I and II (Esd's in Parentheses)

	 I	:	 II
C(1)–C(2)	1.409 (5)		1.413 (2)
C(1)–O(1)	1.243 (2)		1.253 (2)
C(1)–C(6)	1.490 (6)		1.495 (2)
C(2)–C(3)	1.345 (5)		1.349 (2)
C(3)–C(4)	1.483 (5)		1.490 (2)
C(3)–O(2)	1.323 (4)		1.318 (2)
C(4)–C(5)	1.49 (1)	1.49 (1)[a]	1.512 (2)
C(5)–C(6)	1.43 (1)	1.48 (1)	1.513 (2)
C(2)–H(C(2))	0.96 (3)		0.94 (1)
O(2)–H(O(2))	0.94 (5)		1.01 (2)
C(11)–C(11)[b]			1.366 (4)
C(11)–H(C(11))			0.92 (2)
O(1)–C(1)–C(2)	121.1 (2)		121.1 (1)
C(6)–C(1)–C(2)	118.4 (4)		119.3 (3)
O(1)–C(1)–C(6)	120.5 (4)		119.6 (1)
C(1)–C(2)–C(3)	122.0 (3)		121.6 (1)
C(2)–C(3)–C(4)	122.5 (4)		122.6 (1)
C(2)–C(3)–O(2)	118.9 (3)		123.5 (1)
C(4)–C(3)–O(2)	118.6 (3)		113.9 (1)
C(3)–C(4)–C(5)	113.4 (5)	113.9 (5)	111.3 (1)
C(4)–C(5)–C(6)	116.1 (8)	113.8 (3)	111.5 (1)
C(1)–C(6)–C(5)	116.5 (6)	116.5 (5)	113.0 (1)
C(11)[b]–C(11)–C(11)[c]			120.0 (0)
C(1)–C(2)–H(C(2))	118 (2)		116.3 (8)
C(3)–O(2)–H(O(2))	111 (3)		112 (1)

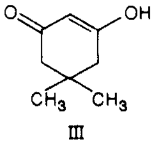
[a] Bond lengths and angles involving C(5A). [b] Symmetry: $^2/_3 - x$, $^1/_3 - y$, $^1/_3 - z$. [c] Symmetry: $^2/_3 + y$, $^1/_3 - x + y$, $^1/_3 - z$.

standard (methyl carbon signal at 17.35 ppm).

Bulk polycrystalline samples of I and of II were used in the solid-state NMR studies. Crystals of II were removed from their mother liquor only seconds before transferring them into the NMR spinner. No attempt was made to dry the samples since single-crystal observations had suggested that the crystals underwent desolvation when exposed to the air. A strong resonance peak at 129.4 ppm, observed only in the spectrum of II, was assigned to included benzene. Surprisingly, the intensity of this peak was not affected by sample grinding or air drying. A proton-decoupled single-pulse FT spectrum was obtained immediately following the CP/MAS experiment without removing the sample or changing the probe, showing the presence of a single resonance peak at 128.5 ppm due to adsorbed or latent liquid benzene in the sample.

Molecular Modeling. Molecular mechanics calculations were performed by using Allinger's MM2 program[14] in order to determine a minimum energy conformation for 1,3-cyclohexanedione in the enol form. Geometry optimization gave a distorted enol geometry for which calculated asymmetry paramters[15] gave a ΔC_s of 3.38°, indicative of a sofa conformation. This value compares favorably with the experimental asymmetry parameters determined from our crystal structures for I and II of 2.29° and 1.96° for I and 0.88° for II.

Infrared Analyses. Nujol mulls of I, II, and dimedone (4,4-dimethyl-1,3-cyclohexanedione), III, were prepared, and their infrared spectra were determined on a Beckman Acculab I grating spectrophotometer. Broad OH stretching bands were observed between 3000 and 1700 cm^{-1} for each of the compounds. IR patterns: I (CHD:benzene), 3080 (br), 2678 (br), 2562 (s, br), 1850 (br), 1610 (s, br), 1600 (m), 1580 (m), 1323 (s), 1280 (s, br), 930 (s), 705 (s); II (CHD), matches Sadtler reference spectra 48019 p (grating) and 17349 (prism); III (Dimedone), matches Sadtler reference spectra 8697 (grating) and 14904 (prism).



