Symmetry and dynamics of molecular rotors in amphidynamic molecular crystals

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Rotary biomolecular machines rely on highly symmetric supramolecular structures with rotating units that operate within a densely packed frame of reference, stator, embedded within relatively rigid membranes. The most notable examples are the enzyme FoF1 ATP synthase and the bacterial flagellum, which undergo rotation in steps determined by the symmetries of their rotators and rotating units. Speculating that a precise control of rotational dynamics in rigid environments will be essential for the development of artificial molecular machines, we analyzed the relation between rotational symmetry order and equilibrium rotational dynamics in a set of crystalline molecular gyroscopes with rotators having axial symmetry that ranges from two- to fivefold. The site exchange frequency for these molecules in their closely related crystals at ambient temperature varies by several orders of magnitude, up to $\text{ca. } 4.46 \times 10^8 \text{ s}^{-1}$.

solid-state NMR | line shape analysis | spin-lattice relaxation | molecular design | crystal engineering

Biomolecular machines are remarkably complex and sophisticated supramolecular systems that have evolved over a few billion years to carry out all the functions of living organisms within the viscous environments of cell membranes and cell compartments (1). By comparison, the development of artificial molecular machines over the last few decades has evolved from the design of molecules that emulate the structure and motion of macroscopic objects (2, 3), to elegant examples of photo- (4) and electroactive rotary molecular motors (5), chemoactive linear motors (6) and actuators (7), among many others (8, 9). Although there is much important knowledge to be gathered from the syntheses and dynamics of molecules in solution, lessons from biological systems and potential materials applications have led to subsequent efforts toward the design and characterization of artificial molecular rotors linked to surfaces (10–12) and in the bulk of crystalline solids (13, 14).

In order to engineer molecular rotors capable of functioning in the crystalline state, one must consider that molecules tend to pack so tightly (15) that large amplitude motions are generally forbidden. However, a promising approach to circumvent the consequences of close packing is to use a strategy that decouples the structurally rigid elements responsible for the architecture of the crystal lattice from those engineered to experience the desired motion (14). Recently, this has been accomplished in a systematic manner with a series of 1,4-bis(triarylpropynyl)benzene and related structures, which emulate some aspects of the structure and function of macroscopic gyroscopes (Fig. 1). Dynamic analyses by variable temperature (VT) nuclear magnetic resonance confirmed that structures with increasingly bulky stators experience thermally activated Brownian rotation in the form of 180-degree jumps with exchange frequencies as high as $\text{ca. } 10^9 \text{ s}^{-1}$ at 300 K (16, 17). The term “amphidynamic crystals” was proposed to convey the coexistence of mobile and rigid components within an ordered solid (14).

Knowing that packing interactions are the result of short-range dispersion forces, one may expect that the shape of the rotator in close-packed crystals will be matched by the van der Waals

Fig. 1. (A) Representation of a set of gyroscopes suggesting internal rotation, even in a close-packed crystal. (B) Molecular analogs with a 1,4-phenylenes as rotators, linked by acetylenes to bulky triphenylmethyl groups acting as a stator. (C) A molecular rotor with two phenylenes and a central diamantane rotator.

surface formed by close neighbors. With that in mind, one can recognize that flat phenylenes with a C_2 axial symmetry and a rectangular cross-section should be less than ideal rotators. As illustrated in Fig. 2, a set of periodic rotary potentials suggests that rotators with a given rotational symmetry order (C_n) will have energy profiles with “ n ” minima and maxima, angular displacements of $360/n^\circ$, and barriers that become smaller as the rotator approaches the shape of a cylinder when $n \rightarrow \infty$. As the number of energy minima n increases, there is a greater spatial resolution that may be addressed with external stimuli when a suitable dipole is included in the structure (18, 19). Increasing the symmetry of the rotators is also interesting because it allows the formation of gears with n teeth when the vertices of the rotator are extended in a radial manner. Very-high-order rotational symmetries are observed in natural systems such as the bacterial flagellum, with $n = 24$ –26 and $n = 34$ –36 in the motor MS and C rings, and a helical structure with 11 units per turn in the flagellar filament (20).

