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Authors: Abraham Colin-Molina, Marcus J. Jellen, Joelis Rodríguez-Hernández, Miguel Eduardo Cifuentes-Quintal, Jorge Barroso, Rubén A. Toscano, Gabriel Merino, and Braulio Rodríguez-Molina

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# Hydrogen Bonded Crystalline Molecular Machines with Ultrafast Rotation and Displacive Phase Transitions

Abraham Colin-Molina,1 Marcus J. Jellen,2 Joelis Rodríguez-Hernández,3 Miguel Eduardo Cifuentes-Quintal,4 Jorge Barroso,4 Rubén A. Toscano,1 Gabriel Merino,4\* Braulio Rodríguez-Molina.1\*

1 Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510, Ciudad de México, México.

2 Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States.

3 Centro de Investigación en Química Aplicada (CIQA), Blvd. Enrique Reyna Hermosillo, No. 140, Saltillo, Coahuila 25294, México.

4 Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida. Km 6 Antigua Carretera a Progreso. Apdo. Postal 73, Cordemex, 97310, Mérida, Yuc., México.

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**Abstract:** Two new crystalline rotors, **1** and **2**, assembled through N-H...N hydrogen bonds, using halogenated carbazole as stators and diaza[2.2.2]bicyclooctane (DABCO) as the rotator, are described. The dynamic characterization through 1H T<sub>1</sub> relaxometry experiments indicate very low rotational activation barriers of 0.67 kcal/mol for **1** and 0.26 kcal/mol for **2**, indicating that DABCO can reach a THz frequency at room temperature in the latter. These  $E_a$  values are supported by solid-state density functional theory computations. Interestingly, both supramolecular rotors show a phase transition between 298 and 250 K, revealed by differential scanning calorimetry and single-crystal X-ray diffraction. The subtle changes in the crystalline environment of these rotors that can alter the motion of an almost barrierless DABCO are discussed here.

#### Introduction

Inspired by nature, several research groups around the world have developed artificial molecular machines with internal dynamics or functional properties.1,2,3,4,5,6 A considerable effort has been invested in both the design and synthesis of compounds with different types of motion in solution7,8 and the solid-state,9,10 aiming to understand better the type and frequency of the motion at the nanoscale. Thus, several motors, rotors, and rotaxanes have been reported recently.11,12,13,14 Among those, solid-state systems with fast intramolecular motion are of particular interest to developing responsive materials (muscles, actuators, sensors, porous materials), akin to the functions of living organisms.15

Molecular rotors are crystalline entities composed of static groups (*stators*) surrounding smaller dynamic components (*rotators*). Previous reports have shown that stators should be voluminous to generate pockets within the crystal lattice and provide enough space for the rotator to undergo the intended motion. For this purpose, molecular components such as trityl, triptycene, pentiptycene, steroids, and more recently carbazole derivatives have been used as stators. 16, 17 From these, carbazole-based rotors are attractive to us given their good tendency to crystallize, high thermal stability, and in some cases, interesting solid-state emission. 18,19,20

The choice of the rotator also plays an essential role in achieving fast intramolecular motion. <sup>21</sup> Globular rotators like bicyclo[2.2.2]octane (BCO), <sup>22</sup> 4,4-diazabicyclo[2.2.2]octane (DABCO), <sup>23</sup>, <sup>24</sup> *p*-carborane, <sup>25</sup> or fullerene, <sup>26</sup> might display rotational frequencies faster than those reached with phenylene groups,<sup>27,28</sup> due to their larger size and symmetry that may enable

volume-conserving motions. With this in mind, the pairing of the appropriate molecular components should facilitate the development of molecular rotors with fast rotation. Such a combination of constituents shall not be restricted to covalent bonds, and therefore the use of supramolecular interactions, like hydrogen or halogen bonds, can be invoked to develop novel rotors with very low rotational barriers.<sup>29</sup>

The directional nature of hydrogen bonds can be used to generate novel structures with a great deal of complexity. <sup>30</sup> The directionality and cooperativity of this supramolecular interaction have been successfully employed in the solid-state to create cocrystals with emergent physicochemical properties not present in the initial components.<sup>31</sup> By using this strategy, a cocrystalline rotor, with an unsubstituted carbazole stator and DABCO rotator, has been recently reported by us, showing dynamics at the molecular and macroscopic scales.<sup>32</sup> These results prompted us to design new molecular architectures, given the fact that carbazole can be bestowed with numerous functional groups across its skeleton, bearing derivatives for attractive interactions during crystallization, and consequently improving the internal dynamics of the rotator.



