

C₅-Symmetric Chiral Corannulenes: Desymmetrization of Bowl Inversion Equilibrium via “Intramolecular” Hydrogen-Bonding Network

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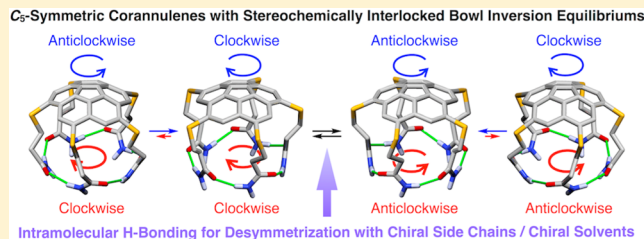
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Supporting Information

ABSTRACT: Because of a rapid conformational inversion, bowl-shaped C₅-symmetric corannulenes, though geometrically chiral, have not been directly resolved into their enantiomers. However, if this inversion equilibrium can be desymmetrized, chiral corannulenes enriched in either enantiomer can be obtained. We demonstrated this possibility using pentasubstituted corannulenes **4** and **5** carrying amide-appended thioalkyl side chains. Compound **4** displays chiroptical activity in a chiral hydrocarbon such as limonene. Because compound **5** carries a chiral center in the side chains, its enantiomers **5_R** and **5_S** show chiroptical activity even in achiral solvents such as CHCl₃ and methylcyclohexane. In sharp contrast, when the side chains bear no amide functionality (**1** and **2_R**), no chiroptical activity emerges even in limonene or with a chiral center in the side chains. Detailed investigations revealed that the peripheral amide units in **4** and **5** are hydrogen-bonded only “intramolecularly” along the corannulene periphery, affording cyclic amide networks with clockwise and anticlockwise geometries. Although this networking gives rise to four stereoisomers, only two, which are enantiomeric to one another, are suggested computationally to exist in the equilibrated system. In a chiral environment (chiral solvent or side chain), their thermodynamic stabilities are certainly unequal, so the bowl-inversion equilibrium can be desymmetrized. However, this is not the case when the system contains a protic solvent that can deteriorate the hydrogen-bonding network. When the enantiomeric purity of limonene as the solvent is varied, the chiroptical activity of the corannulene core changes nonlinearly with its enantiomeric excess (majority rule).



INTRODUCTION

Corannulene is a bowl-shaped π -conjugated molecule whose carbon network skeleton is equivalent to a partial structure of fullerene C₆₀.^{1,2} However, in contrast to the closed architecture of C₆₀, corannulene thermally undergoes a very rapid bowl-to-bowl inversion (Figure 1) whose rate in CHCl₃ has been estimated at 25 °C to be greater than 2×10^5 s⁻¹.³ Although the inversion can be decelerated by enlarging the bowl structure,⁴ it still remains a difficult task to design corannulenes with a small inversion activity. Meanwhile, this nonplanar molecular geometry possibly endows the corannulene family with unique properties and functions.⁵ One of those is concerned with an issue of dynamic molecular chirality. For example, pentasubstituted corannulene derivatives with a symmetry group of C₅, such as **1**, are chiral because of their bowl shape, so a pair of enantiomers can be expected (Figure 1). However, the enantiomers are not resolved because of their thermal racemization in solution associated with rapid bowl-to-bowl inversion of the corannulene skeleton. In regard to this

issue, Siegel and co-workers reported that when pentamethylcorannulene is modified with a chiral ruthenium complex, the resultant organometallic adduct is enriched in either diastereoisomer and shows chiroptical activity in solution.⁶ However, to date, no chiroptically active “genuine” C₅-symmetric corannulenes have been reported.

Without covalently modifying the carbon network skeleton, how one can desymmetrize the bowl inversion equilibrium of C₅-symmetric corannulenes? For this interesting challenge, we herein report a molecular design strategy using “intramolecular” hydrogen bonding (H-bonding), which is made possible by the bowl-shaped nonplanar corannulene structure. Major players for this project include C₅-symmetric corannulenes **4** and **5** carrying amide-appended thioalkyl side chains (Figure 1). A density functional theory (DFT) computational study⁷ using simplified molecular model **3** (Figure 1) suggested that the

