

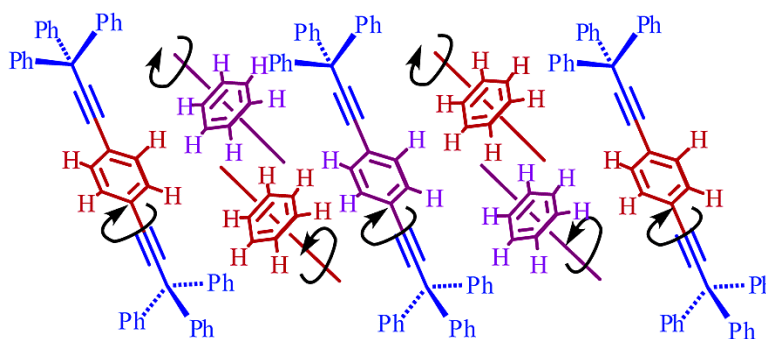
Article

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Molecular “Compasses” and “Gyroscopes.” III. Dynamics of a Phenylene Rotor and Clathrated Benzene in a Slipping-Gear Crystal Lattice

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Abstract: Samples of 1,4-bis(3,3,3-triphenylpropynyl)benzene **3** were prepared by Pd(0)-catalyzed coupling of 3,3,3-triphenylpropyne (**1**) and 1,4-diiodobenzene. The structure of compound **3** is such that the central phenylene can play the role of a gyroscope wheel, while the alkyne bond and trityl groups can act as an axle and shielding frameworks, respectively. Crystals grown from benzene and dichloromethane were characterized by X-ray diffraction, variable-temperature ^{13}C CPMAS NMR, quadrupolar echo solid-state ^2H NMR, and thermal analyses. The rotational dynamics of benzene molecules and phenylene groups were characterized in terms of 6-fold rotation and 2-fold flipping models, respectively. The possibility of a gearing mechanism between adjacent benzene molecules and phenylene groups suggested by the clathrate structure was investigated. However, it was found that 6-fold rotation of benzene molecules at 300 K occurs in the gigahertz regime (or higher) and 2-fold flipping of phenylene groups in the kilohertz range in a structure that can be described as a slipping-gear lattice. The rotational dynamics of the phenylene group in the solvent-free structure were remarkably similar to those in the clathrate, and both are among the fastest known for phenylene rotation in solids. The results presented here provide a valuable starting point for the design and analysis of crystalline solids with correlated molecular motions.

1. Introduction

Numerous developments in X-ray diffraction¹ and solid-state NMR² have paved the way for the study of internal molecular motions in crystalline solids. We recently became interested in the rational design of crystalline solids that can support fast molecular motions. We reasoned that crystals built with molecules that experience volume-conserving conformational motions should have many interesting physicochemical properties. In particular, we are interested in electrooptic materials based on dipolar units that can reorient under the influence of electric, magnetic, and optical stimuli. The desired molecular structures must permit the reorientation of a polar group while maintaining a static framework that supports a very robust crystal lattice. In analogy with macroscopic objects and to suggest some of their properties and functions, we refer to these structures as *molecular compasses* and *molecular gyroscopes*.

One of several promising molecular architectures currently explored in our group for the synthesis of molecular compasses

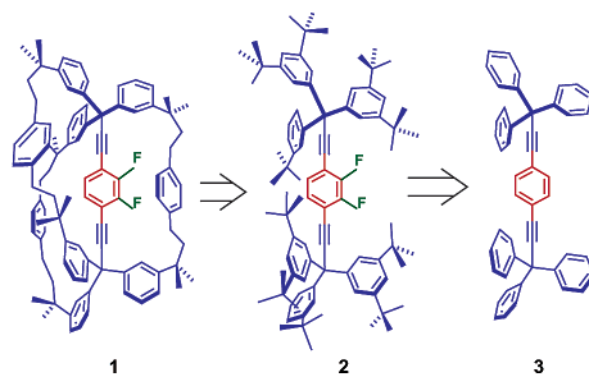


Figure 1. Molecular compasses and gyroscopes based on 1,4-bis-(triarylpropynyl)benzenes. The central difluorobenzene should be shielded from contacts with neighboring molecules and solvent of crystallization. Shielding may be accomplished by bridges across the two trityl groups (**1**) or by bulky *tert*-butyl groups (**2**).

and gyroscopes is based on 1,4-bis(triarylpropynyl)benzenes (Figure 1). We expect that sterically guarded 1,4-diethynylphenylenes should be able to reorient in the solid state, while the triarylmethyl (trityl) framework remains static in the crystal lattice. Rotation of aryl groups attached to triple bonds should be essentially frictionless in the gas phase,³ and steric shielding will be accomplished with groups bridging across the two triaryl methanes, such as structure **1**, and with bulky substituents such as the *tert*-butyl groups in compound **2**.

Working toward the synthesis of compounds **1** and **2**, we recently reported a simple procedure for the preparation of 4-bis-

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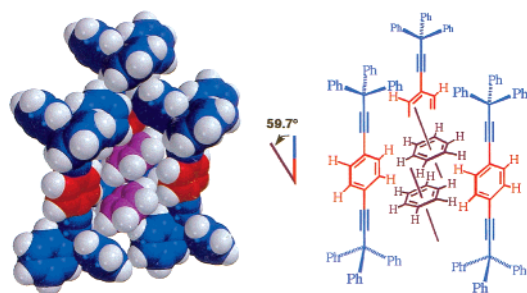


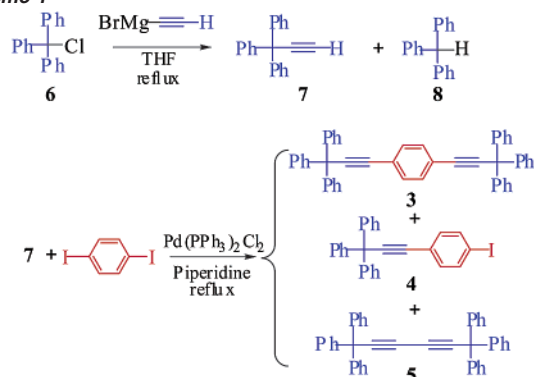
Figure 2. Space-filling models and line formulas illustrating the packing arrangement of rotor **3** and the benzene dimer. Trityl groups, 1,4-phenylenes, and benzene are colored in blue, red, and purple, respectively. A fourth molecule in the forward plane that closes a four-pillar cage was omitted for clarity. The angle formed by the phenylene 1,4-axis and benzene 6-fold axis is 59.7°.