Figure 1. Left: synthesis of supramolecular of rotors 1 and 2. Right: Molecular conformations observed in their corresponding crystals.

In this work, we describe the synthesis and dynamic characterization of two symmetric rotors that feature either 3,6-dichloro- (rotor 1) or 3,6-dibromo-9*H*-carbazole stators (rotor 2), encasing a DABCO rotator (Figure 1). From the X-ray data diffraction, it is determined that these carbazole derivatives are excellent stators that tether the globular DABCO by means of strong NH...N hydrogen bonds. According to the variable temperature 1H spin-lattice experiments, both rotors display rotational barriers of less than 1 kcal/mol, among the lowest  $E_a$  for supramolecular rotors reported to date. Interestingly, both compounds show a displacive phase transition that is unusual in

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purely organic compounds, evidenced by variable temperature single crystal X-ray diffraction,  $_1$ H relaxometry, and calorimetric experiments. It is found that only the internal motion of compound **1** is affected by this transition. A series of density functional theory (DFT) computations are carried out, using periodic boundary conditions, to understand how the crystal structure and bonding of these rotors enable such low  $E_a$  values. Our computed barriers support the experimental values, and the noncovalent interaction index (NCI) provide a way to understand the existent contacts in the cocrystals. Both insights of these sophisticated internal dynamics in ultrafast crystalline rotors can be useful to take advantage of their functionality on future applications.

#### **Results and Discussion**

#### Synthesis and X-ray studies of cocrystals 1 and 2

Our purpose is to use halogenated carbazoles to produce bulky stators and facilitate attractive interactions among the halogen atoms on the periphery.<sup>33</sup> This approach is not trivial given that the substitutions reduce the ability of the carbazole derivatives to form the desired 2:1 cocrystals with DABCO, affording the 1:1 species instead (not discussed here). Let us focus on the supramolecular nature of these rotors because the lack of a covalent bond may result in low electronic barriers to rotation and, in conjunction with the globular shape of the DABCO, very high rotational frequencies could be obtained (Figure 1).

The desired crystalline rotors were obtained as small crystals using a 2:1 ratio (stator/rotator) by slow evaporation of a THF solution or by mechanochemical synthesis using Liquid-Assisted Grinding. Out of three possible precursors, named 3,6-dichloro-*9H*-carbazole (compound **3**), 3,6-dibromo-*9H*-carbazole (compound **4**), and iodocarbazole (compound **5**, not included), only two of them were successfully cocrystallized with DABCO.

Solution 1H NMR afforded the first indication that the rotors displayed the desired hydrogen bond in solution. The corresponding stators (3 or 4) and the DABCO rotator were dissolved in CDCl<sub>3</sub> in a 2:1 ratio and the -NH signal of the halocarbazole indicated major changes in its chemical shifts with respect to the starting materials ( $\Delta\delta = 0.67$  and  $\Delta\delta = 0.45$ , for 1 and 2, respectively). Given that the solubility in chloroform of the carbazole derivatives was slightly limited, we shifted to THF-*d*<sub>8</sub> to solubilize them completely, but the spectroscopic changes were less noticeable (see Figure S1 and S2). Fortunately, the better solubility in THF allowed us to grow crystals suitable for single crystal X-ray studies from the evaporation of the corresponding solutions (Figure S3, S4 and Table S1).

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Figure 2. a) Molecular structure of rotor 1, b) Cavity around the DABCO (magenta) surrounded by four neighboring stators, c) Molecular structure of rotor 2, d) Segment of the cavity around the DABCO (magenta) surrounded by six stators. In both cases, the hydrogen-acceptor distances and D-H...A angles (°) are indicated with standard deviations.