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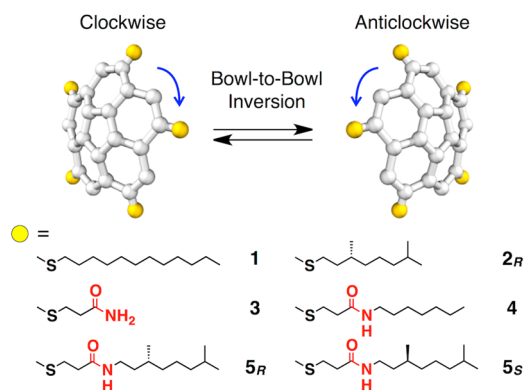


Figure 1. Chemical structures of C_5 -symmetric chiral corannulenes and a schematic representation of the bowl-to-bowl corannulene inversion, where arc-shaped arrows represent tentative definitions of the clockwise and anticlockwise substituent arrays along the corannulene periphery.

bowl shape of the corannulene core enables its peripheral amide units to be H-bonded only “intramolecularly”.⁸ As shown in Figure 2, when all of the amide units are H-bonded along the corannulene periphery at the same time, cyclic amide networks adopting clockwise and anticlockwise chiral geometries (as shown by the red-colored arc-shaped arrows representing the directions of five H-bonded N–H \rightarrow O=C amide units) are constructed.⁸ Since the corannulene core is intrinsically chiral

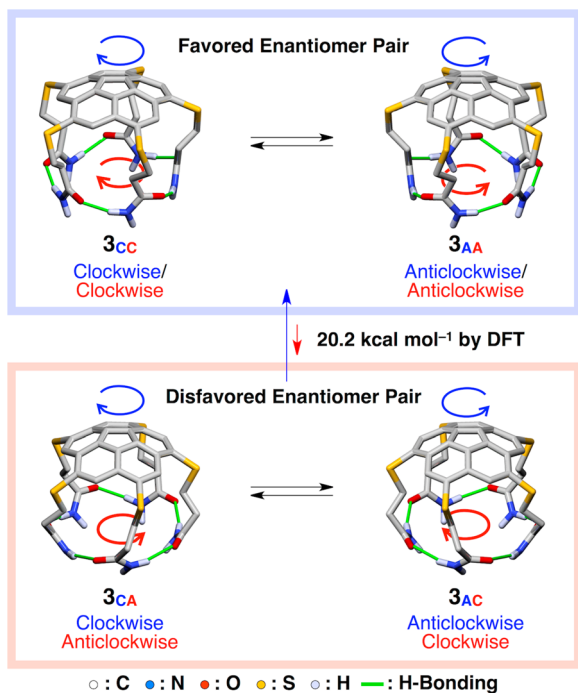


Figure 2. Schematic representations of the bowl inversion equilibrium using simplified molecular model 3 for C_5 -symmetric corannulenes carrying thioalkyl side chains featuring intramolecularly H-bonded amide units. Blue- and red-colored arc-shaped arrows represent the directions of H \rightarrow SR and H-bonded N–H \rightarrow O=C arrays, respectively, along the corannulene periphery. Subscripts C and A for 3 denote the clockwise and anticlockwise directions (tentatively defined), respectively. Four possible stereoisomers were energy-minimized at the SCS-MP2/def2-TZVPP//DFT-D3-TPSS/def-TZVP level.⁹

as a result of its C_5 symmetry (as shown by the blue-colored arc-shaped arrows representing the directions of five H \rightarrow SR peripheral substituents), this networking interaction is supposed to generate four stereoisomers that are equilibrated thermodynamically in the system. These stereoisomers are denoted as 3_{CC} , 3_{AA} , 3_{CA} , and 3_{AC} , where $3_{CC}/3_{AA}$ and $3_{CA}/3_{AC}$ are enantiomer pairs; the subscripts C and A denote clockwise and anticlockwise directions, and their colors are correlated with those of the arc-shaped arrows (Figure 2). However, as also suggested computationally, enantiomer pair $3_{CC}/3_{AA}$ is energetically more favorable than $3_{CA}/3_{AC}$ by 20.2 kcal mol⁻¹.⁹ Thus, we suppose that only one enantiomer pair, $3_{CC}/3_{AA}$, substantially exists in the equilibrated system. In other words, the stereochemistry of the cyclic amide network, once established, unambiguously determines that of the corannulene core or vice versa. As highlighted in the present work, the bowl inversion equilibrium of C_5 -symmetric corannulenes 4 and 5 can be desymmetrized in chiral environments as a result of this particular stereochemical feature.