(3,3,3-triphenylpropynyl)benzene **3** and a preliminary study of its solid-state dynamics.^{4,5} Crystals grown from benzene contain one molecule of **3** (Figure 2, in blue and red) and two molecules of benzene (shown in purple) per unit cell.⁶ The triclinic packing arrangement (space group $P\bar{1}$) can be described in terms of cages formed by four adjacent molecular rotors incarcerating a parallel-displaced⁷ benzene dimer. Phenylene groups and benzene molecules experience gear-like, edge-to-edge contacts with their 1,4- and 6-fold axes, respectively, at an angle of 59.7°.

Using a simple coalescence analysis of the ^{13}C CPMAS NMR, we were able to establish that phenylene group undergoes rapid 2-fold flipping with a rate of $1.3 \times 10^2 \text{ s}^{-1}$ at -18°C . From a sharp signal in the ^{13}C CPMAS NMR spectrum, we deduced that benzene molecules are also in a state of rapid rotation. Knowing that phenylene groups and benzene molecules are within close distances, the question arose whether they could behave as a dynamically geared system. Although the transfer of momentum from six-cogged to two-cogged gears should be inefficient, the prospect of observing geared crystalline lattices with angular momentum transfer from benzene molecules to phenylene units in a concerted fashion is a very intriguing possibility.

Many specific mechanisms must exist for redistribution of thermal energy in crystalline solids, and the concerted rotation of molecular segments in a crystal lattice may be one possibility. The simplest feature of a supramolecular geared system, such as the benzene clathrate of **3**, would entail the rate of rotation of the phenylene group about its 1,4-axis to be commensurate to the rate of rotation of benzene molecules along their 6-fold axis. Looking for a simple qualitative answer, we have analyzed the solid-state structure and thermal properties of crystals of **3**

Scheme 1



grown from benzene and a new desolvated crystal form obtained from dichloromethane. The dynamic behavior of the phenylene groups and benzene molecules in the crystal lattice of the benzene clathrate was investigated by variable-temperature ^{13}C CPMAS NMR measurements and quadrupolar echo ^2H NMR line-shape analyses between 200 and 330 K. Results clearly show that 2-fold flipping of the phenylene group at ambient temperatures occurs in the kilohertz regime, while rotation of benzene molecules about their 6-fold axis occurs with frequencies that are above 100 MHz. Although results from these experiments suggest a description of the benzene clathrate of **3** as a slipping-gear lattice, they provide us with a starting point for the design of crystals with correlated rotation. Rapid 2-fold flipping was also observed for isolated phenylene groups in solvent-free crystals grown from dichloromethane.

2. Results and Discussion

2.1. Synthesis. Samples of 1,4-bis(3,3,3-triphenylpropynyl)-benzene **3** and its deuterated analogue, 1,4-bis(3,3,3-triphenylpropynyl)- d_4 -benzene **d4-3**, were synthesized by a simple two-step procedure from triphenylmethyl chloride (trityl chloride) **6** as illustrated in Scheme 1.

Substitution of the chloride by ethynylmagnesium bromide in refluxing THF under an argon atmosphere by the method of Masson et al. gave 3,3,3-triphenylpropyne **7** in 80% yield.⁸ The formation of triphenylmethane **8** as a side product, and formation of triphenylmethyl peroxide in the presence of oxygen, suggest the formation of trityl radicals as a side reaction. The second and final step was accomplished by Pd(0)-catalyzed coupling of 2.5 equiv of alkyne **7** with 1,4-diiodobenzene or 1,4-dibromobenzene in refluxing piperidine to yield rotors **3** and **d4-3**, respectively. There was no significant difference in reaction times and yields when either of the two aryl halides were used. Analysis of the crude reaction mixtures by GC (carbowax column, 300 °C) and ^1H NMR indicated a crude reaction yield of ca. 80% with the mono-coupling product **4** and alkyne dimer **5**⁹ in ca. 5% each. Column chromatography in hexanes: C_6H_6 : CH_2Cl_2 = 90:5:5, and recrystallization gave pure samples of **3** and **d4-3** in nonoptimized yields of 13 and 11%, respectively. The structures of **3** and **d4-3** were confirmed by ^{13}C and ^1H NMR, high-resolution mass spectrometry, and single-crystal X-ray diffraction data.

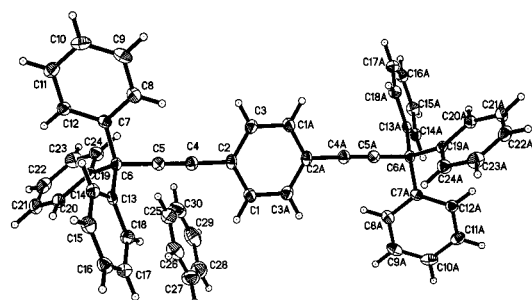
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Table 1. Unit Cell Parameters of the Two Crystalline Structures for Molecular Rotor **3**

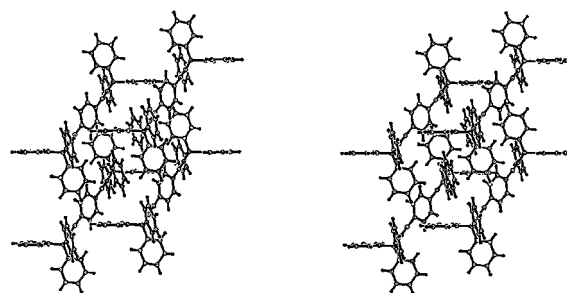
	benzene clathrate		solvent-free
temp (K)	298(2)	100(2)	100(2)
habit	prisms	prisms	prisms
system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.6601(15)	8.5157(19)	9.1500(14)
<i>b</i> (Å)	9.6711(17)	9.547(2)	10.3067(16)
<i>c</i> (Å)	14.600(2)	14.467(3)	10.5004(17)
α (deg)	76.245(4)	77.315(4)	61.736(3)
β (deg)	76.679(4)	76.469(4)	85.731(3)
γ (deg)	72.968(3)	72.970(4)	72.477(3)
vol (Å ³)	1118.5(3)	1078.4(4)	829.0(2)
<i>Z</i>	1	1	1
dens (Mg/m ³)	1.139	1.181	1.223

**Figure 3.** Ortep diagram of the X-ray structure determined from diffraction data measured at 298 K of trityl rotor **3** recrystallized from benzene. Thermal ellipsoids drawn at the 30% probability level.