III

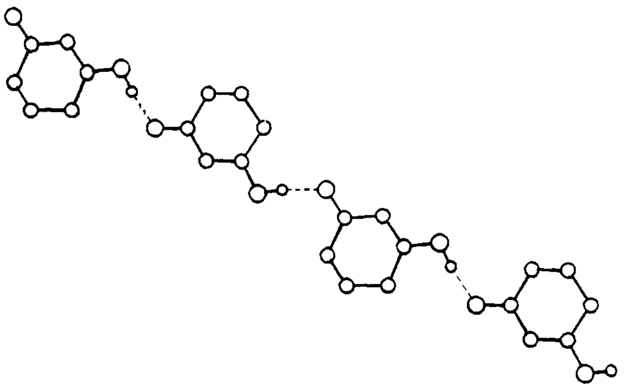


Figure 1. Extended chain of CHD molecules as found in the crystal structure of I. The planar chain extends along the *a* axis in the (001) plane of the unit cell and is constructed from intermolecular hydrogen bonds occurring between the enol hydroxyl group and the carbonyl oxygen of glide related molecules. The O···O hydrogen-bond distance is 2.561 (4) Å. The hydrogen-bond stereochemistry is anti–anti.

Results

1,3-Cyclohexanedione (CHD) can be crystallized in two different forms, distinguishable by morphology, thermal properties, NMR spectra, and X-ray crystallography. Form I is obtained by solution recrystallization from a variety of organic solvents and exists as flat, clear trapezoidal plates. Form II is obtained by solution recrystallization only from benzene or deuterio-substituted benzenes. Crystals of II contain 18 molecules of CHD and 3 molecules of benzene in the unit cell, and they have a distinctly different morphology than crystals of I, which contain no solvent. The composition of II was ultimately determined by X-ray crystallography, but inclusion of benzene could be monitored by solution ^{1}H or ^{13}C NMR of dissolved crystals. Included guest molecules can also be observed by ^{13}C CP/MAS NMR studies.

The intramolecular geometry of CHD is basically the same in both of its crystal forms. CHD exists as the enolic tautomer, exhibiting a difference of 0.073 Å between the enol C—O and the keto C=O bond lengths and 0.064 Å between the endocyclic double bond (C(2)=C(3)) and the C(1)—C(2) conjugated single bond. The CHD ring conformation is in the sofa form in both I and II with C(5) 0.45–0.60 Å out of the plane of the other atoms in the molecule. This conformation is the expected form for a cyclohexyl ring containing three adjacent sp^2 carbons and three sp^3 carbons. Occupancy refinements indicate that C(5) is disordered in I and occurs with equal probability above and below the plane of the molecule (the second position is designated C(5A)).

The packing patterns of I and II, Figures 1 and 2, are distinctly different, but the supermolecular substructures in the two crystals are actually solid-state stereoisomers of one another. These substructures are composed of chains of CHD supermolecules formed by intermolecular hydrogen bonds between the hydroxyl hydrogen and the carbonyl oxygen of neighboring molecules. The O–O distance between hydrogen-bonded oxygens is 2.561 (4) Å in I and 2.579 (1) Å in II, both distances being considerably shorter than van der Waals distance (3.0 Å for O···O interactions[16]) and shorter than most inter- or intramolecular O···O hydrogen-bond distances.[17] In I, the hydrogen-bonded chains are formed between glide-related molecules and the chains are extended and flat, with neighboring chains aligned parallel to one another, Figure 3a.

The hydrogen-bonded chains of II are cyclic, with six CHD molecules per ring, Figure 2. The stereochemical configuration of the hydrogen-bonded chains is different than that observed for I. The difference can be illustrated by referring to the schematic diagram below which shows the orientations that are possible for the OH group and for the =O···H moiety, assuming that the conjugated system and the hydrogen bond are coplanar. For I,

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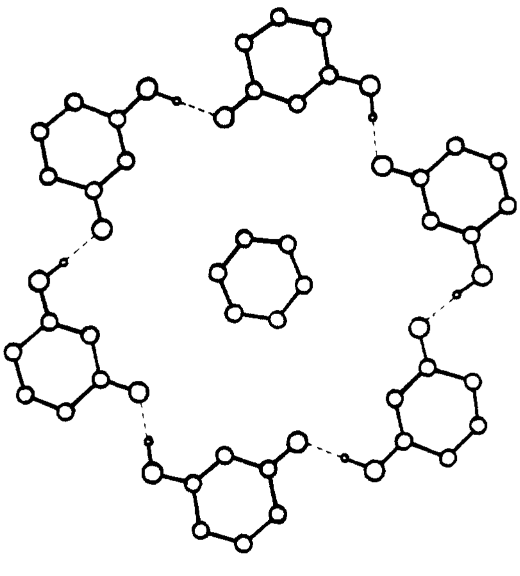


