

# Thermosalient Amphidynamic Molecular Machines: Motion at the Molecular and Macroscopic Scales

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**SUMMARY:** The supramolecular amphidynamic rotor **1**, composed of two carbazole molecules acting as the stator and a DABCO rotator, exhibits remarkable thermosalience above 316 K. During this process, the crystals spontaneously transduce collective molecular displacements into macroscopic movement due to a phase transition, which is described by single crystal X-ray analyses from 100 K to 320 K. The fast rotation in the low-temperature phase (I) occurs with a low activation energy  $E_a(\text{I}) = 2.6 \text{ kcal mol}^{-1}$  and a pre-exponential factor  $A(\text{I}) = 10^{12} \text{ s}^{-1}$ . Increased symmetry of the cavity in the high-temperature phase (II) resulted in slower dynamics, regardless of a smaller rotational barrier,  $E_a(\text{II}) \approx 0.5 \text{ kcal mol}^{-1}$ , due to the large reduction in the pre-exponential factor to  $A(\text{II}) \approx 10^7 \text{ s}^{-1}$ . These results demonstrate that a relatively small distortion of

lattice framework lead to drastic dynamic effects at both molecular and macroscopic scales, helping to understand responsive crystalline materials.

## 1. INTRODUCTION

*Dynamic* crystals are ordered three-dimensional supramolecular constructs that are responsive to external stimuli, usually by macroscopic mechanical reconfiguration.<sup>1–3</sup> The manifestation of the dynamic nature of these crystalline materials is easily observable as restorative effects, such as elastic or plastic deformation where crystals recover their original shape or remain permanently deformed, respectively, albeit they retain their macroscopic integrity. In other cases, disintegrative effects might ensue, where crystals splinter, explode or move due to either ejection of debris or rapid reshaping. In case of disintegrative outcome, the crystals are inevitably destroyed, and this process occasionally appears as transfer of momentum and motion of their fragments.<sup>5–10</sup> *Amphidynamic* crystals, on the other hand, are crystals with moving elements within their structure, that combine long-range order with ultrafast internal dynamics.<sup>11–17</sup> They contain a small, fast-rotating component (rotator) bound by either covalent bonds or intermolecular interactions to a framework (stator) with crystalline periodicity.

While the combination of the macroscopic and internal molecular dynamics in a single material has not been previously observed, such system may provide important insights into multiscale phenomena and their coexistence could shed light in the fundamental mechanism of molecular machines with technological applications, *i.e.* artificial muscles, which show controllable motions that collectively transduce thermal energy into mechanical work.<sup>18</sup> Finding these two properties in a single structure requires the occurrence of deformations, such as elastic bending, or rapid dynamic phenomena characteristic of thermosaliency with pronounced softness and anisotropy in the strength of intermolecular interactions.<sup>1–3,19–22</sup>

These properties are not generally anticipated for amphidynamic crystals, which typically feature rigid frameworks to enable internal rotation.<sup>23</sup> 1,4-diazabicyclo[2.2.2]octane (DABCO) is known to be an excellent globular rotator with two conveniently *para*-positioned basic nitrogen atoms available for hydrogen bonding. Here we report the first example of a molecular crystal that is dynamic at two levels of structural hierarchy—at a molecular scale, by having a rapidly rotating DABCO, and at a macroscopic scale, by being mechanically responsive due to the thermosalient effect during the rearrangement of the stator (**Scheme 1**).

## 2. RESULTS AND DISCUSSION

Commercially available carbazole, DABCO and DABCO-*d*<sub>12</sub> were used as received. The formation of the supramolecular complex between DABCO and carbazole was monitored by <sup>1</sup>H NMR spectroscopy from a 2:1 (mole ratio) mixture of carbazole and DABCO (or DABCO *d*<sub>12</sub>) in CDCl<sub>3</sub> and THF-*d*<sub>8</sub> (**Figure S1**). Slow evaporation of the THF solution afforded large crystalline blocks of carbazole-DABCO-carbazole cocrystals (**1**) (**Figure S2**).