2.2. X-ray Analysis: A Potential Crystalline Gear Chain.

X-ray quality prisms of rotor **3** were obtained by slowly cooling a saturated hot benzene solution. X-ray diffraction data were acquired at 298 K, and the structure was solved in the triclinic space group $P\bar{1}$. Diffraction data acquisition and structure refinement parameters are listed in Table 1. With coincident molecular and crystallographic inversion centers, the unit cell consists of only one molecule of **3** and two molecules of benzene. The molecular structure of **3** and its relation with a benzene molecule are shown in Figure 3. The alkyne groups deviate only slightly from linearity. The angle between C2, the center of the C4–C5 bond, and C6 is only 3°. The triphenylmethyl groups adopt an anti-conformation with the plane of the 1,4-phenylene nearly parallel to the vector given by the bond between the methane (C6) and ipso carbons (C7) corresponding to one of the three aryl groups. The twisting of the phenyl groups in each trityl substituent gives rise to chiral propeller conformations with dihedral angles $\angle_{\text{alkyne}-\text{C}_{\text{methane}}-\text{C}_{\text{ipso}}-\text{C}_{\text{ortho}}}$ of ± 29.8 , ± 50.5 , and ± 45.1 . The different sense of rotation in each trityl group renders them enantiomeric, as required by the molecular center of inversion.

As expected for a rigid, rodlike structure, all molecules of **3** are aligned in the same direction with complementary face-to-edge contacts between enantiomeric trityl propellers. A stereoview of the packing diagram down the *c*-axis in Figure 4 illustrates a cage formed by four molecules of **3** encapsulating the benzene molecules in a parallel-displaced dimeric arrangement. Benzene dimers possess an interplanar distance of 3.59 Å, which is nearly identical to that calculated for the lowest energy parallel-displaced gas-phase dimer. However, a translation of 3.31 Å in the clathrate is significantly longer than a 1.64 Å translation calculated in the gas phase. This results in

**Figure 4.** Stereoview of the packing structure of molecular rotor **3** viewed down the *c*-axis.

	A	B	C	D
B1	2.93	2.98	2.67	6.69
	3.37	3.48	3.17	6.93
B2	6.69	2.67	2.98	2.93
	6.93	3.17	3.48	3.37

Figure 5. Clathrate structure of rotor **3** with trityl groups removed to illustrate the two closest H–H distances in Å between each phenylene group (A–D) and benzene molecules (**B1** and **B2**). Edge-to-edge distances which could lead to dynamic gearing (**B1**–C and **B2**–B) are noted in bold face.

center-to-center distances of 4.88 Å. It is also noteworthy that each benzene molecule experiences an aromatic C–H– π interaction¹⁰ with a hydrogen from a neighboring trityl group directed to the center of the benzene molecule at a distance of 2.94 Å.

Regarding the possible transfer of angular momentum from rotating benzene molecules to phenylene groups, it is known that benzene can undergo rapid in-plane rotation about its 6-fold axis, while rotation of the phenylene groups is restricted along their 1,4-axis. A close inspection of the clathrate structure is facilitated by analysis of a caged dimer in Figure 5, where the trityl groups have been removed for clarity. Benzene molecules in the figure are labeled **B1** and **B2** and phenylene groups with letters A–D. Each benzene molecule is in close proximity with the other one in the dimer, and with four surrounding molecular rotors. There are no benzene-to-phenylene distances shorter than the sum of the van der Waals radii of two hydrogen atoms¹¹ ($2 \times 1.2 \text{ Å} = 2.4 \text{ Å}$). However, as indicated in the table in Figure 5, the hydrogen atoms in each benzene molecule are relatively close to hydrogen atoms in three of the four surrounding phenylenes ($d_{\text{H-H}} = 2.67\text{--}3.48 \text{ Å}$). From the three closest phenylene rotors, there is only one that experiences edge-to-edge interactions with a given benzene. These edge-to-edge contacts involve molecules labeled **B1**–C and **B2**–B. With edge-to-edge distances as close as 2.67 Å, one may speculate that

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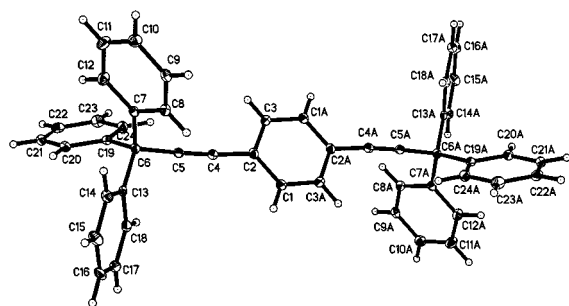


Figure 6. ORTEP diagram of rotor **3** in desolvated crystals with thermal ellipsoids drawn at a 30% probability level. Crystals were grown from CH_2Cl_2 .

in-plane rotation of a benzene molecule may gear with rotation of the phenylene group along the 1,4-axis. Clockwise rotation of **B1** would result in anticlockwise rotation of **C**. However, transfer of motion from a six-cogged benzene gear to a two-cogged phenylene may lead to frequent slipping. It is interesting to speculate that additional pathways for transfer of (linear and) angular momentum through contacts with neighboring rotors, and from one benzene to another, may follow dynamic pathways with high degree of order restricted by lattice symmetries.

2.3. Thermal Stability of the Benzene Clathrate: DSC and TG Analysis. To characterize the rotational dynamics of the benzene clathrate by solid-state VT NMR experiments, we needed to determine its thermal stability. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements were carried out on freshly crystallized samples of compound **3**. From the TGA measurement, a weight loss of 20% was observed between 100 and 130 °C, which is due to the evaporation of benzene from the clathrate. DSC analysis run with the same sample showed an endothermic transition at 100 °C followed by an exothermic peak at 105 °C and sharp melting at 316 °C. The transitions at 100 and 105 °C correspond to desolvation followed by a reconstructive solid-to-solid-phase transition. Clathrate single crystals left at ambient temperature, and pressure lost benzene and turned opaque within 2 to 3 days.