RESULTS AND DISCUSSION

Amide-appended C_5 -symmetric corannulenes 4, 5_R , and 5_S , together with non-amide references 1 and 2_R (Figure 1), were synthesized from 1,3,5,7,9-pentachlorocorannulene as a common precursor according to methods analogous to those reported by Scott and co-workers¹⁰ with minor modifications, and they were unambiguously characterized by ¹H and ¹³C NMR spectroscopy along with mass spectrometry (Figures S1–S16 in the Supporting Information).⁹ In our previous study in 2009, we reported that a C_5 -symmetric deca-substituted liquid-crystalline (LC) corannulene (achiral) with amide-appended thioalkyl side chains self-assembles into a hexagonal columnar geometry,¹¹ for which “intermolecular” H-bonding interaction among the peripheral amide units is crucial. As an extension of this work, compound 4 was synthesized because of curiosity about how its C_5 -symmetric chiral corannulene core stereochemically affects the assembly behavior and LC properties. However, 4 did not assemble into an LC mesophase but afforded a polycrystalline solid material. Nevertheless, in the course of this study, we encountered an unexpected phenomenon that 4 does not self-assemble in an apolar solvent such as methylcyclohexane (MCHex), which usually facilitates H-bonding interactions of amides. The occurrence of a H-bonding interaction in 4 was confirmed by the IR spectrum of its MCHex solution at 20 °C, where stretching vibrations due to the H-bonded amide NH and C=O groups were observed at 3331 and 1650 cm⁻¹,¹² respectively (Figure S17a).⁹ Meanwhile, in a dynamic light scattering (DLS) analysis, compound 4 displayed, over a wide range of its concentration from 3 to 300 μ M, a unimodal scattering peak with an almost constant hydrodynamic diameter of \sim 1.3 nm (Figure 3a). This was also the case in CHCl₃ (Figure 3b, blue) as well as a protic solvent such as EtOH that can deteriorate H-bonding interactions (Figure 3b, red). These DLS profiles are analogous to that of 1 bearing no H-bonding amide groups (Figure 3b, orange). Therefore, we carried out diffusion-ordered spectroscopy (DOSY) of 4, which provided a diffusion coefficient of 7.1×10^{-10} m² s⁻¹ in CDCl₃ at 20 °C (Figure S18b).⁹ Again, this value is close to that of nonassembled reference 1 (8.4×10^{-10} m² s⁻¹; Figure S18a), indicating that 4 is unassembled but dispersed in MCHex at a unimolecular level. All of these observations allow us to conclude that the amide units in 4 are H-bonded but only “intramolecularly”. Amide-appended

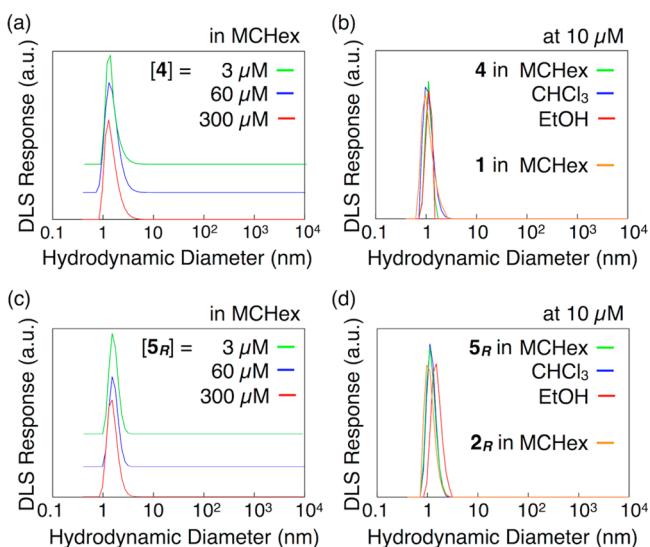


Figure 3. Dynamic light scattering (DLS) profiles of (a) **4** in methylcyclohexane (MCHex) at 3 μM (green), 60 μM (blue), and 300 μM (red); (b) **4** at 10 μM in MCHex (green), CHCl_3 (blue), and EtOH (red) and **1** at 10 μM in MCHex (orange); (c) **5_R** in MCHex at 3 μM (green), 60 μM (blue), and 300 μM (red); and (d) **5_R** at 10 μM in MCHex (green), CHCl_3 (blue), and EtOH (red) and **2_R** at 10 μM in MCHex (orange).