As shown with the segment of the crystal structure in **Figure 1A**, at room temperature, the crystals of the rotor **1** are monoclinic, space group *P*2<sub>1</sub>/*c* (**Table S1**). The asymmetric unit comprises two carbazole stators that tether one DABCO rotator through two short N—H⋯N hydrogen bonds, with N⋯N distances of 2.863(1) Å and 2.878(1) Å and D—H⋯A angles of 174.3(1)° and 173.9(1)°, respectively. The carbazole moieties that hold the rotator are almost perpendicular to each other with a mean inter-planar angle between their two planes of 82.5(1)°. This results in the rotator being encased in a rhomboid cavity of four carbazole molecules (**Figure 1B**), as this disposition of the carbazole moieties seems to enhance the T-shape-like CH---π interaction between neighboring supramolecular rotors (see also **Figures S13-S15**). The DABCO

rotators are disordered at room temperature, and the structure was modeled with two positions with occupancies of 57 and 43 % at 290 K (**Figure 1C**). As anticipated from the reduced thermal motion, the size of the thermal ellipsoids is reduced at low temperature (200 K and 100 K), in line with the expected dynamic nature of the rotator (**Table S9**).

As in the case of previously reported molecular rotors with globular rotators,<sup>28,29</sup> the average  $C_{3v}$  point symmetry of DABCO is at the origin of a dynamic process that is too fast to be monitored on the timescale of variable temperature (VT)  $^{13}\text{C}$  CPMAS ( $10^2$ – $10^4$  s $^{-1}$ ) or by  $^2\text{H}$  NMR ( $10^4$ – $10^7$  s $^{-1}$ ) spectroscopy.<sup>30,31</sup> We anticipated that rotational processes in **1** could modulate  $^1\text{H}$ – $^1\text{H}$  dipolar magnetic interactions to provide an effective nuclear relaxation mechanism, similar to that observed with other crystalline rotators.<sup>32–37</sup> The method relies on  $^1\text{H}$   $T_1$  spin-lattice relaxation measurements carried out by saturation recovery in the solid state as a function of temperature, followed by the plot of the  $\ln(1/T_1)$  values as a function of the inverse temperature,  $1/T$ , to obtain the linear form of the Arrhenius equation, as shown in the plot of **Figure 2A**. The resulting plot gives a slope that depends on the activation energy for rotation with a maximum relaxation value (shortest  $T_1$ ) occurring when the frequency of rotational site exchange matches the Larmor frequency of the spectrometer used. In our case, with an  $^1\text{H}$  NMR Larmor frequency of 600 MHz ( $6 \times 10^8$  s $^{-1}$ ), we expected that the  $T_1$  minimum of the globular and highly symmetric DABCO would be observed at very low temperatures.<sup>38,39</sup>

The  $^1\text{H}$   $T_1$  relaxation times of **1** were recorded between 350 K and 193 K and were fit to single exponential functions, (for changes in the  $^1\text{H}$  line shape upon temperature variations, see **Figures S17-S18**). The  $T_1$  was notably reduced from 20 s at 295 K to 2 s at 193 K, indicating that the motion of DABCO is a thermally activated process (see **Table S7** and **Figures S19-S30**). The

$\ln(1/T_1)$  vs  $1/T$  plot revealed a linear relationship from 300 K to 193 K with a steady increase in the  $1/T_1$  axis but without reaching the expected maximum (**Figure 2A**), indicating that the motion of DABCO has a frequency higher than 600 MHz at the lowest temperature attainable with our spectrometer. Nevertheless, the activation energy of rotation ( $E_a$ ) obtained from the slope<sup>30,40</sup> yielded a value of 2.6 kcal mol<sup>-1</sup>, which is comparable to other ultrafast supramolecular rotors.<sup>41</sup> A sharp deviation from linearity observed above 300 K in the  $1/T_1$  plot in **Figure 2A** is strongly suggestive of a phase transition.