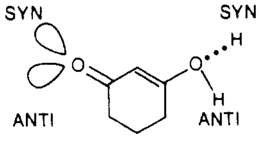
Figure 2. Cyclamer host-guest complex of six CHD molecules and one benzene guest molecule, as found in the crystal structure of II. The complex is planar and is located on a $\bar{3}$ special position in the crystal. The backbone of the cyclamer is constructed from intermolecular hydrogen bonds with O···O distances of 2.579 (1) Å. The hydrogen-bond stereochemistry is syn-anti. The benzene molecule is crystallographically ordered and can only be removed from the solid-state structure by heating the sample or by vacuum methods.

Table III. Hydrogen Bond Geometries

	I	II
O(1)···O(2),[a] Å	2.561 (4)	2.579 (1)
O(1)···H(O(2)),[a] Å	1.63 (5)	1.57 (2)
O(2)-H(O(2)), Å	0.94 (5)	1.01 (2)
O(1)···H(O(2))[a]-O(2),[a] deg	170 (5)	174 (2)

[a] Symmetry operations. I: $x - {}^1/_2, {}^1/_2 - y, z$. II: $x - y + {}^2/_3, x + {}^1/_3, {}^1/_3 - z$.

the hydrogen-bond configuration is anti-anti, while for II it is syn-anti (specifying the hydroxyl orientation first and the carbonyl hydrogen-bond orientation second). Despite these stereochemical differences, the hydrogen-bond geometries, including bond lengths and angles, are nearly identical, Table III.



In the presence of benzene, CHD adopts the syn-anti configuration, allowing formation of a cyclamer which encloses one ordered benzene molecule. The benzene is situated precisely on a special position in crystals of II and has a slight ring pucker with S_6 symmetry. There are no unusually close intermolecular interactions between the benzene hydrogens and the CHD host structure, but it is of interest to note that the interior of the cyclamer cavity consists of six keto oxygen atoms located in a crown ether type array and that the benzene hydrogen atoms are pointing directly toward the syn lone pair electron positions of the keto oxygens. Since the H···O distance involved, 3.00 (2) Å, is considerably larger than the van der Waals distance 2.4 Å), it is unlikely that this interaction is a stabilizing one. Nevertheless, it is the closest host-guest contact and the *orientation* of the proton and the carbonyl groups are favorable for hydrogen-bond formation.

The CHD ring and the included benzene form a nearly planar structure, where only the C(5) or C(5A) atoms are substantially out of plane (the oxygens are found from 0.03 to 0.09 Å out of plane). Three cyclamer rings from adjacent layers overlap each CHD ring, Figure 3b. The benzene molecules, isolated from one another by two layers of intervening CHD rings, are isolated in cavities which are 10.5 Å apart.