The X-ray diffraction data of both compounds show the intended hydrogen-bonded triad, but with two completely different supramolecular arrays, with two stator orientations (Figure 2).34 In rotor 1, the two carbazole components are placed at a perpendicular conformation surrounding a highly disordered DABCO.35 In this rotor, there are two hydrogen-acceptor bond N-H...N distances of 1.892(3) and 2.028(3) Å. In both interactions, the angle NH...N is close to linearity 176.9(2)° and 176.4(3)°, respectively, suggesting that these hydrogen bonds are strong. The corresponding DFT computations provided excellent values for the lattice constants of 1 with an error of 1.3-1.6%. In particular, the computed hydrogen bond lengths of 1.88 Å and an NH...N angle of 177.6° are in good agreement with the experimental results. Although it is a difficult task to estimate the hydrogen bond interaction energy within the crystal, TPSS-D3(BJ)/def2-TZVP computations in the gas phase (including the ZPE correction) indicate that this value is of 10.0 kcal/mol.

The molecular rotor **2** also show two hydrogen bonds that tie a disordered DABCO, <sup>36</sup> with slightly longer hydrogen-acceptor bond distances (2.11 Å) and lower linearity (163.3°) compared to rotor **1**. This deviation results from the twisted conformation in this rotor, which resembles a *'tilted ladder'* where the *'steps'* of 3,6-dibromo-*9H*-carbazole are antiparallel components that lie on different planes while tethering the DABCO, which is inclined approximately 22°. In **2**, the crystal packing displays the expected symmetric type-II halogen bond, with a Br...Br distance of 3.735 Å and an angle of *ca*. 170°.37 The globular DABCO is surrounded by planar neighboring halocarbazoles, residing within a rectangular cavity. The computed lattice constant values in **2** have an error percentage of 0.4-2.6%. Note that the crystal has a triclinic phase, so the lattice parameters  $\alpha$ ,  $\beta$ , and  $\gamma$  are no longer

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90°, and the computations yield an error of less than 0.7%. The computed hydrogen bond distances and NH...N angles in the crystal are 1.87 Å and 178.1°, respectively, and the estimated interaction energy in the gas phase for this hydrogen bond is again 10.1 kcal/mol.

# Bulk characterization, internal dynamics by 1H T1 spin-lattice relaxation and DFT computations in the solid state

In order to study the internal dynamics of these supramolecular rotors, larger amounts of each cocrystal were prepared mechanochemically using the Liquid-Assisted Grinding (LAG) approach.<sup>38</sup> The phase purity of the samples was corroborated by powder X-ray diffraction data using Le Bail fittings (see Figure S15 and S16), The thermal stability of molecular rotors was studied by DSC and TGA analyses showing good stability under 120 °C (see Figures S7-S11). Given that the hydrogen bond acts as the supramolecular axis as evidenced by FTIR in the NH stretching (see Figures S13 and S14), the globular DABCO is expected to show a very fast reorientation process. This rapid motion can be an efficient relaxation process for restoring the bulk magnetization of the sample in the NMR spectrometer.<sup>39</sup>



Figure 3. a)  $_{1}H$  T<sub>1</sub> relaxation experiments of rotor 1, b)  $_{1}H$  T<sub>1</sub> relaxation experiments of rotor 2. c) Computed rotational potential of the DABCO rotator in 1, d) Computed rotational potential of the DABCO rotator in 2.

Considering that the rotation in these systems is a thermallyactivated process and that the reorientation is characterized by a correlation time  $\tau_c$ , variable-temperature 1H T1 experiments were carried out to obtain the corresponding activation parameters.<sup>40</sup> At low temperatures, the reorientation of DABCO should be reduced until they match the Larmor frequency of the observed nucleus, in this case, 1H at 600 MHz. This would be identified when the T1 values reach a minimum.<sup>41</sup> For rotors **1** and **2**, the 1H T1 saturation-recovery experiments were carried out from 360 K to 175 K (see Figures S22-S41), the minimum temperature available in the spectrometer.