The purported phase transition was confirmed by differential scanning calorimetry (DSC) (**Figure 2B**). Thermal analysis confirmed that upon heating, the material undergoes a reversible endothermic phase transition around 316–322 K from the room-temperature phase (hereafter form I) to a high-temperature phase (form II). The reverse transition, from form II to form I, occurs around 297–304 K upon cooling. The transitions are observed in the DSC with saw-tooth profiles that is known to be characteristic for the thermosalient (crystal jumping) effect.<sup>2–4,19–21,24</sup> The crystals can be cycled between the two phases, but display small shifts in the transition temperature in consecutive cycles (**Figure S3**). Subsequently, crystals obtained from THF were inspected by hot-stage microscopy. Indeed, when heated above ~316 K, they exhibit a strong thermosalient effect that appears as sudden motion and jumping off the heated surface (**Video S1**). Depending on the crystal size and quality, the integrity of these crystals can be preserved after at least five thermal cycles, although their surface generally deteriorates after repetitive thermal treatment.

Based on well-supported analysis of the kinematics of the crystal jumps, we conclude that changes of the rhomboid scaffold in two crystallographic directions play a major role in the

observed face-dependence of the thermosalient effect (**Figure 3**, **Figure S4** and **Table S2**). It has been established that the thermosalience is a result of macroscopic stresses that build up in single crystalline specimens when large anisotropic structural changes are distributed unequally across their volume.<sup>1,2</sup> Observations made with crystals laying on a horizontal surface with different faces can be correlated with changes in the crystal structure to assign the molecular origins of the observed macroscopic relaxation (i.e., crystal rolling, displacement, jumping, etc.). We noticed that heated crystals showed translational motion when sitting on their (010)/(0 $\bar{1}$ 0) face, with changes occurring along the crystallographic directions [001] and [100]. The observed translational motion is a result of the molecular rearrangement along the *a* and *c* axes (**Figure 3B**; **Video S2**). By contrast, crystals sitting on their (0 $\bar{1}\bar{1}$ )/(011) face jump due to the realignment of rhomboid scaffold along the crystallographic [001] direction. However, the significant expansion of the scaffold perpendicular to [001] direction causes mechanical instability and macroscopic rotation (**Figure 3C**, **Video S3**). Finally, crystals that are heated at their (100)/( $\bar{1}$ 00) face jump off the stage and towards the viewer due to expansion in the [100] direction and parallel to the length of the crystal (**Figure 3D**, **Video S4**).

Inspection of crystals that were restrained from motion showed significant changes in crystal dimensions above 320 K (**Figure S5** and **Video S5**). The length of a typical crystal changed to +4%, and its width changed to +8%. As shown in **Figure S5** and **Figure S6**, a single crystal can be cycled between the two forms at least five times without notable deterioration.

As shown in **Figure 4A–C**, at the molecular level the rhomboid shape of the rotator scaffold changes to a square shape with an increase in symmetry from monoclinic to tetragonal (**Table S1**). The phase transition results in concomitant realignment of the cages so that although in the high-temperature phase they are still slightly offset, they are better packed (**Figure 4D,E**), in line

with the slightly higher density (**Table S1**). The change in interaction of the lateral carbazole molecules with DABCO affects its position, and in the high-temperature phase II the rotator is also disordered (**Figure S7**).

Detailed analysis of the molecular interactions revealed that during the phase transition from I to II the CH--- $\pi$  distance between carbazole molecules in the rhomboid cavity of **1** has increased from 2.690(2) Å to 2.847(2) Å along the crystallographic direction [100], resulting an expansion of the crystal length. At the same time, a slight contraction is observed with the opposite CH--- $\pi$  distance, from 2.855(1) Å to 2.847(1) Å, along the crystallographic direction [001], which results in contraction of the crystal width (**Figure 4D, E**). The expansivity indicatrix reflects the changes in length along the principal axes, as shown in the **Figure S8**.