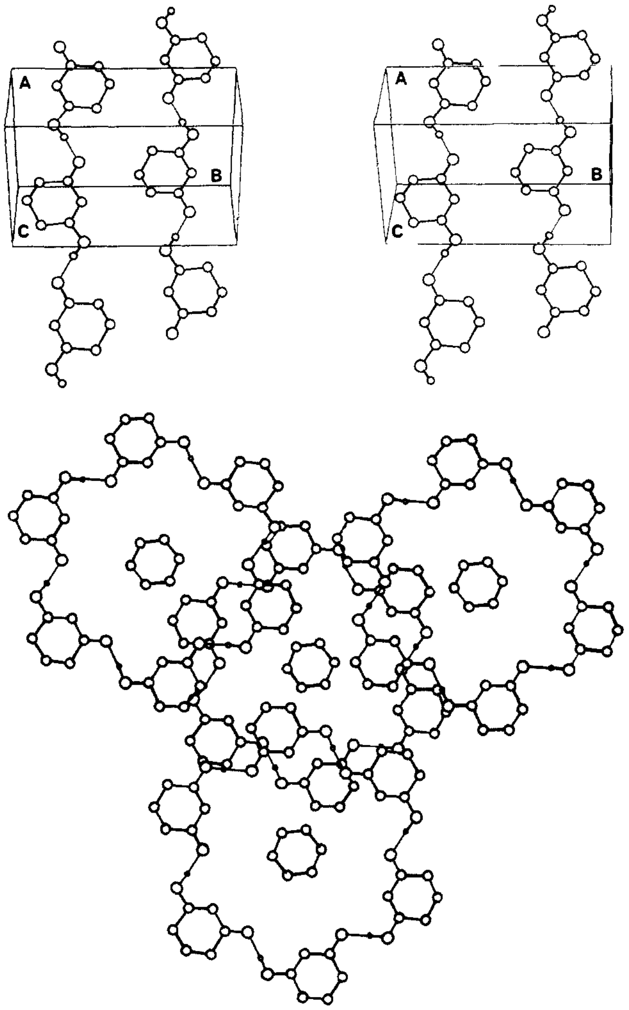


Figure 3. (a, top) Unit cell packing pattern of I viewed along (100), showing parallel alignment of neighboring hydrogen-bonded chains. (b, bottom) Two layers of the cyclamer complex viewed along the (001) direction, showing the 3-fold symmetric arrangement of neighboring complexes and the displacement of nearest-neighbor benzene molecules. The benzene molecules are trapped in cavities rather than in channels of the lattice, so that the benzene molecules aligned along (001) occur 10.5 Å apart and are isolated from one another by intervening hydrocarbon portions of neighboring cyclohexanedione molecules.

High-resolution solid-state NMR studies were done on I and II at room temperature, showing that the isotropic chemical shifts of the CHD carbon atoms in the two structures occur at very nearly the same values, but that internal chemical shift differences between C(1) and C(3) resonances are greater than 1.5 ppm and thus can be used as a diagnostic tool for identifying open-chain or host-guest CHD supermolecular structures. The resonances due to benzene occur as a single peak at 129.40 ppm. Since this peak is visible under CP/MAS conditions, the benzene motion within the crystal is not liquid-like. A freely tumbling and translating molecule (such as benzene in phosphonitrile clathrates[18]) would result in averaged CH dipolar interactions, resulting in loss of signal under CP conditions.

A proton-decoupled single-pulse FT experiment was run on the solid immediately after the CP/MAS experiment, with the sample still in the solid-state probe, and a peak for liquid benzene was seen occurring at the expected position for liquid benzene (128.5) 0.9 ppm upfield from the benzene position in II, Figure 4. Normally, 1 ppm is below the reproducibility of solid-state spectra, but in this case all experimental parameters were identical since the sample was not removed from the probe and no field or

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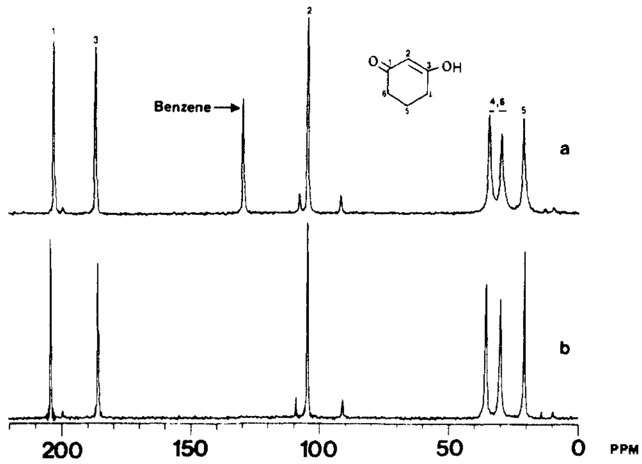


Figure 4. ^{13}CP/MAS NMR spectra of I (a) and II (b) run at a carbon frequency of 37.735 MHz, with a sample spinning speed of 3.8 kHz. The benzene guest species in I is clearly visible in (a) at 129.4 ppm (relative to Me$_4$Si). A difference of about 1.5 ppm is observed for $\Delta\sigma_{C(1)-C(3)}$ between the two samples. Similar chemical shift differences can also be seen for the aliphatic carbon peaks.

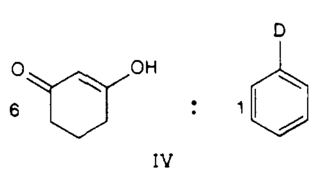
electronic adjustments were made other than the pulse sequence. This 1 ppm difference is real and is indicative of the change in environment of the benzene molecule in the CHD cavity as compared to the liquid phase. The intensity of the liquid benzene peak rapidly decreased with time, and its presence was ascribed to residual solvent adsorbed on the surfaces of the polycrystalline sample.

We also learned from the NMR experiments that extensive sample grinding of II, or exposure of II to air for long periods of time, did not result in rapid changes in concentration of the benzene guest molecules. This benzene could be removed only by heating or applying a vacuum.