In both rotors, the relaxation  $T_1$  times shortened as the temperature of the samples reduced, although the  $T_1$  minima were not observed due to instrumental temperature limitations

(Figure 3). This suggests that the rotational frequencies of the DABCO in 1 and 2 are faster than 600 MHz even at 175 K. The activation energies corresponding to rotation ( $E_a$ ) are obtained from the slope of Ln(1/T1) against the reciprocal of the temperature (1000/T), as reported in other instances, which are remarkably low for both rotors 1 (0.67 kcal/mol for 1 and 0.26 kcal/mol for 2, see Figures S20 and S21). These barriers represent only a fraction of that found in the rotor using unsubstituted carbazole and DABCO (2.6 kcal/mol).32 These values indicate that the rotational frequencies at 295 K for rotors 1 and 2 should be ca. 760 GHz and 1.4 THz, respectively, and both compounds should be able to reach faster frequencies above room temperature, because they are thermally stable cocrystals. Similar fast rotations have only been reported in covalent rotors with bicyclo[2.2.2]octane as the rotational component, with an energy barrier of 1.15 kcal/mol 42 or a distribution of energy barriers ranging from 0.37 to 1.29 kcal/mol. 43 The computed rotational barriers, using periodic boundary conditions, are 1.26 and 0.77 kcal/mol for 1 and 2, respectively. These values are close to the experimental values, although within the limits of the range of any computational method.

#### Dynamic characterization by VT X-ray diffraction

The  $_1H$  T<sub>1</sub> plot of rotor **1** indicates that some data deviate from the projected linearity (Figure 3a). The discrepancies occur below room temperature, and later the linearity is recovered as the temperature approaches 175 K. In contrast, only a small deviation is observed in the plot of rotor **2** (Figure 3b). This  $_1H$  T<sub>1</sub> behavior of compound **1** could come from variations in the vibrational or rotational modes of the molecular components, giving rise to new relaxation pathways within the crystals.44



Figure 4. Changes in the relative orientation of the carbazole stators at different temperatures. a) rotor 1 and b) rotor 2. Cell volume upon cooling from 298 K to 190 K: (c) rotor 1 displays an expansion of the cell at ca. 250 K, d) rotor 2 does not show an evident cell expansion.

To explore in detail this intriguing behavior from a structural point of view, we grew a fresh single crystal of **1** and performed lowtemperature X-ray diffraction studies from 298 K to 200 K (Figure 4). From the analyses of those experiments, it is noted that rotor **1** shows changes in the relative conformation of the molecular components upon cooling, which affect the relative positions of the carbazole and changed the alignment of DABCO, making the N-H...N bond distance (D2) and angle (A2): 2.04 Å /170.9°, 2.05

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Å /170.0°, and 2.04 Å /169.5° at 298, 250, and 230 K, respectively (Figure 4a). The same set of experiments for compound **2** reveal only minor structural variations in the X-ray diffraction data (Figure 4b). However, the phase transition was detected by DSC (see Figure S12).

Despite the observed structural changes in rotor **1**, the X-ray diffraction data refinements at all temperatures show that the crystal system and space-group have not changed ( $P2_1/c$ ), and therefore this process is an isostructural phase transition. Most notably, an expansion of the cell axes and the volume is observed at *ca*. 250 K (Figure 4).45



**Figure 5.** Changes in the atomic positions in rotor **1** at different temperatures. All atoms of the 3,6-dihalocarbazole portion that contain labelled atoms Cl(3) and Cl(4) were overlapped. a) Comparison between 298-250 K, b) Comparison between 250-230 K, and c) Comparison between 230-200 K. The comparison was carried out calculating the centroids of each carbazole moiety.

According to the classification of phase transitions proposed by Buerger,<sup>46</sup> the observed structural changes should correspond to a second-order phase transition called displacive. This kind of transition has been mostly reported in hybrid compounds<sup>47</sup> and metallic salts, <sup>48</sup> and therefore its presence may be of great relevance to fully understand the behavior of crystalline molecular machines. It has been reported that these transformations require small energy and are associated with changes in the atomic positions of the molecular components due to molecular translations or rotations.<sup>49</sup> In the both rotors reported here, in addition to expected changes in their atomic coordinates, the calorimetric experiments clearly indicate a small amount of absorbed heat.