The above correlations confirm that the anisotropic thermal expansion contributes to the occurrence of the thermosalient effect. The hardness of the crystal on the (010) face of form I, determined by nanoindentation, is  $H = 1.1 \pm 3.9$  GPa, and the respective value of the Young's modulus is  $E = 0.04 \pm 0.31$  GPa. These values suggest that the crystals of rotor **1** are very soft, and thus they fulfil one of the prerequisites for occurrence of the thermosalience (**Figure S9**).<sup>4,25–27</sup>

The changes in the cavity of **1** upon transition are accompanied by reorientation of the DABCO rotator with respect to its rotational axis, as evidenced by the significant change in the N—H $\cdots$ N hydrogen bond angle, from *ca.* 174° at room temperature to the ideal value of 180° at 320 K (**Figure 5B**, and **Tables S3–S5**). The realignment of the rotator also influences its dynamics, as shown by the deviation from linearity of the temperature dependence of the  $T_1$  values. Within the temperature range of the phase transition (316–322 K on heating), the relaxation spiked from 22.3

s (at 300 K) to 70.3 s (at 330 K) and subsequently remained constant up to 350 K, the highest temperature that could be attained without significant thermal decomposition of the cocrystal.

In order to further explore the nature of the structural changes that occur as a result of the phase transition and their effects on the rotational dynamics of DABCO we carried out additional NMR experiments. At first sight, the invariance of  $T_1$  and the higher symmetry cavity in the high-temperature phase II suggested that spin-lattice relaxation was no longer determined by DABCO rotation. It seemed reasonable to assume that motion in the high-temperature phase would be much faster than the Larmor frequency of the  $^1\text{H}$  nuclei. However, changes in the line shape of the quadrupolar echo  $^2\text{H}$  NMR spectra of DABCO- $d_{12}$ , which maintained space group (**Table S6**) and the phase transition according to DSC studies (see **Figures S10-S12**), revealed a completely unexpected result (**Figure 6**). The spectrum of the low-temperature phase (e.g., 213–300 K) was narrow and consistent with a 6-fold rotational potential being explored in the fast exchange regime ( $k_r \geq 10^7 \text{ s}^{-1}$ , see **Figure S16**). This result is consistent with the fast dynamics determined by  $^1\text{H}$  spin-lattice relaxation (**Figure 2A**). However, the spectra obtained from the high-temperature phase (**Figure 6**, 320–350 K) were characterized by appearance of a new spectral feature covering a greater width that could be simulated with a 6-fold rotational trajectory (i.e.,  $60^\circ$ -jumps) in the intermediate exchange regime. Simulations suggested a rotational exchange rate  $k_r = 2.2 \times 10^6 \text{ s}^{-1}$  that, similar to the  $T_1$  values, is nearly temperature-independent between 320 K and 350 K.

A relatively slow, almost temperature-independent rotation in the high-temperature, high-symmetry phase II was not anticipated. However, with deuterium-labeled samples at hand we carried out  $^2\text{H}$  NMR spin-lattice relaxation ( $^2\text{H } T_1$ , see **Table S8** and **Figures S32-S43**)

measurements that confirmed the result shown in **Figure 2A**, with  $E_a \approx 2.6$  kcal/mol and a discontinuity occurring in the same temperature range (**Figure S31**). Given the high certainty given by the data shown in **Figure 2A** and **6** and previously reported parameters for relaxation of DABCO in the solid state, we went back and carried a fit of all the  $^1\text{H}$   $T_1^{-1}$  data to estimate the activation parameters ( $E_a$  and  $A$ ) of the two phases using the full Kubo-Tomita relaxation expression (**Equation 1**).<sup>42</sup>

$$T_1^{-1} = C [\tau_c(1 + \omega_0^2\tau_c^2)^{-1} + 4\tau_c(1 + 4\omega_0^2\tau_c^2)^{-1}] \quad (1)$$