2.4. X-ray Structure of the Desolvated Crystals. Desolvated single crystals obtained by slow evaporation from CH_2Cl_2 were shown to be spectroscopically (FT-IR and NMR) and thermally (DSC) identical to those obtained upon loss of benzene from the clathrate (vide infra). Diffraction data and structure refinement parameters for the solvent-free crystals obtained at 100 K are listed in Table 1. The structure was solved in a triclinic $P\bar{1}$ space group with one-half of a molecule per asymmetric unit due to coincident molecular and crystallographic inversion centers.

The molecular structure of rotor **3** in the desolvated crystal is similar to that observed in the benzene clathrate (Figure 6). The trityl groups adopt enantiomeric propeller conformations related by the molecular center of inversion. The diethynyl benzene fragment has a greater deviation from linearity than that in the benzene clathrate. It can be appreciated from the structure in Figure 6 that all four alkyne and the two phenylene ipso carbons lie outside an imaginary straight line subtending the two methane carbons (C6 and C6A) and passing through the center of the phenylene ring.

To compare changes in packing structure with and without solvent, the structure of the benzene clathrate was also determined at 100 K (Table 1). It is worth noting that there are

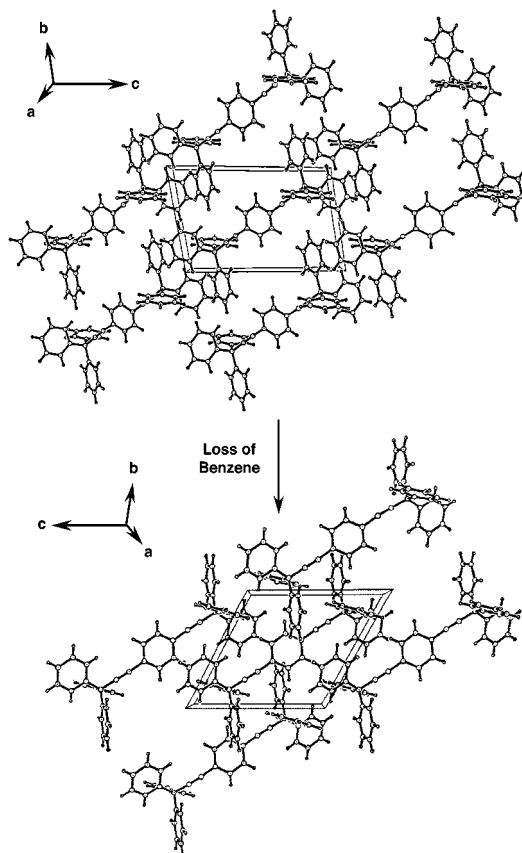


Figure 7. Packing diagrams of compound **3** in the clathrate (top, with benzene molecules removed for clarity) and desolvated structures (bottom).

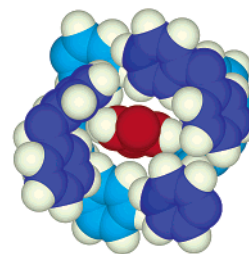


Figure 8. Space-filling view of the local environment of the phenylene group (red) in desolvated crystals of **3** illustrating the “cage” formed by 10 phenyl groups from three trityl groups above (dark blue) and three below (light blue).

no significant modifications in the clathrate upon cooling from 293 to 100 K. Structures with and without solvent had different unit cell dimensions but very similar packing topologies (Figure 7) as expected for a first-order solid-to-solid-phase transition. Small changes in unit cell angles and a modest expansion in the *a*- and *b*-directions (7.4 and 8.0%, respectively) are accompanied by a large 27.4% contraction along the *c*-axis. As suggested in Figure 7, the loss of benzene from the clathrate to the solvent-free crystal lattice is facilitated by a relatively small molecular displacement. Although removal of benzene from the clathrate to the solvent-free structure decreases the volume of the unit cell by 23.2%, the change in density is only 3.6% (at 100 K). The local environment around phenylene groups in the desolvated form is illustrated in Figure 8. Close interdigitation of adjacent molecules results in the formation of a supramolecular “cage” constituted by 10 phenyl groups from six neighboring trityl groups.

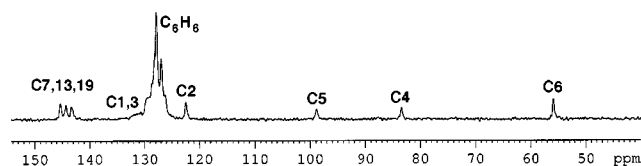


Figure 9. ^{13}C CPMAS NMR spectrum of the benzene clathrate of molecular rotor **3**. For signal labels, please see Figure 3.

2.5. Solid-State ^{13}C CPMAS NMR Chemical Shift Assignments in the Benzene Clathrate. Solution-like spectra can be measured with solid samples by taking advantage of the cross polarization and magic angle spinning technique developed by Pines and co-workers.^{12,13} The cross polarization (CP) method relies on the transfer of magnetization from the highly abundant and sensitive hydrogen atoms to the less sensitive and highly diluted ^{13}C nuclei. The experiment includes simultaneous high power ^1H -decoupling and fast sample spinning (5–20 kHz) at the magic angle (54.7°) to remove the line broadening that comes from static anisotropic interactions mediated by the external magnetic field such as heteronuclear dipolar coupling and chemical shift anisotropy. Although resolution in the solid state is not as high as that observed in solution, chemical shifts determined by the CPMAS method are generally comparable.