A comparison of the crystalline structures at different temperatures reveals the change in the atomic positions of rotor **1**. Figure 5a highlights the displacive rearrangement with a centroid-centroid distance of 0.74 Å suffered by the stator above 250 K, but this change is less noticeable in the range of temperatures between 250 and 200 K (Figures 5b and 5c). The translational changes found below 250 K are considered enough evidence of the displacive transition that occurred inside the crystal with the largest change along the *c*-axis (Figure S5 and Table S2). Similar structural reconfigurations have been reported in molecular systems with ferroelectric response with a DABCO component in their structures.<sup>50</sup>

In contrast, compound **2** only shows small changes in its relaxation behavior (*vide supra*), calorimetric analysis as well as minor variations in the single crystal X-ray data collections at different temperatures (see Figure S6 and Table S3). In order to emphasize the structural differences after the displacive phase

transitions in 1 and 2, the structures at room temperature (before transition) and 230 K (after transition) were superimposed, revealing a displacement of 0.51 Å (rotor 1) or 0.31 Å (rotor 2) occurring on the perpendicular axis to the plane of the stator. It is important to emphasize that the displacive transition described here was not studied in the previously reported parent rotor with unsubstituted carbazole stator, but rather a thermosalient (disintegrative) phase transition at high temperatures.

To rationalize the distinctive behavior between the rotors, it is mandatory to identify the number and type of intermolecular contacts within the crystal. Each carbazole-DABCO-carbazole triad is surrounded by 10 or 14 rotors in compounds 1 and 2, respectively (Figure 6). Although the conformation differs and the number of neighbors is different in each compound, the DFT periodic computations indicated that the interaction energy between a rotor and all its neighbors is ~60 kcal/mol in both cases (58.0 and 60.0 kcal/mol for 1 and 2, respectively). These similar interaction energies could indicate that: A) the type of interactions in the crystal is the same or that B) the interactions are different but compensate each other so that they result in equivalent magnitudes. Hypothesis A was discarded since the number of neighbors and the crystal arrangement for each rotor are different. To explore if hypothesis **B** is valid, it was necessary to distinguish the type and number of contacts. To this end, the NCI (Non-Covalent Interactions) index was used to identify the contacts of each rotor. It is impractical to determine how many and what type of contacts surround a specific rotor from the NCI of the unit cell (see Figure S42). Therefore, we considered the first neighbors of a given rotor to form pairs (moieties).



Figure 6. Non-covalent interactions (NCIs) analyses. Plots in pairs or dimers found in the crystals of rotors 1 and 2.

In the case of rotor 1, there are three different moieties of neighboring units (Figure 6): a) four moieties labeled 1-A with  $\pi$ ...H-C, CH...CH, and C-CI...H-C contacts, b) four moieties labeled 1-B with the similar interactions as seen in 1-A but with different orientation and, c) two moieties 1-C with CI...Cl interactions

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between rotors. In contrast, for the case of **2**, there are five different pairs of neighboring units: a) two moieties **2-A** with  $\pi$ ...H-C, and C-Br...H-C contacts, b) four moieties **2-B** with mostly with  $\pi$ ...H-C contacts, c) two moieties type **2-C**, which exhibit C-Br...hydrogen contacts of the rotator and also with the aromatic carbazole, d) four moieties **2-D** with C-Br...H-C interactions, and e) two moieties **2-E**, which show Br...Br contacts. So, the nature of the interactions in each rotor could be similar, but the number is different, so the conformational differences in the crystal structure between **1** and **2** balance the reduced number of contacts.

The fact that the intermolecular interactions in each rotor have virtually the same energy may suggest that the relaxation anomalies observed in **1** are due to the variation of the cavity hosting the DABCO, considering the significant changes in the *c*-crystallographic axis, which modifies the initial alignment (and dynamics) of the rotator. In the case of rotor **2**, the ladder conformation of the components may act akin to a "shock absorber" and, therefore, small structural changes do not significantly affect the relaxation of the DABCO.