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Fig. 2. (A) Cross-sections of hypothetical rotators with axial symmetry order C_n represented with a heavy line with the enclosure formed by their close neighbors in close-packed crystals with a dotted line. The top row represents the rotators and their environment in their minima and the bottom row in their transition states. (B) Idealized potential energy surfaces [$E(\theta) = 1/2E_0(1 - \cos n\theta)$] for rotators with axial symmetry order C_2 , C_3 , C_6 , and C_∞ illustrating an increasing number of energy minima and a decrease in the height of the energy barriers as the transition state is more efficiently circumscribed within its close-packing enclosure.

An indication of the effects of symmetry on rotational dynamics in crystalline solids was first observed with a molecular rotor with two flat phenylenes (C_2) linked to a more cylindrical diamantane (C_3) rotor (Fig. 1C). The dynamics of the two rotators were determined by VT solid-state NMR (21). Line shape analysis of VT ^{13}C NMR spectra obtained under cross-polarization and magic angle spinning (CP-MAS) showed that the two symmetrically related phenylenes overcome barriers of 13.7 kcal/mol to jump between positions related by 180° with an average frequency of *ca.* 50 s^{-1} at 300 K. The activation energy for the more cylindrical diamantane with a threefold (C_3) rotational symmetry, determined by VT ^1H spin-lattice relaxation was only 4.1 kcal/mol, with a rotational frequency of *ca.* 10^6 s^{-1} for 120° jumps at 300 K (21). Encouraged by this report, we describe here the results of a study on the effects of rotational symmetry on solid-state dynamics in a homologous series of molecular gyroscopes.

The structures selected for this work have a common bis(tri-phenylsilyl) stator (shown in blue in Fig. 3A) and diethynyl axle

and four different rotators (shown in red in the same figure). The rotators with their corresponding axial symmetries (in parentheses) are a 1,4-phenylene (C_2), a 1,4-bicyclo[2.2.2]octane (C_3), a diagonally substituted 1,6-cubane (C_3), and a 1,12-closocarboranediyl (C_5). We report here the synthesis, X-ray structures, and rotational dynamics of the corresponding molecular gyroscopes 1–4. As expected from their analogous molecular structures, the packing motifs of all four crystals are closely related to each other and are largely determined by aromatic interactions between neighboring trityl groups that form a chain of sixfold phenyl embraces (22) (Fig. 3B). In agreement with the close-packing principle, a cross-section of the packing structure around each rotator reveals a boundary with shape and symmetry that closely match those of the rotator (Fig. 3C). Although an excellent correlation between rotational symmetry order and activation parameters exists for compounds 1, 2, and 4, the cubanediyl derivative 3 was found to have a significantly higher activation energy that arises from specific contacts between the rotator and the phenyl groups of two neighboring stators.

Results

Synthesis, Crystallization, and X-Ray Analysis. The synthesis of compounds 1–4 was accomplished by a standard protocol based on the synthesis of axially substituted diacetylene derivatives of the phenylene, bicyclo[2.2.2]octane, cubyl, and carborane rotary units. The corresponding diacetylides were subsequently reacted with two equivalents of triphenylsilyl chloride to yield the desired structures. The synthesis and spectroscopic characterization of compounds 1–4 are described in detail in *SI Appendix*. The crystallization of compounds 1–4 was achieved by slow solvent evaporation of dichloromethane (1, 3, and 4) or acetone (2), and the resulting single crystals were shown to be solvent-free. Crystal structures of molecular rotors 1, 2, and 4 were solved in the triclinic space group P_1 and the cubanediyl structure 3 in the monoclinic space group $P2_1/c$. Whereas compounds 1, 2, and 3 display coincident crystallographic and molecular inversion centers, the carborane-containing rotor 4 is not symmetric, with one of its trityl-acetylene groups bent away from the molecular long axis. The structure of the bicyclo[2.2.2]octane (BCO) rotor is not compatible with an inversion center, so that the crystal symmetry can be satisfied only by a local disorder where BCO adopts with equal probability two positions related by a 60-degree rotation. This disorder transforms the point group of the BCO from a local D_{3h} into an average D_{6h} and the rotational axis from C_3 to C_6 . In spite of differences in unit cell dimensions and molecular and crystal symmetries, all four molecular rotors pack in a relatively similar manner (Fig. 3B). Their crystal structures consist of long chains of molecules aligned in a head-to-tail manner by