The ^{13}C CPMAS NMR spectrum of the benzene clathrate is shown in Figure 9. Signals were labeled in the same manner as those in the ORTEP diagram shown in Figure 3. Specific assignments were confirmed by interrupted decoupling experiments and by taking advantage of partial isotopic labeling. It is well known that interrupted decoupling after cross polarization, and prior to acquisition, results in the loss of signals corresponding to strongly coupled protonated carbons.¹⁴ Signals corresponding to methane (C6), alkyne (C4 and C5), and aromatic ipso carbons (C7, C13, and C19) were partially assigned in this manner. Aromatic signals corresponding to phenylene rotor, benzene of crystallization, and the protonated carbons of the trityl groups were assigned with the help of deuterium labeling experiments as described previously.⁴ The number of signals in the solid-state spectrum is in good agreement with expectations from the symmetry present in the crystal lattice. Single peaks at 55, 83, and 99 ppm correspond to the methane (C6) and alkyne carbons (C4 and C5) of the two crystallographically equivalent molecular halves. Three signals between 142 and 147 ppm correspond to the ipso carbons in each of the three phenyl groups of the two equivalent triphenyl methanes (C7, C13, and C19). Although these signals are equivalent in solution with an average chemical shift of 145.2 ppm in CDCl_3 , they have different magnetic environments in the solid state. A signal at 122 ppm corresponds to the equivalent ipso carbons of the central phenylene (C2 and C2A), and a broad signal at 131 ppm was assigned to the four protonated carbons (C1, C1A, C3, and C3A). We noticed that the width and intensity of the signal at 131 ppm could change slightly from

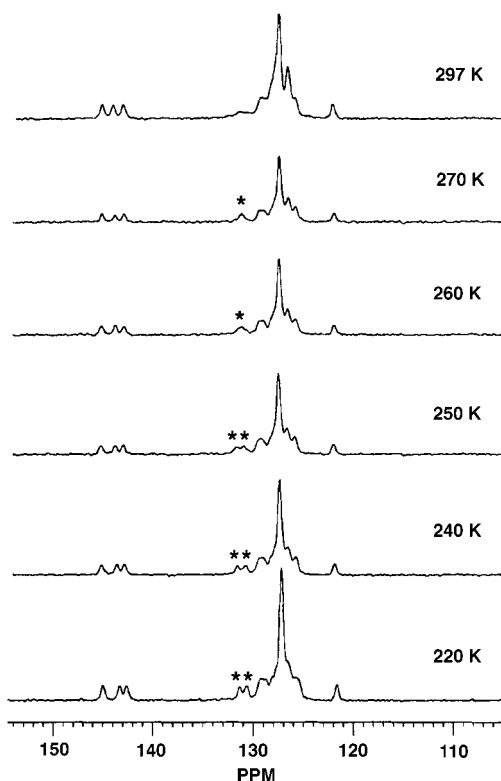


Figure 10. Variable-temperature ^{13}C CPMAS NMR of the benzene clathrate of **3**. The signals corresponding to C1 and C3 are indicated with a star.

experiment to experiment. Knowing that carbon atoms C1 and C3 are crystallographically and magnetically nonequivalent, we recognized that variations in the width and intensity of this signal may reflect dynamic processes related to rotation about the phenylene 1,4-axis.

2.6. Variable-Temperature ^{13}C CPMAS Measurements in the Benzene Clathrate of 3. The results from experiments carried out between 220 and 297 K are shown in Figure 10. As expected, the most important changes in this temperature range occur to the signal assigned to C1 and C3 at 131 ppm. At 297 K, the signal appears weak and broad, suggesting that coalescence of two signals corresponding to each of the two carbons may occur near ambient temperature. However, an increase in intensity and eventual split into two well-resolved singlets at 131.6 and 130.8 ppm was observed as the temperature was lowered to 250 K. With a splitting of 60 Hz between C1 and C3, and a coalescence temperature of ca. 255 K, a time constant for rotation of 7.7 ms (rate of 130 s^{-1}) and an approximate barrier of 12.8 kcal/mol were calculated.

2.7. Variable-Temperature ^2H Quadrupolar Echo Measurements with the Benzene Clathrate of 3. Deuterium NMR in the solid state is largely dominated by the interaction between the nuclear spin and electric quadrupole moment at the nucleus.¹⁵ The orientation-dependence of the quadrupolar coupling characterizes the spectra and makes it one of the most sensitive probes for dynamics in crystalline solids and other rigid media. The spectrum of a single crystal with only one type of $\text{C}-^2\text{H}$ bond would consist of a doublet with a quadrupolar splitting $\Delta\nu$ that depends on the orientation angle β that the bond makes with respect to the external field.^{15,16}

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$$\Delta\nu = \frac{3}{4}(e^2q_{zz}Q/h)(3\cos^2\beta - 1) = \frac{3}{4}QCC(3\cos^2\beta - 1)$$

Q in the equation represents the electric quadrupole moment of the deuteron, e and h are the electric charge and Planck constant, respectively, and q_{zz} is the magnitude of the principal component of electric field gradient tensor, which lies along the C– 2 H bond. The splitting frequency for aromatic C– 2 H bonds, with $QCC = 180$ kHz, changes from 270 kHz when $\beta = 0^\circ$ and 135 kHz for $\beta = 90^\circ$, to 0 kHz when the C– 2 H bond is oriented at the magic angle, that is, $\beta = 54.7^\circ$. Although powdered samples have molecules with all values of β represented, they are not all equally populated. A collection of doublets in all possible orientations gives rise to a broad symmetric spectrum with two maxima and two shoulders known as a Pake or powder pattern. Variations in the powder pattern of a solid sample occur when the C– 2 H bonds experience reorientations that reduce the range of their magnetic interactions by dynamic averaging. The dynamic range covered by line shape analysis techniques is commensurate with the magnitude of the QCC (~ 180 kHz) and goes from ca. 10^4 to 10^8 s $^{-1}$.

For our study, we take advantage of very well-characterized spectral changes occurring upon 2-fold phenyl flipping and free phenyl rotation about its 1,4-axis,¹⁷ as well as in-plane rotation of benzene molecules.¹⁸ Measurements were carried out with a quadrupolar echo sequence on static powdered samples. Spectra were obtained at 46.07 MHz with 90° pulse width of 2.2 μ s, echo and refocusing delays of 30 and 20 μ s, respectively, and a 60 s delay between pulses (20 s for **3**/C₆D₆). Phenylene dynamics were explored with crystals of **3-d₄** grown from C₆H₆. Spectra were acquired in the range between 146 and 324 K to examine benzene dynamics in the C₆D₆ clathrate. It was not possible to decrease the temperature below 146 K due to the probe limitations. Spectra measured with either of the two labeled samples between 200 and 300 K showed no spectral changes. In agreement with the VT ¹³C CPMAS measurements, spectra from the phenylene group correspond to the slow exchange, or static limit (Figure 11, $k_{\text{rot}} < 10^4$ s $^{-1}$). The spectra corresponding to benzene rotation are consistent with discrete jumps rather than continuous rotation. The jump rate, even at 200 K, occurred in the fast exchange limit ($k_{\text{rot}} > 10^7$ s $^{-1}$). Although simulations involving 60° and 120° jumps are indistinguishable from each other, previous ²H NMR^{18b} and neutron scattering¹⁹ studies with crystalline benzene and a benzene clathrate with cyclohexen-1,3-dione^{18a} have shown that nearest neighbor 60° jumps (6-fold rotation) are the most likely. These studies have shown 2-fold flip in the fast exchange limit above 140 K in the case of crystalline C₆D₆ and above 290 K in the case of the cyclohexen-1,3-dione clathrate.^{18a}