Based on the previous analyses, an asymmetric rotor where one and one 3,6-dibromo-9H-carbazole 3.6-dichlorostator simultaneously tether one DABCO rotator was attempted to produce a rotor with modulated properties. The three components (in a 1:1:1 ratio) were dissolved and followed by 1H NMR in solution, and two proton signals at 9.40 and 9.32 ppm were observed (Figure S1). These chemical shifts were taken as indicative of the presence of the asymmetric rotor in solution. When this three-component solution was left to evaporate (either from CHCl<sub>3</sub> or THF), the resulting crystalline precipitate showed a mixture of supramolecular rotors 1 and 2, as evidenced by the Le Bail fitting using powder X-ray diffraction data (see Figures S17, S18 and S19). The self-assembly process of **1** and **2** was not expected and it can be explained in terms of a lower energetic cost that favors the symmetric rotors, although more detailed subsequent studies are needed to gather deeper insights.

### **Summary and Outlook**

Two ultrafast supramolecular rotors **1** and **2** featuring halocarbazoles and DABCO have been obtained by establishing strong N-H...N hydrogen bonds. This interaction was already observable from 1H NMR in solution and transferred to the solid-state rendering symmetric structures and conformations, with **2** also displaying halogen bonds. Preliminary experiments indicate that symmetric rotors are the preferred entities in the solid-state over asymmetric ones.

The two rotors show very distinctive supramolecular arrays with differences in the conformation of the halocarbazole stators. However, both compounds display very low activation barriers to rotation **1** (*ca.* Ea = 0.67 kcal/mol) and **2** (*ca.* 0.26 kcal/mol) for organic crystals, as determined by 1H spin-lattice experiments. These values are supported by DFT computations using periodic boundary conditions. Taken these values into consideration, the rotational frequencies for **1** and **2** at room temperature should be *ca.* 760 GHz and 1.4 THz, respectively.

Notably, both crystalline rotors have different responses when they are cooled down. Rotor **1** has an unexpected cell expansion

during cooling, specifically at 250 K, causing noticeable structural distortions that were pinpointed by 1H spin-lattice and calorimetric measurements. In stark contrast, rotor **2** does not display changes in relaxation behavior. The lack of change is attributed to the conformation of its components that uphold minor structural changes. These insights reveal that is possible to attain very high rotational frequencies in the solid-state and that the internal motion is sensitive to the structural changes in the crystalline environment in this type of molecular machines.

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**Keywords:** Crystalline Molecular Machines • THz Frequency • Displacive Phase Transition • Non-Covalent Interactions • 1H T<sub>1</sub> relaxation .

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- 1 Lancia, F., Ryabchun, A., Katsonis, N., Nat. Rev. Chem., 2019, 3, 536-551.
- 2 Groppi, J., Baroncini, M., Venturi, M., Silvi, S., Credi, A., Chem. Commun., 2019, 55, 12595-12602.
- 3 Kassem, S., Van Leeuwen, T., Lubbe, A. S., Wilson, M. R., Feringa, B. L., Leigh, D. A., Chem. Soc. Rev., 2017, 46, 2592-2621.
- 4 Pezzato, C., Nguyen, M. T., Kim, D. J., Anamimoghadam, O., Mosca, L., Stoddart, J. F., Angew. Chem. Int. Ed., 2018, 57, 9325-9329.
- 5 Harris, J. D., Moran, M. J., Aprahamian, I., Proc. Natl. Acad. Sci. USA, 2018, 115.9414-9422