Fig. 3. (A) Structures of molecular gyroscopes 1—1,4-phenylene rotor, 2—1,4-bicyclo[2.2.2] octanediyl rotor, 3—1,4-cubane rotor, and 4—1,12-carboranediyl rotor. (B) Schematic representation of the packing structures of molecular gyroscopes 1–4 indicating the structural parameters that differ among them. (C) Cross-sections of the local environment around the molecular rotors 1–4 showing how the local environment follows the shape of the rotator.

complementary aromatic edge-to-face interactions (SiPh₃---Ph₃Si) characteristic of a phenyl embrace (22). The primary differences between the four structures arise from the number of geometrically different next neighbors (I, II, etc.), their rotators' centroid-to-centroid distances (m_1), the distances between molecules in neighboring chains (d_1), and the displacement distances along the chain direction between molecules in neighboring chains (d_2). For a detailed analysis of these parameters, see *SI Appendix*.

The rotational dynamics of compounds **1–4** were studied by solid-state NMR techniques using well-characterized polycrystalline samples. The choice of NMR method was determined by the kinetic window needed to characterize the dynamics of the central rotator in the temperature range of 180 K and 320 K. Expecting a relatively high barrier for the characteristic 180-degree rotation of the 1,4-phenylene of molecular gyroscope **1**, we acquired quadrupolar echo ²H NMR measurements as a function of temperature. This method is ideally suited to determine rotational exchange processes in the frequency range of 10⁴–10⁷ s^{−1}.

Dynamics of Phenylene Rotor 1 by VT ²H NMR. Wide-line ²H NMR spectra acquired at 46.073 MHz between 207 K and 321 K with a deuterated phenylene rotor **1** are illustrated in Fig. 4A. The method relies on the analysis of spectral changes that occur when the C–²H bonds experience reorientations that reduce their magnetic interactions in the range of *ca.* 10⁴–10⁸ s^{−1} (23). The experimental spectra were simulated with a model that considers site exchange of the ²H nuclei by 180-degree flips where the only adjustable variable is the rotational exchange rate, k_r (24). The experimental data in Fig. 4 were matched with simulated spectra with k_r values ranging from <10³ s^{−1} at 207 K to 2.0 × 10⁷ s^{−1} at 321 K. An Arrhenius plot, $k_r = k_0 \exp(-E_a/RT)$, of the rotational exchange frequency as a function of inverse temperature in Fig. 4B gives a linear fit with an activation energy $E_a = 8.5 \pm 2.5$ kcal/mol and a preexponential frequency factor $k_0 = 1.1 \times 10^{13}$ s^{−1}.