2.8. Desolvation Analysis by Solid-State NMR. Knowing that the density of the desolvated molecular rotor was analogous

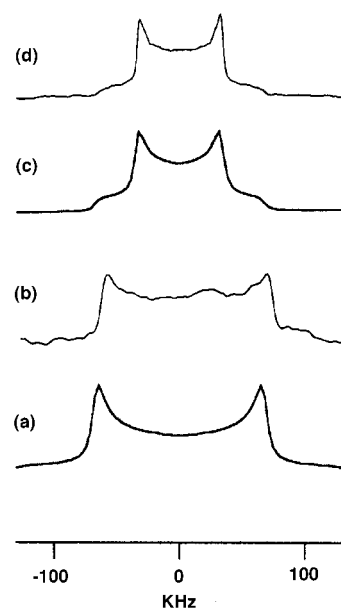


Figure 11. Calculated (a, c) and experimental (b, d) quadrupolar echo ²H NMR spectra of **3-d₄** in C₆H₆ and **3** in C₆D₆ at 298 K. The spectra of **3-d₄**/C₆H₆ (a and b) correspond to motion of the phenylene group in the slow exchange regime ($k_{\text{rot}} = 6 \times 10^3$). The simulated spectra for samples of **3** containing C₆D₆ (c and d) correspond to in-plane rotation of C₆D₆ about its 6-fold axis in the fast exchange limit ($k_{\text{rot}} = 10^8$ s $^{-1}$).

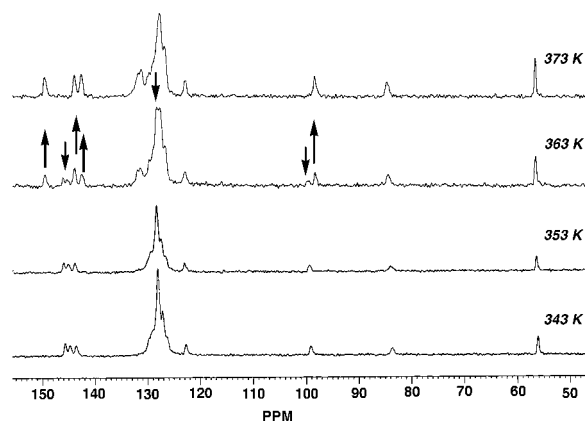


Figure 12. ¹³C CPMAS NMR spectra of benzene-grown crystal of **3** illustrating the growth of the desolvated phase by 363 K.

to that of the benzene clathrate, it seemed possible that phenylene rotation in solvent-free crystals may occur within the range covered by the ²H line shape analysis method. To explore that, we decided to investigate the desolvation process by ¹³C NMR and then to carry out a detailed ²H NMR analysis in the desolvated samples. Desolvation analysis of the benzene clathrate by ¹³C CPMAS was carried out with freshly grown crystals of **3**. The temperature was increased by 5° increments from 294 to 373 K. Representative spectra are illustrated in Figure 12.

In full agreement with the TGA and DSC experiments, a first-order reconstructive phase transition can be observed as the signals corresponding to the clathrate disappear and the signals of the desolvated crystals grow-in sharply at 363 K (90° C). The evolution of the sample at that temperature is highlighted in the figure by upward arrows corresponding to the new phase and downward arrows that correspond to the disappearing benzene clathrate. The ¹³C CPMAS spectrum of the desolvated sample obtained in situ in Figure 12 (top spectrum) was identical

(16) This equation assumes negligible asymmetry in the electric field gradient tensor: $\eta = (q_{xx} - q_{yy})/q_{zz} = 0$. Deviations from this condition are generally small for aromatic deuterons.

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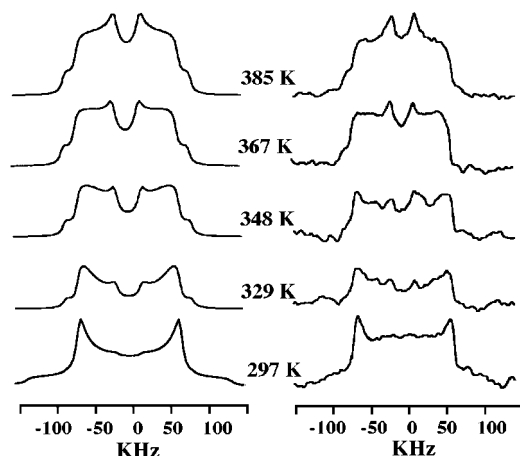


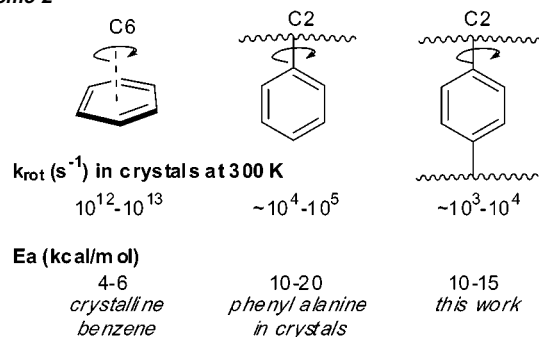
Figure 13. Experimental (right) and simulated (left) solid-state ^2H NMR of desolvated samples of **3-d₄**. The rotation rate constants used for fitting, from bottom to top, are ($\times 10^6 \text{ s}^{-1}$) as follows: 0.015, 0.4, 1.3, 2.2, and 3.8.

to spectra acquired with desolvated crystals grown from CH_2Cl_2 (not shown).