6 Braga, D., Grepioni, F., Maini, L., d'Agostino, S., Eur. J., Inorg. Chem., 2018, 3597-3605.

- 7 Kumbhar, H. S., Deshpande, S. S., Shankarling, G. S., ChemistrySelect, 2016, 1, 2058-2064.
- 8 Wu, Y., Wang, G., Li, Q., Xiang, J., Jiang, H., Wang, Y., Nat. Commun., 2018, 9, 1953
- 9 Kaleta, J., Bastien, G., Wen, J., Dracinsky, M., Tortorici, E., Cisarova, I., Beale, P. D., Rogers, C. T., Michl, J., J. Org, Chem., 2019, 84, 8489-8467.
- 10 Inukai, M., Fukushima, T., Hijikata, Y., Ogiwara, N., Horike, S., Kitagawa, S., J. Am. Chem. Soc., 2015, 137, 12183-12186.
- 11 Harada, J., Yoneyama, N., Sato, S., Takahashi, Y., Inabe, T., Cryst. Growth Des., 2019, 19, 291-299.
- 12 Zhang, Z.-X., Zhang, T., Shi, P.-P., Zhang, W.-Y., Ye, Q., Fu, D.-W., J. Phys. Chem. Lett., 2019, 10, 4237-4244.
- 13 Balema, T. A., Ulumuddin, N., Murphy, C. J., Slough, D. P., Smith, Z. C., Hannagan, R. T., Wasio, N. A., Larson, A. M., Patel, D. A., Groden, K., McEwen, J.-S, Lin, Y.-S., Sykes, E. C. H., J. Phys. Chem. C, 2019, 123, 23738-23746.
- 14 Dong, J., Zhang, K., Li, X., Qian, Y., Zhu, H., Yuan, D., Xu, Q.-H., Jiang, J., Zhao, D., Nat. Commun., 2017, 8, 1142.
- 15 Urry, D.W., Angew. Chem. Int. Ed., 1993, 32, 819-841.
- 16 Meng, H., Zhao, C., Nie, M., Wang, C., Wang, T., Nanoscale, 2018, 10, 18119-18123. 17 Thibeault, D., Auger, M., Morin, J.-F., Eur. J. Org. Chem., 2010, 3049-36067.

18 Aguilar-Granda, A., Colin-Molina, A., Jellen, M.J., Núñez-Pineda, A., Cifuentes Quintal, M.E., Toscano, R.A., Merino G., Rodríguez-Molina, B., Chem. Commun., 2019, 55, 14054-14057.

- 19 Parrot, E. P. J., Tan, N. Y., Hu, R., Zeitler, J. A., Tang, B. Z., Pickwell-MacPherson, E., Mater. Horiz., 2014, 1, 251-258.
- 20 Alam, P., Leung, N. L. C., Cheng, Y., Zhang, H., Liu, J., Wu, W., Know, R. T. K., Lam, J. W. Y., Sung, H. H. Y., Williams, I. D., Tang, B. Z., Angew. Chem. Int. Ed. 2019, 58, 4536-4540.
- 21 Karlen, S. D., Reyes, H., Taylor, R. E., Khan, S. I., Hawthorne, M. F., Garcia-Garibay, M. A., Proc. Nat. Acad. Sci. USA, 2010, 107, 14973-14977.
- 22 Rodríguez-Molina, B., Pérez-Estrada, S., Garcia-Garibay, M. A., J. Am. Chem. Soc., 2013, 135, 10388-10395.
- 23 Jiang, X., Duan, H.-B., Jellen, M. J., Chen, Y., Chung, T. S., Liang, Y., Garcia-Garibay, M. A., J. Am. Chem. Soc., 2019, 141, 16802-16809.
- 24 d'Agostino, S., Fornasari, L., Grepioni, F., Braga, D., Rossi, F., Chierotti, M. R., Gobetto, R., Chem. Eur. J., 2018, 24,15059-15066.
- 25 Prokop, A., Vacek, J., Michl, J., ACS Nano, 2012, 6, 1901-1914.
- 26 Lorbach, A., Maverick, E., Carreras, A., Alemany, P., Wu, G., Garcia-Garibay,
- M. A., Bazan, G. C., Phys. Chem. Chem. Phys., 2014, 16, 12980-12986.
- 27 Setaka, W., Inoue, K., Higa, S., Yoshigai, S., Kono, H., Yamaguchi, K., J. Org. Chem., 2014, 79, 8288-8295. 28 Bracco, S., Miyano, T., Negroni, M., Bassanetti, I., Marchio, L., Sozzani, P.,
- Tohnai, N., Comotti, A., Chem. Commun., 2017, 53, 7776-7779.
- 29 Aakeroy, C. B., Panikkattu, S., Chopade, P. D., Desper, J., CrystEngComm, 2013. 15. 3125-3136.
- 30 Li, Z., Wu, L.-Z., 2015, Hydrogen Bonded Supramolecular Structures, Springer.
- 31 Liu, R., Wang, H., Jin, W. J., Cryst. Growth Des., 2017, 17, 3331-3337.
- 32 Colin-Molina, A., Prasad-Karothu, D., Jellen, M. J., Toscano, R. A., Garcia-Garibay, M. A., Naumov, P., Rodríguez-Molina, B., Matter, 2019, 1, 1033-1046.