$$\tau_c^{-1} = \tau_0^{-1} \exp(E_a/RT) \quad (2)$$

The constant  $C$  in **Equation 1** represents the strength of the dipolar interactions involved in the relaxation process, and the value  $C = 5 \times 10^8 \text{ s}^{-2}$  was taken from our previously published work.<sup>38,40</sup> The  $\tau_c$  corresponds to the site exchange rotational correlation time, and  $\omega_0$  is the spectrometer frequency. The rotational correlation times are given by the Arrhenius equation (**Equation 2**), where  $\tau_0^{-1} = A$  is the rotational pre-exponential factor. As estimated from the slope in **Figure 2A**, we find that fast rotation in the low-temperature phase I has an activation energy of  $E_a(\text{I}) = 2.63 \text{ kcal mol}^{-1}$  and a normal pre-exponential factor of ca.  $A(\text{I}) = 4.4 \times 10^{12} \text{ s}^{-1}$  (**Figure 7**, dashed black line). By contrast, the fit of the relaxation dynamics of the high-temperature phase II (**Figure 7**, dashed red line) is consistent with much lower activation energy,  $E_a(\text{II}) \approx 0.5 \text{ kcal mol}^{-1}$ , and much smaller pre-exponential factor  $A(\text{II}) = 1.1 \times 10^7 \text{ s}^{-1}$ , giving values that account very well the  $^2\text{H}$  NMR data shown in **Figure 6**.

An interpretation of the changes in the activation barrier in terms of structural parameters is intuitively simple and generally based on hindrance along the rotational potential. It has also been shown that an increase in the symmetry of the potential leads to shorter angular displacements

between sites, such that their barriers tend to be lower.<sup>43</sup> This appears to be also the case with the supramolecular rotor **1**. By contrast, structural interpretations of changes in the pre-exponential factor are less intuitive. For an elementary rotary process, the pre-exponential factor can be associated with an oscillation that occurs in the potential energy well, which may be viewed as “an attempt frequency”. A relatively steep potential caused by a relatively high barrier ( $E_a = 2.6$  kcal mol<sup>-1</sup>) in the low-temperature phase would have a relatively large force constant that may explain the relatively large observed attempt frequency, with  $A = 4.4 \times 10^{12}$  s<sup>-1</sup>. By contrast, a nearly barrierless potential in phase II would render the rotator unbound or diffusive, without a restorative force that leads to the suggested rapid oscillatory motion. It seems reasonable that the pre-exponential factor under those conditions would reflect events that transfer angular momentum from the cavity to the rotator, such as collisions with the neighbors. While a simplified pictorial illustration of these conditions is shown in **Figure 8**, further insights are likely to require the use of molecular dynamics simulations.

## Conclusions

We report the first supramolecular rotor with fast rotating DABCO and static carbazole components held together by hydrogen bonds, which also displays a remarkable thermosalient effect. Crystals were shown to undergo a phase transition with a large structural reconfiguration around 316 K, which cause the crystals to change shape and jump off a hot surface. Upon transition from the low- to the high-temperature phase, the symmetry of the crystal lattice and hence of the cavity hosting the rotator increases, and this affects the dynamics of the rotator in a counterintuitive manner. By using <sup>1</sup>H (and <sup>2</sup>H) spin-lattice relaxation and line shape analysis of quadrupolar echo <sup>2</sup>H NMR, we found that, contrary to what would be expected from solely kinetic considerations, the rotation slows down significantly when going from the low-

temperature phase I to the high-temperature phase II, despite an approximately 5.2-fold reduction in the rotational barrier from  $\sim 2.6$  to only  $\sim 0.5$  kcal mol<sup>-1</sup>. We showed that this reduction is brought about by a five order of magnitude change in the pre-exponential factor, from  $4.4 \times 10^{12}$  s<sup>-1</sup> in phase I to  $1.1 \times 10^7$  s<sup>-1</sup> in phase II. Our results indicate that changes in structure resulting from the phase transition are concurrently responsible for changes in dynamics effects occurring at the molecular scale and changes in dynamics that occur in the macroscopic scale in the form of crystal motility due to lattice expansion in certain directions.