paraffinic side chains are known to promote stacking of disk-shaped π -conjugated molecules by an “intermolecular” H-bonding interaction.¹³ However, as suggested computationally (Figure 2), the bowl shape of the corannulene core likely facilitates only “intramolecular” H-bonding of the peripheral amide units. In regard to this possibility, a CDCl_3 solution of **4** at 15 $^\circ\text{C}$ displayed a broader ^1H NMR spectral feature (Figure S2) than the non-amide reference **2_R** (Figure S1). However, upon heating to 55 $^\circ\text{C}$ (Figure S3) or mixing with a small amount of CD_3OD (Figure S4) to deteriorate the H-bonding network, the spectrum became considerably sharp. Hence, the bowl inversion of **4** is likely decelerated as a result of its intramolecular H-bonding network.

In circular dichroism (CD) spectroscopy (Figure 4b), compound **4** in (*R*)-limonene at 20 $^\circ\text{C}$ (green solid curve) displayed a clear Cotton effect in an absorption range of the corannulene moiety, where the observed spectral pattern is the mirror image of that measured in (*S*)-limonene (green dashed curve). As expected from the nonassembling behavior of **4** (Figure 3a), its apparent molar ellipticities ($[\theta]$) evaluated at 337 and 378 nm in (*R*)-limonene remained unchanged with the concentration of **4** ($[\text{4}]$) even when $[\text{4}]$ was varied over a wide range from 3 to 300 μM (Figure S22a). In contrast to **4**, side-chain-chiral **5_R** and **5_S** exhibited chiroptical activity even in an achiral solvent such as MCHex, displaying mirror-imaged CD spectra of one another (Figure 4a, blue and red solid curves, respectively). One may also notice that the CD spectral pattern thus observed for **5** in MCHex is essentially the same as that of **4** in limonene (Figure 4b, green curves). As shown by the DLS profiles in Figure 3c,d together with other supporting data (Figures S17b, S18c, S19, S20, and S22b,c),⁹ compound **5** does not self-assemble in solution, most likely because its amide units, just as in the case of **4**, are H-bonded only “intramolecularly”. Again, this “intramolecular” H-bonding^{8b} is crucial for **5** to exert chiroptical activity, as addition of a protic solvent such as EtOH (30 vol %) to an MCHex solution of **5_R**

resulted in complete disappearance of its CD activity (Figure S21).⁹

By means of vibrational circular dichroism (VCD) spectroscopy, we successfully confirmed that the amide units in **4** adopt a chiral geometry in limonene. As shown in Figure 4d, compound **4** in (*R*)- (blue solid curve) and (*S*)-limonene (red solid curve) at 20 $^\circ\text{C}$ displayed mirror-image VCD spectra of one another with a clear Cotton effect around a stretching vibrational band due to the H-bonded amide $\text{C}=\text{O}$. Likewise, Figure 4c shows that compounds **5_R** (blue solid curve) and **5_S** (red solid curve) are VCD-active even in MCHex at 20 $^\circ\text{C}$, displaying mirror-image spectra of one another. The VCD spectral patterns thus observed for **4** and **5** are consistent with those simulated for stereoisomers **3_{AA}** and **3_{CC}** in Figure 2 (Figure S25).^{9,16} As already described, the side-chain amide units in **4** and **5** are H-bonded only “intramolecularly” and certainly form a chiral cyclic amide network along the corannulene periphery. The observed VCD activities clearly indicate that the cyclic amide network, when located in a chiral environment, is enriched in either a clockwise or anticlockwise geometry (Figure 2). Consequently, the bowl inversion equilibrium is desymmetrized, giving rise to a preferred handedness of the C_5 -symmetric corannulene core.