Discussion

The crystal structures of I and II show that 1,3-cyclohexanedione exists in two different crystal forms containing stereoisomeric hydrogen-bonded chains of CHD molecules. In II, these chains form a supermolecular host–guest complex which traps neutral molecules and serves as a small molecule analogue of macromolecular host–guest structures. Finite arrays of cyclic hydrogen-bonded monomers which form structures with cavities or holes in them are termed *cyclamers*, or cycla-*n*-mers where *n* denotes the number of monomers per ring. The CHD cyclahexamer, II, is a highly specific complexing agent since it will complex benzene and deuteriobenzenes but will not complex thiophene, pyridine, alcohols, or chloroform. The benzene guest molecule is not disordered, as evidenced by small thermal parameters for benzene carbons and hydrogens and the lack of residual or diffuse electron density peaks within the cyclamer cavity. The appearance of a sharp benzene resonance in the ^{13}C solid-state NMR pattern is indicative of restricted benzene motion, corroborating the X-ray results. The benzene molecules may be hopping rapidly between symmetry equivalent positions about the 3-fold axis, a motion not uncommon for planar molecules in the solid state,[19] but NMR relaxation studies would be needed to characterize such motions.[20]

Crystals of II complexed with perdeuteriobenzene and with monodeuteriobenzene were also prepared. The inclusion of deuteriobenzenes was confirmed by solution ^{2}H NMR analysis of the crystals after isolating them from the deuterated benzene solvents. Although the X-ray powder pattern of the monodeuteriobenzene host–guest complex, IV, matches that of II, the different molecular symmetries of the guest molecules in II and IV require that certain crystallogrpahic features be different.[21]

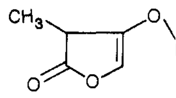


IV

In II the benzene molecule is on a $\bar{3}$ special position, a symmetry not possible for monosubstituted benzenes. A disordered structure with random orientations of static deuteriobenzene molecules would have on the average one-sixth of a deuterium at each aromatic proton position and could thus exhibit $\bar{3}$ symmetry. A crystallographically indistinguishable structure, however, would also occur if the deuteriobenzene molecules were dynamically disordered by a hopping motion within the cavities. Further studies are needed to resolve these ambiguities.

A comparison of the hydrogen-bond geometries in I and II shows that they are remarkably similar, Table III. Both compounds have a very short hydrogen bond of less than 2.6 Å, as found for Dimedone, III.[22] Such short hydrogen bonds also occur for intramolecular hydrogen bonds in compounds such as naphthazarin[23] or 4-bromo-5-hydroxyflavone.[24] Rarely do intermolecular hydrogen bonds occur with O···O distances less than 2.8 Å (exceptions include complexes between strong acids and strong acceptors such as triphenylphosphine oxide[25] and symmetrical acid salts such as HF_2^-[26]). Emsley has classified hydrogen bonds with short distances like these as "strong hydrogen bonds", and he has demonstrated that structures with such bonds have characteristic spectral properties.[27] Acyclic β-diketomethanes have O···O distances of 2.42–2.53 Å (10 known structures), and exhibit the expected low-frequency infrared OH stretching bands. Similar low-frequency bands were observed in the infrared spectra of the cyclic diketomethanes, I–III.

The structures of I–III are the only saturated cyclic β-diketomethane structures in the literature. The remarkable consistency in hydrogen-bond lengths between these three structures suggests that *the short intermolecular hydrogen bond between β-diketomethanes may be a characteristic feature of cyclic β-diketomethanes* just as the short intramolecular hydrogen bond is characteristic of acyclic β-diketomethanes. In support of this claim, there is also a short intermolecular hydrogen bond found in α-methyltetronic acid, V.[28]



V

Since these intermolecular bonds are nearly as short as the intramolecular bonds in acyclic structures, it may be possible to observe dynamic proton exchange between oxygens on neighboring cyclic β-diketomethane molecules analogous to intramolecular proton transfer in acyclic systems. There is no evidence for crystallographic disorder in compounds I–III, but a reasonable mechanism for proton hopping involving very small molecular rearrangements can be envisaged for I or for III. Somewhat larger molecular motions would be required to accommodate proton transfer in II since exchanging groups (hydroxyl and keto groups)

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are in different orientations in the cyclamer.