## EXPERIMENTAL PROCEDURES

**Synthesis of carbazole-DABCO-carbazole rotor (1).** In a flask of 20 mL, 0.2 g (1 eq, 1.78 mmol) of DABCO and 0.6 g (2 eq, 3.56 mmol) of 9*H*-carbazole were dissolved in 8 mL of dry THF. The solution was left to evaporate at room temperature, and after 3 days colorless crystals of the desired rotor were obtained, these crystals were filtered and recovered for their solid-state characterization.

**Thermal analysis.** Differential scanning calorimetry of carbazole-DABCO-carbazole rotor (1) was carried out on a simultaneous TGA-DSC Netzsch STA 449 F3 Jupiter and TA DSC-Q2000 instruments. Crystals were taken on a Tzero aluminum pan and heated from room temperature (298 K) to the selected temperature at rate of 10 K min<sup>-1</sup> under nitrogen atmosphere.

**Single-crystal X-ray diffraction.** The X-ray diffraction data of carbazole-DABCO-carbazole rotor (1) at 100 K, 290 K and 320 K were collected on a Bruker Kappa APEX DUO diffractometer equipped with Cobra cooling device (Oxford Cryosystems), and graphite-monochromated MoK<sub>α</sub> radiation ( $\lambda = 0.71073$  Å). X-ray diffraction data of Carbazole-DABCO-*d*<sub>12</sub>-carbazole at 290, 320 K also collected by using MoK<sub>α</sub> radiation. X-ray diffraction data at 100

K and 200 K were also collected on a Bruker APEX II DUO Quasar diffractometer equipped with CryoJet XL low-temperature monochromatized CuK $\alpha$  radiation ( $\lambda = 1.54178$  Å). The APEX II program was used to determine the unit cell parameters and to collect the data.<sup>44</sup> The frames were integrated with the Bruker SAINT<sup>45</sup> software package, and the data were corrected for absorption effects using SADABS.<sup>46</sup> The structures were solved by direct methods and refined against  $F^2$  by the full matrix least-squares technique using the SHELX crystallography packages<sup>47</sup> with Olex2 as a GUI and graphics program.<sup>48</sup> All hydrogen atoms bonded to carbon atoms were introduced in calculated positions and refined using the appropriate riding model. The rotator (DABCO) shows dynamic disorder at 100 K, 290 K and 320 K. The disordered parts of DABCO were refined using the restraints on geometrical and atomic displacement parameters. Finalized CIFs were verified by using PLATON<sup>49</sup> did not show any missing symmetry. Geometrical calculations were done using PLATON<sup>49</sup> and PARST.<sup>50</sup> The packing diagrams were generated using Mercury 3.10.3<sup>51</sup> and X-Seed,<sup>52</sup> and the images were rendered with POV-Ray.<sup>53</sup>

**Microscopy.** The thermomicroscopic behavior of carbazole-DABCO-carbazole rotor (**1**) was observed with a Nikon LV100 fluorescence microscope coupled with a heating stage. High-speed recordings were obtained with a HotShot 1280 CC camera (NAC) mounted on a Stereozoom SMZ745T trinocular stereoscope (Nikon) and the heating was controlled by a hot stage. The videos showing thermosalient effects were recorded at a speed of 1500 frames per second. The scanning electron microscopy (SEM) observations were carried out with a QUANTA FEG 450 electron microscope with a primary electron energy of 2–5 kV. A crystal of carbazole-DABCO-carbazole rotor (**1**) was placed in a graphite crucible and covered with oil to record the SEM image with a steady heating rate of 1 K min<sup>-1</sup> by recording one frame per second.

**Nanoindentation.** The nanoindentation measurements of a single crystal of carbazole-DABCO-carbazole rotor (**1**) were performed on (010) face with an Agilent G200 nanoindenter equipped with an XP head by using Berkovitch diamond indenter. Each indentation was performed using the continuous stiffness method to a depth of 1000 nm with a strain rate of 0.05, an amplitude of 2 nm, and a frequency of 45 Hz.<sup>54</sup> Before performing indentation on the rotor crystals, the stiffness and the geometry of the tip were determined and calibrated by using Corning 7980 silica reference sample (Nanomechanics S1495-25). In order to ensure that the tip was fully engaged, the modulus was measured between 200 and 1000 nm. The value of the Poisson's ratio was assumed to be 0.30.