As can be seen from Figure 4a, the spectral interference for CD spectroscopy by the solvent absorption is much less in MCHex than in limonene (Figure 4b). Therefore, by using the CD spectral data of **5_R** in MCHex over a wide temperature range from -40 to 40 $^\circ\text{C}$, we evaluated the intrinsic molar ellipticity of its corannulene core at 337 nm as $[\theta] = 2.9 \times 10^4 \text{ deg cm}^{-2} \text{ dmol}^{-1}$ (Figure S26).^{9,14} On the basis of this value, the % diastereomeric excess (% de) of **5** at 20 $^\circ\text{C}$ in MCHex was estimated as 32%, which was enhanced to 45% when the temperature was lowered to -40 $^\circ\text{C}$. It is noteworthy that when (*R*)-limonene was used as the solvent, the % de of **5_R** was considerably enhanced to 80% even at 20 $^\circ\text{C}$ (Figure 4b, blue solid curve). On the contrary, in (*S*)-limonene, **5_R** was substantially CD-silent (Figure 4b, blue broken curve). Consistently, **5_S** showed enhanced chiroptical activity in (*S*)-limonene (Figure 4b, red broken curve) but was hardly CD-active in (*R*)-limonene (Figure 4b, red solid curve). Therefore, the side-chain chiral centers of **5** likely cooperate with the chiral solvent, either positively or negatively, in desymmetrizing the bowl inversion equilibrium of the corannulene core (Figure 2). In regard to the chiral solvent effect, we observed the following interesting phenomenon. When the enantiomeric purity of limonene as the solvent was decreased, the CD intensity of **4** at 337 nm decreased as expected. However, this spectral change was not linear but instead was sigmoidal with respect to the applied change in the % enantiomeric excess (% ee) of limonene (Figure 4e). The same held true for the CD intensity change at 378 nm. As shown in Figure 4f, an analogous nonlinear response also resulted in a comparable study on **5**, where the apparent $[\theta]$ values at 337 and 378 nm changed sigmoidally as the % ee of limonene was changed. Such a nonlinear phenomenon, known as the “majority rule”, has mostly been reported for helical polymers (including their noncovalent analogues), whose handednesses are determined by a cooperative interaction among multiple chiral entities involved.¹⁵

Why do compounds **4** and **5**, though not polymeric, obey the majority rule (Figure 4e,f)? This is not surprising when one considers that the cyclic amide network (Figure 2) is a thermodynamically preferred structure that enables all of the