Dynamic Analysis of Bicyclo[2.2.2]Octane, Cubyl, and Carborane Rotors 2, 3, and 4 by VT ¹H Spin-Lattice Relaxation. Based on their higher rotational symmetry order and their packing structures, we expected molecular gyroscopes **2, 3, and 4** to have rotational frequencies greater than 10⁶ s^{−1} at ambient temperature. Given the challenge of preparing deuterated samples of these compounds, their motion was explored by ¹H NMR spin-lattice relaxation (T_1) at 300 MHz. Spin-lattice relaxation can be used to probe dynamic processes occurring at frequencies near the Larmor frequency of the nucleus being studied, i.e., ¹H at 300 MHz in our experiments. Spin-lattice relaxation is particularly useful when the stimulated nuclear transitions responsible for restoring

thermal equilibrium are dominated by the modulation of dipolar interactions caused by the rapid motion of internal rotors (25). If this process has a characteristic correlation time τ_c that follows Arrhenius kinetics, its activation energy E_a and preexponential factor τ_0^{-1} (k_0) (Eq. 1) are determined by fitting the measured T_1 values as a function of temperature to the Kubo–Tomita relaxation expression (Eq. 2), where C is a constant that depends on the number of H atoms, and ω_o is the spectrometer frequency (26).

$$\tau_c^{-1} = \tau_0^{-1} \exp(E_a/RT), \quad [1]$$

$$T_1^{-1} = C[\tau_c(1 + \omega_o^2\tau_c^2)^{-1} + 4\tau_c(1 + 4\omega_o^2\tau_c^2)^{-1}]. \quad [2]$$

¹H T_1 values were obtained by inversion recovery measurements at 300 MHz by transferring the ¹H spin magnetization to ¹³C nuclei in a set of variable time delays. Experiments between 180 and 396 K with molecular rotors **2** and **4** showed that the entire spectrum relaxes with a single T_1 value with variations that follow the expected “V-shape” dependence (Fig. 5). The maximum relaxation rate (shortest T_1) was observed at 235 K for the bicyclo[2.2.2]octane rotor **2** and at 215 K for the carborane rotor **4**. As illustrated in Fig. 5, the two datasets fit well to the Kubo–Tomita expression to give activation energies of 3.5 ± 0.2 kcal/mol and 3.0 ± 0.1 kcal/mol for compounds **2** and **4**,

Fig. 4. (A) Experimental (darker line) and simulated (lighter line) ²H NMR spectra of **1**. (B) Arrhenius plot of the exchange data in A.

Fig. 5. Experimental results (crosses) and fit to the Kubo–Tomita relaxation expression (lines) of the ¹H spin-lattice relaxation of compounds **2** (Top) and **4** (Bottom).

respectively. The preexponential values determined by the fits were $\tau_o^{-1} = 3.6 \times 10^{10} \text{ s}^{-1}$ for compound **2** and $\tau_o^{-1} = 6.4 \times 10^{10} \text{ s}^{-1}$ for compound **4**. With these parameters, the calculated rotational exchange frequencies for compounds **2** and **4** at 300 K are 1.05×10^8 and $4.46 \times 10^8 \text{ s}^{-1}$, respectively, both significantly higher than that of the phenylene group, which at the same temperature rotates at *ca.* $9.0 \times 10^6 \text{ s}^{-1}$.

As inversion recovery measurements with crystals of molecular rotor **3** showed no changes in the ^1H T_1 values, we concluded that the rotational exchange dynamics of the cubanediyl rotor were far from the $3.0 \times 10^8 \text{ s}^{-1}$ (300 MHz) regime. Knowing that high-resolution variable temperature ^{13}C CP-MAS NMR is suitable for dynamic processes with exchange frequencies k_{ex} that are comparable to the frequency difference $\Delta\nu$ in Hz between the nonequivalent signals, usually between 50 and 1,000 Hz (27), we explored the dynamics of the cubanediyl derivative with this method.