## **Solid-State NMR experiments**

### **VT <sup>2</sup>H NMR spin-echo experiments**

The solid-state <sup>2</sup>H NMR spin-echo experiments were performed on a Bruker AV600 instrument at 92.1 MHz (deuterium resonance frequency) with a 5 mm wideline probe and 90-degree pulse of 2.9  $\mu$ s. To suppress the undesired artifacts, a quadrupolar-echo sequence with phase recycling was used. An echo delay of 50  $\mu$ s was used after the refocusing delay of 46  $\mu$ s, and the recycle delay between pulses was 5 s. In the experiment, about 100 mg of sample was placed in a short borosilicate glass NMR tube. 64 scans were acquired for all temperatures explored. All spectra in this work were obtained using a line broadening of 1.5 kHz in data processing.

### **VT <sup>1</sup>H and <sup>2</sup>H spin-lattice relaxation time ( $T_1$ )**

<sup>1</sup>H  $T_1$  measurements were carried out using a commercial magnet set at a magnetic field strength  $B_0$  of 14.1 T, at which the proton frequency ( $\nu_0 = \omega_0/2\pi$ ) is 600.0 MHz. A tank circuit was built for this purpose using an inductor made of bare copper wire wound in a coil form. Polycrystalline

sample of the co-crystal was packed in borosilicate glass tubes (5 mm diameter, 1.0 cm length) capped with Teflon tape plugs and placed in the copper coil.  $T_1$  experiments were recorded using a saturation recovery pulse sequence combined with a spin-echo, the saturation state was attained with a pulse comb ( $3*\pi/2$ ) which was followed by a time recovery  $\tau$ . The spectra at different  $\tau_s$  were integrated to then build saturation recovery traces that were fitted to a single exponential function.  $^1\text{H}$  and  $^2\text{H}$   $T_1$  experiments were recorded in the range of 193 – 350 K.

## **SUPPORTING INFORMATION**

Tables with crystallographic parameters, reversibility studies,  $^1\text{H}$  NMR solution data for rotor **1**, variable-temperature  $^1\text{H}$   $T_1$  saturation-recovery experiments, DSC results, thermal expansion analysis, nanoindentation results, and face indexing. Data File 1 (CCDC Numbers): 1842963-1842965, 1879529, 1894394, 1894383, 1870056-1870057.

## **ACKNOWLEDGMENTS**

B.R.-M. thanks UNAM PAPIIT IA201117 for financial support. A.C.-M. thanks to CONACYT for a scholarship (576483). This research was partially carried out using the Core Technology Platform resources at New York University Abu Dhabi. We thank M. C. García Gonzalez, D. Martínez Otero, A. Nuñez Pineda, M. A. Peña González, E. Huerta Salazar, J. Weston and L. Li for their technical assistance. We thank Dr. A. Aguilar-Granda for valuable scientific discussions. The work at UCLA was supported by grants NSF DMR-1700471 and MRI-1532232.

## **AUTHOR CONTRIBUTIONS**

A.C.-M. synthesized, characterized and crystallized the compound, made the initial Differential Scanning Calorimetry and Thermogravimetry studies, carried out the powder X-ray diffraction

analyses, made the initial discovery of the thermosalient effect and made the solid state  $^2\text{H}$  NMR simulations. D.P.-K. carried out the Hot-Stage Microscopy and SEM observations, reversible Differential Scanning Calorimetry, nanoindentation analyses and X-ray studies at room and high temperature. M. J. J. acquired the powder X-ray diffraction, Variable Temperature solid-state  $^2\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR and  $^1\text{H}$  and  $^2\text{H}$   $T_1$  relaxometry measurements. R. A.-T. collected and refined the X-ray structures at room and low temperatures. M.A.G.-G., P.N. and B.R.-M. designed and supervised the research, analyzed the data and wrote the paper with input from all the authors.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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## MAIN SCHEME AND FIGURES LEGENDS