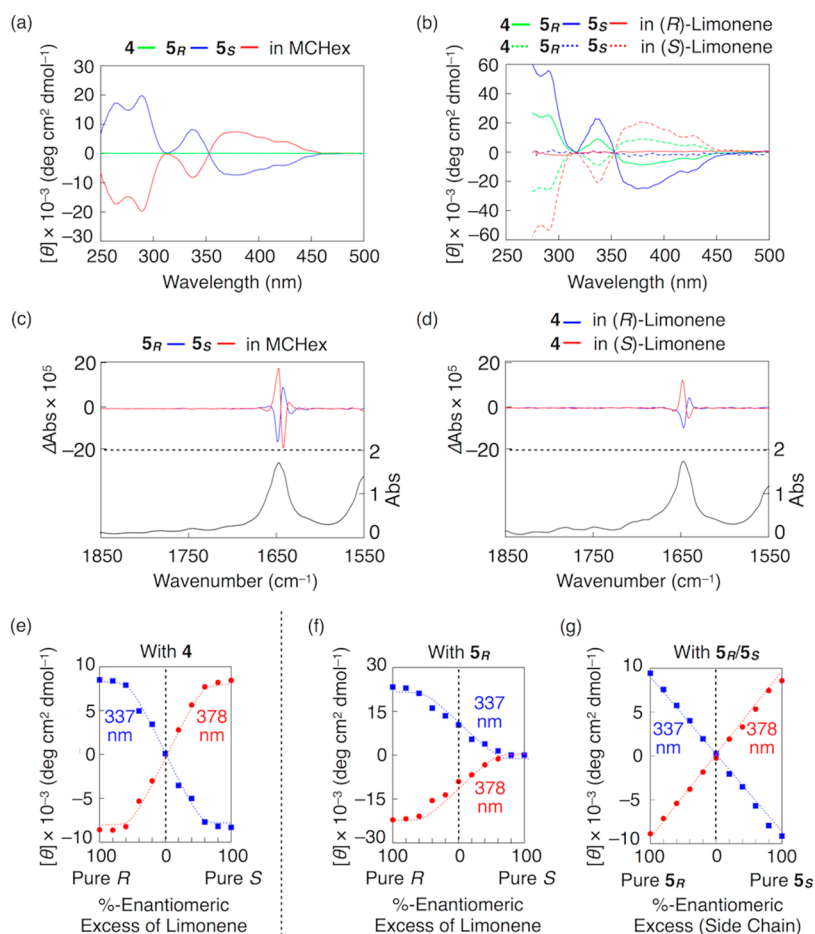


Figure 4. (a, b) Circular dichroism (CD) spectra at 20 °C of **4** (green), **5_R** (blue), and **5_S** (red) (20 μM) in (a) methylcyclohexane (MCHex) and (b) (*R*)- (solid curves) and (*S*)-limonene (dashed curves). (c, d) Vibrational circular dichroism (VCD, upper) and IR (lower) spectra at 20 °C of (c) **5_R** (blue and black curves) and **5_S** (red curve) in MCHex and (d) **4** in (*R*)- (blue and black curves) and (*S*)-limonene (red curve). (e–g) Changes in apparent $[\theta]$ values at 337 (blue plots) and 378 nm (red plots) of (e) **4** and (f) **5_R** in limonene as functions of the % enantiomeric excess (% ee) of limonene and (g) **5** in MCHex as functions of the % ee of the side-chain chiral centers of **5**.

amide units to be H-bonded at the same time. Suppose that **4** is dissolved in a solvent composed of a 3:2 mixture of the limonene enantiomers (20% ee) and also that this solvent stereochemically prefers three neighboring amide units in **4** to be H-bonded clockwise and the remaining two to be H-bonded anticlockwise (Figure 5, left). However, this preference cannot be accepted thermodynamically, since the

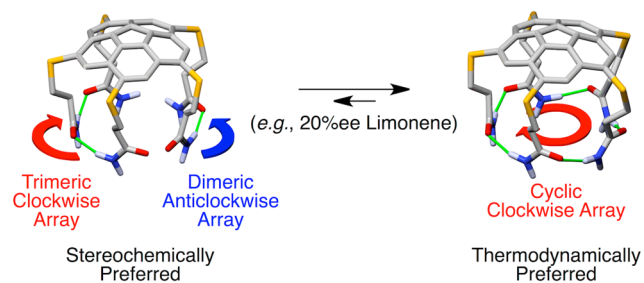


Figure 5. Schematic representation of a possible mechanism explaining why *C*₅-symmetric corannulenes **4** and **5** exert a sign of chiroptical amplification (majority rule) in response to a change in the % ee of limonene. The molecular model for the cyclic clockwise array (right) is a DFT-optimized structure identical to that utilized in Figure 2.

cyclic amide network (Figure 5, right) would not be accomplished. Hence, the minor H-bonded array (blue) should flip into its opposite geometry so as to join the major array (red). Because of the presence of such a large thermodynamic bias originating from the bowl shape of the corannulene core (Figure 2), the chiroptical response likely obeys the majority rule. Just in case, we examined the chiroptical behaviors of **5_R** and **5_S** when they were mixed at different mole ratios in MCHex. As expected from the nonassembling behavior of **5**, the apparent $[\theta]$ values at 337 and 378 nm both changed linearly with the % ee of **5** employed (Figure 4g).

CONCLUSIONS

Inspired by an unexpected observation that *C*₅-symmetric corannulene **4** (Figure 1), though carrying amide-appended side chains, does not self-assemble in solution, we noticed that its peripheral amide units are H-bonded only “intramolecularly” along the corannulene periphery. This finding was successfully extended to a strategy for desymmetrizing the bowl inversion equilibrium of *C*₅-symmetric corannulenes (Figure 2). Consequently, a “genuine” chiroptical feature of the *C*₅-chiral corannulene skeleton was first unveiled. Obviously, the observed spectral pattern essentially differs from that of the organometallic adduct between pentamethylcorannulene and a chiral ruthenium complex.⁶ It is also noteworthy that except for

polymeric and supramolecular hosts of large dimensions,^{17,18} no unimolecular hosts other than our chiral corannulenes have been reported to sense chiral hydrocarbons. Furthermore, no other unimolecular hosts obey the majority rule in their responses to chiral stimuli.¹⁵