Dynamic Analysis of Cubyl Rotor **3 by VT ^{13}C CP-MAS NMR.** As suspected, the variable temperature ^{13}C CP-MAS spectra of the molecular rotor **3** carried out at 75.468 MHz (Fig. 6A) revealed a remarkably slow dynamic process with exchange frequencies in the range of 40–320 s^{-1} between 263 and 288 K. Three of the four relatively well-resolved sp^3 -carbon signals detected at 263 K around 45–50 ppm were shown to coalesce and broaden as the temperature was increased up to 288 K. The number of signals in the low-temperature spectrum is consistent with the crystallographic and molecular inversion center, which requires only three signals for the six protonated cubanediyl carbons. The higher field signal at 45 ppm, assigned to the static quaternary cubanediyl carbons, remains constant as a function of temperature. Line shape analyses of these signals at eight temperatures were carried out assuming that they correspond to positions involved in an exchange process that interconverts them by 120-degree jumps (Fig. 6A). The spectra were simulated reasonably well with exchange rates that vary between 40 and 320 s^{-1} (28). An Arrhenius plot showed a linear fit with an activation energy $E_a = 12.6 \pm 2.5 \text{ kcal/mol}$ and a preexponential factor $k_o = 9.63 \times 10^{11} \text{ s}^{-1}$ (Fig. 6B).

Discussion

The short-range, nondirectional nature of van der Waals forces suggests that a coarse mean field approximation may be applicable to molecules and molecular fragments that have no cavities and no protuberances, such that close-packing forces in molecular rotors should tend to generate surfaces that conform to the shape of the rotor. We postulated that the higher the rotational symmetry order, and the more cylindrical the shape of the rotors, the lower the barriers to rotation and the greater rotational frequencies. Indeed, the cross-sections of the crystal structures along the rotor on a plane perpendicular to the rotational axis in Fig. 3C confirm that the close-packing envelope conforms coarsely to the size, shape, and symmetry of the rotor. The cross-section of the phenylene rotator in **1** approaches a rectangle and the environment around the disordered bicyclo[2.2.2]octane rotator of **2** resembles a hexagon. As the highest axial symmetries of the cubyl rotator in **3** and the *para*-carborane rotator in **4** are rotation-inversion given by S_6 and S_3 axis, respectively, their cross-sections approach a hexagon and decagon. The activation energies obtained by solid state NMR from crystals of **1** ($8.5 \pm 2.5 \text{ kcal/mol}$), **2** ($3.5 \pm 0.2 \text{ kcal/mol}$), and **4** (3.0 ± 0.1) confirm the expected correlation between structure and dynamics. However, a large activation energy of $12.6 \pm 2.5 \text{ kcal/mol}$ in the case of the cubanediyl rotor **3** highlights the atomically coarse nature of crystal packing surfaces. To understand the origin of this unexpected high-energy barrier, we analyzed the packing structure of **3** in more detail. As illustrated in Fig. 6C and D, the shape of the rotor pocket approaches that of the cubanediyl (red), which can be represented as a pair of triangles

Fig. 6. (A) Experimental (black lines) and simulated (blue lines) ^{13}C CP-MAS spectra of the aliphatic carbons of molecular rotor **3**. (B) Arrhenius plot of the exchange data in A. (C) Closeup of a space-filling model of the cubanediyl rotor **3** viewed down the rotational axis. (D) Schematic view of the cross-section of the ground and transition states of the cubanediyl group corresponding to the space filling model in C to illustrate the steric clashing of two pairs of hydrogens in the transition state. Carbon atoms corresponding to cubanediyl groups are shown in red, hydrogen atoms in white, and other atoms in blue.

related by a 60-degree rotation followed by inversion (point group S_6). The pocket is defined by the neighboring triphenylsilyl groups of four adjacent molecules, which create a van der Waals boundary (shown in gray in Fig. 6D) that conforms coarsely to the symmetry of the rotator. As illustrated in the space filling model in Fig. 6C and in the corresponding schematic view of Fig. 6D, there are two hydrogen atoms (blue circles) from neighboring phenyl groups that intrude in the pocket, effectively blocking the motion of the central cubanediyl. As such, the transition state for rotation between adjacent energy minima has severe steric interactions between the corresponding hydrogen atoms. This specific steric interaction accounts for the slow rotation of the cubanediyl despite its high symmetry and small moment of inertia. This result suggests that barriers arising from steric interactions with neighboring atoms projecting into rotator “hollows” (15) should be important for the smaller rotators, but perhaps less significant for rotators as large as those in the bacterial flagellum, which are *ca.* 20–45 nm in diameter.