The spectrum of the desolvated phase was partially assigned by analogy with the spectrum of the clathrate as well as by dipolar dephasing¹⁴ and variable-temperature experiments. It is primarily characterized by a larger chemical shift dispersion of signals corresponding to the trityl group. While a group of 15 protonated trityl carbons in the clathrate occur between 126 and 129 ppm, they cover an expanded range between 126 and 132 ppm in the solvent-free phase. Two trityl signals at 131 and 132 ppm overlap with a signal from the phenylene rotor. The three nonequivalent ipso carbons in the clathrate at 144, 145, and 146 ppm separate from each other to resonate at 141, 143, and 150 ppm. Although the spectrum of desolvated samples is not affected by heating to 378 K, sample cooling suggests that phenylene rotation occurs in an analogous fashion to that observed in the clathrate. This conclusion is primarily supported by measurements carried out below 230 K, which revealed the emergence of two phenylene signals at 130 and 132.5 ppm ($\Delta\nu \approx 187.5 \text{ Hz}$). Although limited resolution prevented us from establishing a precise coalescence temperature, it appears that phenylene rotation at ambient temperature in the solvent-free phase also occurs in the kilohertz frequency range.

2.9. Phenylene Rotational Dynamics in the Desolvated Sample by VT ^2H Quadrupolar Echo Measurements. Ambient temperature phenylene rotation in the millisecond time scale was confirmed by VT ^2H quadrupolar echo measurements. Measurements carried out with the desolvated sample between 297 and 385 K showed spectral changes consistent with a dynamic process described by rotation of the phenylene group about the 1,4-axis (Figure 13). As in previous experiments, spectra were obtained with a 90° pulse width of $2.0 \mu\text{s}$, echo and refocusing delays of 30 and $20 \mu\text{s}$, respectively. The delay between pulses was chosen at 60 s. As illustrated in Figure 13, spectra were suitably simulated with a model that assumes a $\text{QCC} = 180 \text{ kHz}$ and an anisotropy parameter of $\eta = 0$. A 2-fold flipping motion with rotation rates ranging between ca. 1.5×10^4 at 297 K and $3.8 \times 10^6 \text{ s}^{-1}$ at 385 K was suggested by the fitting results (Figure 13, right). An Arrhenius plot built with the rate of calculated rotation yielded an activation energy of 14.6 kcal/mol, which is only $\sim 2 \text{ kcal/mol}$ higher than that estimated in the benzene clathrate.

Scheme 2



2.10. Benzene, Phenyl, and Phenylene Rotation in the Solid State.

It is clear from our study that the rates of rotation of the phenylene group and benzene molecules in the clathrate structure of **3** are not correlated in a simple manner. The rate of the 6-fold rotation for benzene molecules in the dimer falls in the fast exchange regime of the ^2H line shape analysis methods ($k_{\text{rot}} = 10^8 \text{ s}^{-1}$) under the conditions where the clathrate is thermally stable (ca. 200–300 K). Although there are only a few examples, it is known that benzene molecules in crystals reorient about their 6-fold axis with very low activation barriers and with very high preexponential factors.^{18,19} The rates of degenerate 6-fold rotation in the solid state¹⁹ are affected in a relatively modest manner as compared to the rates of isotropic rotation observed in liquids. The rotational correlation time $2\tau_c$ of benzene molecules in liquid benzene at 298 K is $1.28 \times 10^{-12} \text{ s}$.²⁰ The estimated rate of free rotation, determined by the principal moment of inertia along the 6-fold axis at the same temperature, is $1.7 \times 10^{12} \text{ s}^{-1}$.²¹ The activation energy for 6-fold rotation of benzene in benzene crystals is only 3.95 kcal/mol, and the suggested preexponential factor is $2 \times 10^{13} \text{ s}^{-1}$.^{19b} The enclathration of benzene with 1,3-cyclohexanedione, in a structure that contains six aromatic $\text{C-H}\cdots\text{O}=\text{C}$ hydrogen bonds, gives rise to a slightly higher activation energy of 6 kcal/mol and a preexponential factor of $8 \times 10^{13} \text{ s}^{-1}$.^{19a} Rates of benzene rotation in these solids fall in the 10^{13} s^{-1} range at ambient temperature. A graphical summary of benzene, phenyl, and phenylene rotational dynamics, with order of magnitude rates in known crystals at ambient temperatures, is shown in Scheme 2.

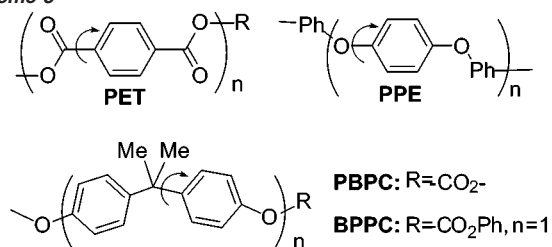
While the small 60° jump angle and the highly symmetric environment of benzene give rise to very large rates of in-plane rotation, introduction of a single point of attachment slows down the dynamics of phenyl groups in a dramatic manner. As expected from space-filling environments and local symmetry of the phenyl group, literature studies report a degenerate 2-fold flipping process as the dominant mechanism. The 2-fold rotation of phenyl groups studied by ^2H NMR in crystals of phenylalanine and phenylalanine-containing peptides^{17,22} has shown that phenyl flips tend to occur in the 10^4 – 10^5 s^{-1} range near ambient temperatures. The reported activation energies range from 10 to 20 kcal/mol (Scheme 2). In a recent study of

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Scheme 3



crystalline penicillin V dynamics by X-ray and ^{13}C CPMAS NMR, Wendeler and co-workers documented the rate of phenyl flipping in various crystalline salts.²³ Crystals of the free acid, H^+ , and with Li^+ , Na^+ , Rb^+ , and Cs^+ were shown to influence the rate of phenyl rotation over 8 orders of magnitude at ambient temperature. The rates of rotation for the Li^+ salt were the slowest ($\sim 0.1 \text{ s}^{-1}$ at 300 K), and the rates in the Rb^+ salt were the fastest ($5 \times 10^8 \text{ s}^{-1}$). Differences in activation energy for phenyl flip in these crystals ranged by a factor of 2, between 12.3 and 26.5 kcal/mol. Interestingly, differences in flipping rates in these cases arise primarily from differences in the calculated preexponential factors which varied by as much as 5 orders of magnitude (ca. 10^{14} – 10^{18} s^{-1}).²⁴ In another example of phenyl flipping in crystals reported by Casarini and co-workers, rates of rotation of 3.5×10^2 and $1.2 \times 10^3 \text{ s}^{-1}$ were calculated at ambient temperature for the two formally enantiotopic phenyl groups of diphenyl sulfoxide.²⁵

If a single point of attachment reduces the rates of rotation of phenyl groups in crystals, one may expect that the linkage of a benzene ring along its 1,4-axis may restrict its rotational dynamics even further. However, coalescence analysis by ^{13}C CPMAS NMR in the case of **3** revealed rates of rotation of ca. 10^3 s^{-1} at ambient temperature, and an activation energy of only 12.8 kcal/mol was deduced. Although this analysis is of limited precision, it is remarkable that rotation of the phenylene group in desolvated samples, determined by deuterium line shape analyses over a wider temperature range (Figure 13), has a remarkably similar activation energy of only 14.6 kcal/mol.