**Scheme 1.** Chemical structure of the rotor **1** composed of carbazole (stator) and DABCO (rotator).

**Figure 1.** (A) Molecular structure of the rotor **1**, with the corresponding N···N distances and N—H···N angles indicated. (B) Top-down view (space-filling) of the cavity comprised by adjacent carbazole moieties that encase a single DABCO rotator. (C) Temperature effects on the structure of the rotator. All thermal ellipsoids are drawn at 50% probability. See also **Figures S13-S15** and **Tables S3-S5 and S9**.

**Figure 2.** Evidence for a phase transition in the rotor **1** from  $T_1$  relaxometry and DSC. (A) Plot of the natural logarithm of the  $^1\text{H}$   $1/T_1$  relaxation rate vs. the reciprocal temperature ( $1000/T$ ). The deviation from the linearity at ca. 300 K indicates a phase transition. (B) DSC analyses showing thermal effects with saw-tooth profile characteristic for a reversible thermosalient phase transition. See also **Figure S3**.

**Figure 3.** Thermosalient effect of the rotor **1** and its crystal face-dependence. (A) Cartoons of the crystal habit showing the plane indices and direction of motion. (B–D) Snapshots of the crystals recorded using high-speed camera (frame rate:  $1500\text{ s}^{-1}$ ) and dependence of the effect on the resting face of the crystals. Crystals sitting on their (010)/(0 $\bar{1}$ 0) face move sideways, crystals (on the (011)/(0 $\bar{1}$  $\bar{1}$ ) plane jump and rotate, while crystals sitting on their (100)/( $\bar{1}$ 00) face jump off the hot plate and towards the viewer.

**Figure 4.** Structural changes during the phase transition of rotor **1** between form I and form II. (A,B) Changes in the shape of the cavity and the orientation of DABCO. (C) Comparison of the unit cells before and after the phase transition. The values of the characteristic unit cell parameters in the two phases are given. (D,E) Mechanism of the phase transition and changes in the relevant molecular planes.

**Figure 5.** Changes in the crystal structure during the phase transition of the rotor **1** from phase I to phase II. (A) Changes in the inner cavity due to the phase transition. (B) Realignment of the DABCO rotator and respective changes in the hydrogen bonding geometry.

**Figure 6.** Experimental (solid blue line) and simulated (dotted red line)  $^2\text{H}$  NMR spectra of carbazole DABCO- $d_{12}$  rotor as a function of temperature. The spectra acquired at 300 K and 310 K correspond to phase I and the spectra above 320 K correspond to phase II (simulations were carried out with a cone angle =  $70^\circ$ , QCC = 165 kHz and pulse delay = 50  $\mu\text{s}$ ). See also **Figure S16**.

**Figure 7.** Analyses of the  $^1\text{H}$   $T_1$  data for molecular rotor **1** using the Kubo-Tomita equation.<sup>42</sup> See also **Figure S31**.

**Figure 8.** Qualitative depiction of the different potential energy surfaces leading to different dynamics in the carbazole-DABCO rotor **1** (with selected sites represented by Newman projections) in crystal phases I and II.

#### DESCRIPTIVE TITLES OF SUPPLEMENTAL VIDEOS, ZIP FILE AND SUPPLEMENTAL INFORMATION

**Supplemental Information.** Tables S1-S9 and Figures S1-S40.

**Data File 1.** Crystallographic information (CIF Files).

**Supplemental Video 1.** Macroscopic motion of a crystal under a heated surface.

**Supplemental Video 2.** Thermosalient effect along the crystallographic directions [001] and [100] showing macroscale motion.

**Supplemental Video 3.** Thermosalient effect perpendicular to the crystallographic direction [001] showing macroscale motion.

**Supplemental Video 4.** Expansion in the crystallographic direction [100] showing macroscale motion.

**Supplemental Video 5.** Changes in the crystal dimensions above phase transition under Hot-Stage SEM.