33 Colin-Molina, A., Pérez-Estrada, S., Roa, A. E., Hernández-Ortega, S., Rodriguez, M., Brown, S., Rodríguez-Molina, B., Chem. Commun. 2016, 52,12833-12836.

34 Rotor 1 was refined in a monoclinic centrosymmetric space group P21/c. Although the diffraction patterns at low and room temperatures can be indexed in the tetragonal space group  $P4_1$  ( $P4_3$ ) the structure could not be refined successfully in this space group. In the case of rotor **2**, the only space group that gave good quality figures of merit was P-1 at low and room temperature.

- 35 The DABCO rotator was solved with a four-site disorder, showing occupancies of 0.338, 0.256, 0.215, 0.191, at room temperature.
- 36 In rotor 2 the DABCO rotator was solved with a two-site disorder, with 0.60 and 0.40 occupancies at room temperature.
- 37 Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G., Terraneo, G., Chem. Rev., 2016, 116, 2478-2601.
- 38 Hasa, D., Rauber-Schneider, G., Voinovich, D., Jones, W., Angew. Chem. Int. Ed., 2015, 54, 7371-7375.
- 39 Beckmann, P. A., Dougherty Jr. W. G., Kassel, W. S., Solid State Nucl. Magn. Reson., 2009, 36, 86-91.
- 40 R. Kubo and K. Tomita, J. Phys. Soc. Jpn., 1954, 9, 888-919.
- 41 V.I. Bakhmutov, 2004, Practical NMR relaxation for chemists, Wiley.
- 42 Rodríguez-Molina, B., Pérez-Estrada, S., Garcia-Garibay, M.A., J. Am. Chem. Soc., 2013, 135, 10388-10395.
- 43 Simonov, S., Zorina, L., Wzietek, P., Rodríguez-Fortea, A., Canadell, E., Meziere, C., Bastien, G., Lemouchi, C., Garcia-Garibay, M.A., Batail, P., Nano
- Lett., 2018, 18, 3780-3784. 44 Harris, R.K., Wasylishen, R. E., Duer, M. J., 2009, NMR crystallography, Wiley.
- 45 DSC experiments at low temperatures displayed an endothermic event as indicated in the SI.
- 46 Buerger, M. J., 1951, Phase transformation in Solids, John Wiley and Son.
- 47 Liu, Y., Zhu, C.-L., Zheng, X.-Y., Qin, L.-L., Yang, S.-X., Liu, Z.-Q., R. Soc. Open Sci., 2018, 5, 180738.
- 48 Matvienko, A. A., Maslennikov, D. V., Zakharov, B. A., Sidelnikov, A. A., Chizhik, S. A., Boldyreva, E. V., IUCrJ, 2017, 4, 588-597.
- 49 Anwar, J., Zahn, D., Adv. Drug Deliv. Rev., 2017, 117, 47-70.
- 50 Ye, H.Y., Zhang, Y., Noro, S.-I, Kubo, K., Yoshitake, M., Liu, Z.-Q., Cai, H.-L., Fu, D.-W., Yoshikawa, H., Agawa, K., Xiong, R.-G., Nakamura, T., Sci. Rep., 2013, 3, 2249.

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cycles by second at room temperature!