Despite limitations in our data, a review of the literature reveals that the phenylene group in compound **3** performs as an excellent molecular rotor. There are fewer examples of phenylene rotation in solids reported, and most of them relate to phenylene-containing polymers. A few examples of phenylene rotation in crystalline samples reveal a very slow process. In one case, measurements carried out with drawn crystalline fibers of poly(ethyleneterephthalate) (PET, $\text{R} = \text{CH}_2\text{-CH}_2\text{-}$, Scheme 3) measured by ^{13}C exchange NMR give 2-fold flipping rate constants of 1.5 s^{-1} at 293 K.²⁶ Phenylene flip in crystals of 1,4-diphenoxy benzene, a model for poly(phenyl-*O*-(phenylene)) (PPE), was shown to occur at a rate of 1.3 s^{-1} at 300 K.²⁷ Similarly, studies with crystalline bisphenol phenyl carbonate (BPPC, $\text{R} = \text{-CO}_2\text{Ph}$), a model for poly(bisphenyl carbonate) (PBPC), revealed two crystalline forms, one with “immobile”²⁸

phenylene rings and one with “facile” flipping motion.²⁹ The “mobile” polymorph was shown to belong to the space group C_2 with two independent half molecules per asymmetric unit. As expected from its crystal symmetry, two dynamic environments were indeed observed. The most mobile phenylene was shown to undergo flipping motions at a rate of $5 \times 10^6 \text{ s}^{-1}$ at 305 K. Phenylene motion in the static polymorph was slower than 10^2 s^{-1} , as suggested by the ^2H NMR data.

In the case of more complex polymeric samples, rotational rate constants and activation energies reflect the structural and dynamic heterogeneity of each material. Despite a range of dynamics properties, a 2-fold flipping model has been proven suitable in most cases. Deuterium line shape analyses with poly-(butylene terephthalate) (PBT) at 70 °C revealed a crystalline phase with very slow motion ($k_{\text{rot}} < 10^2 \text{ s}^{-1}$), an amorphous phase with fast flips at a rate of $k_{\text{rot}} \approx 5.5 \times 10^5 \text{ s}^{-1}$, and a slower interphase with flipping rates of $k_{\text{rot}} \approx 1.2 \times 10^5 \text{ s}^{-1}$. An activation energy of only 5.9 kcal/mol calculated for rotation in the amorphous region suggests a fluidlike environment. Dynamic studies with phenyl deuterated PET were interpreted in terms of distributions of rate constants and narrow distribution of flip angles giving rotational rate constants of $< 10^3 \text{ s}^{-1}$ at ambient temperature.³⁰ Rates of phenylene flip in the case of bisphenol-containing polymers have also been measured in the 10^4 – 10^6 s^{-1} range in the amorphous regions.³¹ Activation energies measured in the amorphous phase of various polymers range between 6 and 20 kcal/mol.

3. Conclusions

An ideal crystalline geared lattice would be characterized by the concerted rotation of individual molecular rotors, such that they can influence each other over long distances by mechanisms that transfer angular momentum from one to another in a structurally predetermined manner. Extended correlated motions in crystals would require precise rotational symmetry with clockwise and anticlockwise rotors acting on each other without interference. Parity rules that determine the motion of molecular gears in a chain have been analyzed by Mislou,³² and the transfer of angular momentum at the molecular level in molecular gear trains of triptycyl ethers has been analyzed in solution by Iwamura and co-workers.³³ An ideal crystalline geared lattice would “operate” under thermal equilibrium by exchanging energy between molecular modes and extended phonons. Unless activation energies and preexponential factors are identical for different rotors, geared lattices would only operate under a limited temperature range when their rotational motions become isochronous or commensurate. Regarding the benzene clathrate of compound **3**, it is clear that in-plane rotation of the benzene molecules and 2-fold phenylene flipping occur with very different rates and very different activation energies. While a lower limit of $k_{\text{rot}} > 10^8 \text{ s}^{-1}$ was deduced for in-plane

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benzene rotation (even at 200 K), rates of $k_{\text{rot}} > 10^{12} \text{ s}^{-1}$ at ambient temperatures are likely. In contrast, phenylene rotation by a 2-fold flipping mechanism at ambient temperature falls in the range of $10^3\text{--}10^4 \text{ s}^{-1}$ with activation energies of 12–15 kcal/mol. Although the 2-fold phenylene flip in compound **3** is much slower than the rate of benzene rotation, it is much faster than phenylene flips reported in most literature examples. We speculate that crystalline geared lattices will require systems with molecular rotors that experience steric contacts that constitute each other's main rotational barriers. Geared rotors should also have matching cogs and rotational periods. Intrigued by the benzene clathrate formed by compound **3**, we are now exploring the preparation of analogous clathrates with substituted benzenes and molecular rotors with substituted phenylenes. We believe that there is much to be learned in the construction and analysis of crystalline solids with structurally programmed motions. We also expect that phenylene flipping in molecular rotors with intramolecular steric shielding, such as compound

2 (Figure 1), will increase the rate of phenylene rotation and will help us achieve the preparation of fast molecular compasses and molecular gyroscopes.

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Supporting Information Available: Experimental details on the synthesis of compounds **3**, **4**, and **7**, ^1H and ^{13}C NMR spectra of compounds **3** and **4**, 2-D HMBC analysis of **4**, details of the variable-temperature solid-state ^{13}C CPMAS and ^2H NMR acquisition (PDF). Crystallographic information files (CIF) of compound **3** grown from benzene and from methylene chloride. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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