Conclusions

This work has shown that 1,3-cyclohexanedione (CHD) forms stereoisomeric hydrogen-bonded supermolecules in the solid state. One of these supermolecules is a cyclic structure, called a cyclamer, which serves as a host in complexing benzene, perdeuteriobenzene, and monodeuteriobenzene. CHD monomers, which are enolic, form supermolecules by aggregating via strong intermolecular hydrogen bonds with O···O hydrogen-bond distances of 2.51–2.57 Å, nearly as short as the O···O intramolecular hydrogen-bond contacts found in acyclic *β*-diketomethanes. High-resolution solid-state NMR spectroscopy and X-ray crystallography were used as complementary tools to elucidate the structures of the host–guest complexes and the dynamic properties of the included guest species.

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Registry No. I, 504-02-9; II, 103620-43-5; IV, 103620-45-7; C_6D_6·6I, 103620-44-6.

Supplementary Material Available: Tables 1 and 2 listing fractional atomic coordinates and anisotropic thermal parameters for compounds I and II (2 pages); tables of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

Electrocatalytic Reduction of Nitrite to Ammonia Based on a Water-Soluble Iron Porphyrin

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Abstract: In aqueous solution at either pH 4.5 or 6.7, the water-soluble porphyrin $[\mathrm{Fe^{III}(H_2O)(TPPS)}]^{3-}$ ($\mathrm{H_2TPPS^{4-}}$ = tetraanonic form of *meso*-tetrakis(*p*-sulfonatophenyl)porphyrin) is an effective electrocatalyst for the reduction of nitrite ion to ammonia with hydroxylamine or N_2O also appearing as significant products, depending upon the reaction conditions. The reductions proceed via the nitrosyl complex $[\mathrm{Fe^{II}(NO^+)(TPPS)}]^{3-}$ as an intermediate. The nitrosyl complex forms at pH <3.0 by a reaction between the Fe(III) porphyrin and NO arising from disproportionation of HONO or, at 4.0 < pH >7.0, following reduction of Fe(III) to Fe(II) ($E_{1/2}$ = –0.23 V vs. SSCE) via an acid–base reaction. Reduction of the nitrosyl complex occurs by sequential 1-electron steps at $E_{1/2}$ = +0.35 and –0.63 V vs. SSCE, the second of which is pH-dependent at pH <2.6. Evidence for a third 1-electron step has been found by differential pulse polarography at pH 2.1. The first two reductions are followed by a multiple-electron wave which is greatly enhanced as the pH is decreased from 4 to 2.6. Although NH_3 is the ultimate reduction product at –0.9 V, NH_2OH appears to be an intermediate stage in the reduction and electrolysis to the 2-electron stage at –0.63 V gives increasing yields of N_2O. The redox properties of the nitrosyl complex and probable mechanism of reduction of NO_2^- to NH_3 are discussed and compared with earlier results obtained on polypyridyl complexes of Os and Ru.

The enzyme nitrite reductase (found in bacteria, fungi, and plants) converts nitrite to ammonia in a net 6-electron, five-proton reduction process.[1] The enzyme utilizes an iron isobacteriochlorin as the active site. Chlorins, bacteriochlorins, and isobacteriochlorins are all derived from a parent porphyrin by the hydrogenation of one or two pyrrollic double bonds.[2] One line of current research has emphasized the study of synthetic iron isobacteriochlorins and related complexes in order to determine the distinctive features of the active site that allow it to catalyze the reduction of nitrite.[3] However, recent results have shown that a number of simple iron complexes are capable of reducing NO catalytically to ammonia,[4] suggesting that the key to the redox chemistry may lie in the Fe–NO fragment and be relatively insensitive to the nature of the additional ligands coordinated to the iron center.

Studies of the reductive chemistry of the bound nitrite and nitrosyl ligands have concentrated on the stoichiometric or near stoichiometric reduction of these ligands coordinated to Fe, Ru, or Os.[5,6] Results obtained for polypyridine complexes of ruthenium and osmium have demonstrated the facile interconversion of bound nitrite and nitrosyl[7] and also the chemical and electrochemical reduction of bound nitrosyl to coordinated ammonia.[5,6] The results of detailed electrochemical studies have allowed a mechanism to be proposed based on a series of 1-electron reductions, initially at the nitrosyl ligand, which lead to a series of detectable intermediates.[6]

There are numerous examples in the literature of iron nitrosyl porphyrins,[8] and detailed electrochemical studies on the complexes Fe(NO)(TPP) and Fe(NO)(OEP) ($\mathrm{OEP^{2-}}$ = dianion of octaethylporphine, $\mathrm{TPP^{2-}}$ = dianion of *meso*-tetraphenylporphine) in

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