Conclusions

As expected by the shape-conforming nature of the short-range forces responsible for close-packing interactions of molecular crystals, the rotational frequencies and activation energies for a set of crystalline rotors correlate well with the symmetry of their corresponding rotational axes. An exception discovered in the case of the smallest cubyl rotator highlights the coarse nature of close-packing surfaces. One of the most remarkable results of this study is a barrier of only 2.98 kcal/mol for the *p*-carborane rotator **4**, which, despite being in a crystalline solid, is similar in

magnitude to the gas phase rotational barrier for the methyl groups of ethane to pass each other (3.0 kcal/mol). It is also worth noting that Brownian rotation with frequencies that cover up to *ca.* 10 orders of magnitude can be achieved with a relatively simple molecular design in close-packed, amphidynamic molecular crystals.

Materials and Methods

For the synthesis of compounds **1–4** and their characterization, detailed crystallographic analyses, sample preparation, acquisition parameters, and representative examples of the primary inversion recovery and the full VT-¹³C NMR data, please see [SI Appendix](#). Wide-line ²H NMR measurements of **1** were carried out at 46.073 MHz on a Bruker Avance instrument using a single channel solenoid probe with a 5-mm insert. Measurements were carried out between 207 and 321 K with temperature calibration using the ²⁰⁷Pb shift of a lead nitrate standard (29). Variable temperature ¹H spin-lattice relaxation (*T*₁) measurements for compounds **2** and **4** were made with the inversion recovery method using ¹³C CP-MAS detection. The sample

was prepared as a fine powder tightly packed into a 4-mm ZrO₂ rotor with a ZrO₂ cap, and then spun at 10 kHz for the duration of the experiment. Measurements were carried out between 180 and 396 K, with temperature calibration using the ²⁰⁷Pb shift standard. The pulse sequence started with an inversion (π) pulse on the ¹H channel (300.13 MHz) followed by a variable delay (50 μ sec–10 sec). The intensity of the remaining ¹H magnetization was determined after a $\pi/2$ pulse by cross-polarization and acquisition of the ¹³C free induction decay. Signal averaging was set to eight scans, and the recycle delay was set to the longest of the experimental variable delay times (10 s). The dynamics of cubyl rotor **3** were studied by line shape analysis of the ¹³C signals corresponding to the four unique cubyl carbons in the crystal structure. The CP-MAS ¹³C NMR spectrum (at 75.47 MHz) was acquired at nine temperatures from 263–295 K, with temperature calibration using the ²⁰⁷Pb NMR lead nitrate chemical shift standard. The spectra were acquired with a 1-ms cross-polarization time and a 30-s recycle delay, and a spinning rate of 10 kHz. Line shape simulations were performed using the program *g*-NMR (28).

1. Goodsell DS (2009) *The Machinery of Life* (Springer Science, New York), 2nd Ed.
2. Mislow K (1988) Molecular machinery in organic chemistry. *Chemtracts Org Chem* 2:151–174.
3. Kelly TR, ed. (2005) Molecular machines. *Topics in Current Chemistry* (Springer, Heidelberg), Vol 262.
4. Fletcher SP, Dumur F, Pollard MM, Feringa BL (2005) A reversible, unidirectional molecular rotary motor driven by chemical energy. *Science* 310:80–82.
5. Hawthorne MF, et al. (2004) Electrical or photocontrol of the rotary motion of a metallocarborane. *Science* 303:1849–1851.
6. Leigh DA, Wong JKY, Dehez F, Zerbetto F (2003) Unidirectional rotation in a mechanically interlocked molecular rotor. *Nature* 424:174–179.
7. Fang L, et al. (2009) Acid-base actuation of [c2]daisy chains. *J Am Chem Soc* 131:7126–7134.
8. Browne WR, Feringa BL (2006) Making molecular machines work. *Nat Nanotechnol* 1:25–35.
9. Kottas GS, Clarke LI, Horinek D, Michl J (2005) Artificial molecular rotors. *Chem Rev* 105:1281–1376.
10. Gimzewski JK, et al. (1998) Rotation of a single molecule within a supramolecular bearing. *Science* 281:531–533.
11. Zheng X, et al. (2004) Dipolar and nonpolar altitudinal molecular rotors mounted on an Au(111) surface. *J Am Chem Soc* 126:4540–4542.
12. Du L, Liao S, Khatib HA, Stoddart JF, Zink JJ (2009) Controlled-access hollow mechanized silica nanocontainers. *J Am Chem Soc* 131:15136–15142.
13. Khuong TAV, Nunez JE, Godinez CE, Garcia-Garibay MA (2006) Crystalline molecular machines: A quest toward solid-state dynamics and function. *Acc Chem Res* 39:413–422.
14. Garcia-Garibay MA (2005) Crystalline molecular machines: Encoding supramolecular dynamics into molecular structure. *Proc Nat Acad Sci USA* 102:10771–10776.
15. Dunitz JD, Gavezzotti A (2009) How molecules stick together in organic crystals: Weak intermolecular interactions. *Chem Soc Rev* 38:2622–2633.
16. Khuong TAV, Zepeda G, Ruiz R, Kahn SI, Garcia-Garibay MA (2004) Molecular compasses and gyroscopes: Engineering molecular crystals with fast internal rotation. *Cryst Growth Des* 4:15–18.
17. Garcia-Garibay MA, Godinez CE (2009) Engineering crystal packing and internal dynamics in molecular gyroscopes by refining their components. Fast exchange of a phenylene rotator by ²H NMR. *Cryst Growth Design* 9:3124–3128.
18. Akutagawa T, et al. (2009) Ferroelectricity and polarity control in solid state flip-flop supramolecular rotors. *Nat Mater* 8:342–347.
19. Vacek J, Michl J (2001) Molecular dynamics of a grid-mounted molecular dipolar rotor in a rotating electric field. *Proc Nat Acad Sci USA* 98:5481–5486.
20. Minamino T, Imada K, Namba K (2008) Molecular motors of the bacterial flagella. *Curr Opin Struct Biol* 18:693–701.
21. Karlen SD, Ortiz R, Chapman OL, Garcia-Garibay MA (2005) Effects of rotational order on the solid state dynamics of phenylene and diamantane rotators. *J Am Chem Soc* 127:6554–6555.
22. Scudder M, Dance I (1998) Crystal supramolecular: hexagonal arrays of sextuple phenyl embraces amongst chemically diverse compounds. *J Chem Soc Dalton* 329–344.
23. Hoatson GL, Vold RL (1994) ²H-NMR spectroscopy of solids and liquid crystals. *Solid State NMR III*, ed B Blümich (Springer, New York), pp 1–67.
24. Macho V, Brombacher L, Spiess HW (2001) The NMR-WEBLAB: An Internet approach to NMR lineshape analysis. *Appl Magn Reson* 20:405–432.
25. Fyfe CA (1983) *Solid State NMR for Chemists* (CFC Press, Guelph, Ontario).
26. Kubo R, Tomita K (1954) A general theory of magnetic resonance absorption. *J Phys Soc Jpn* 9:888–919.
27. Sandström J (1983) *Dynamic NMR Spectroscopy* (Academic, New York).
28. Adept Scientific Inc. (2003) *g-NMR v. 5.0* (Adept Scientific Inc, Bethesda, MD).
29. Bielecki A, Burum DP (1995) Temperature dependence of ²⁰⁷Pb MAS spectra of solid lead nitrate. An accurate, sensitive thermometer for variable-temperature MAS. *J Magn Res A* 116:215–220.