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of synthesis; analytical data obtained by mass spectrometry and NMR, IR, absorption, and CD spectroscopy; and results of DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380.
- (2) For reviews, see: (a) Wu, Y. T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843. (b) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868.
- (3) Lovas, F. J.; McMahon, R. J.; Grabow, J. U.; Schnell, M.; Mack, J.; Scott, L. T.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **2005**, *127*, 4345.
- (4) (a) Abdourzak, A. H.; Sygula, A.; Raibideau, P. W. *J. Am. Chem. Soc.* **1993**, *115*, 3010. (b) Seiders, T. J.; Baldrige, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517. (c) Eliseeva, M. N.; Scott, L. T. *J. Am. Chem. Soc.* **2012**, *134*, 151669.
- (5) (a) Valenti, G.; Bruno, C.; Rapino, S.; Fiorani, A.; Jackson, E. A.; Scott, L. T.; Paolucci, F.; Marcaccio, M. *J. Phys. Chem. C* **2010**, *114*, 19467. (b) Zabula, A. V.; Filatov, A. S.; Spisak, S. N.; Rogachev, A. Y.; Petrukhina, M. A. *Science* **2011**, *333*, 1008. (c) Bauert, T.; Zoppi, L.; Koller, G.; Siegel, J. S.; Baldrige, K. K.; Ernst, K.-H. *J. Am. Chem. Soc.* **2013**, *135*, 12857. (d) Stuparu, M. C. *Angew. Chem., Int. Ed.* **2013**, *52*, 7786. (e) Kuvychko, I. V.; Dubceac, C.; Deng, S. H. M.; Wang, X. B.; Granovsky, A. A.; Popov, A. A.; Petrukhina, M. A.; Stauss, S. H.; Boltalina, O. V. *Angew. Chem., Int. Ed.* **2013**, *52*, 7505. (f) Juriček, M.; Strutt, N. L.; Barnes, J. C.; Butterfield, A. M.; Dale, E. J.; Baldrige, K. K.; Stoddart, J. F.; Siegel, J. S. *Nat. Chem.* **2014**, *6*, 222.
- (6) Bandera, D.; Baldrige, K. K.; Linden, A.; Dorta, R.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 865.
- (7) (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, No. 154104. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456.
- (8) (a) Rebek, J., Jr. *Acc. Chem. Res.* **1990**, *23*, 12. (b) Mishiro, K.; Furuta, T.; Sasamori, T.; Hayashi, K.; Tokitoh, N.; Futaki, S.; Kawabata, T. *J. Am. Chem. Soc.* **2013**, *135*, 13644.
- (9) See the Supporting Information.
- (10) Bancu, M.; Rai, A. K.; Cheng, P. C.; Gilardi, R. D.; Scott, L. T. *Synlett* **2004**, 173.
- (11) Miyajima, D.; Tashiro, K.; Araoka, F.; Takezoe, H.; Kim, J.; Kato, K.; Takata, M.; Aida, T. *J. Am. Chem. Soc.* **2009**, *131*, 44.

(12) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981.

(13) (a) Brunsveld, L.; Folmer, B. B. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071. (b) De Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687.

(14) (a) Brunden, K. R.; Uratani, Y.; Cramer, W. A. *J. Biol. Chem.* **1984**, *259*, 7682. (b) Scholtz, J.; Marqusee, S.; Baldwin, R. L.; York, E. J.; Bolen, D. W. *Proc. Natl. Acad. Sci. U.S.A.* **1991**, *88*, 2854. (c) Dolarin, C.; Jiang, H.; Leger, J. M.; Guionneau, P.; Huc, I. *J. Am. Chem. Soc.* **2005**, *127*, 12943. (d) Greenfield, N. J. *Nat. Protoc.* **2006**, *1*, 2527.

(15) (a) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138. (b) Jin, W.; Fukushima, T.; Niki, M.; Kosaka, A.; Ishii, N.; Aida, T. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10801. (c) Van Gestel, J.; Palmans, A. R. A.; Titulaer, B.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 5490.

(16) (a) Smulders, M. M. J.; Buffeteau, T.; Cavagnat, D.; Wolffs, M.; Schenning, A. P. H. J.; Meijer, E. W. *Chirality* **2008**, *20*, 1016. (b) Aparicio, F.; Nieto-Ortega, B.; Najera, F.; Ramirez, F. J.; Navarrete, J. T. L.; Casado, J.; Sanchez, L. *Angew. Chem., Int. Ed.* **2013**, *52*, 1.

(17) (a) Aimi, J.; Oya, K.; Tsuda, A.; Aida, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 2031. (b) Ghosh, S.; Li, X. Q.; Stepaneko, V.; Würthner, F. *Chem.—Eur. J.* **2008**, *14*, 11343. (c) Isare, B.; Linares, M.; Zargarian, L.; Fermanjian, S.; Miura, M.; Motohashi, S.; Vanthuyne, N.; Lazzaroni, N.; Bouteiller, L. *Chem.—Eur. J.* **2010**, *16*, 173.

(18) (a) Green, M. M.; Khatri, C.; Peterson, N. C. *J. Am. Chem. Soc.* **1993**, *115*, 4941. (b) Nakashima, H.; Koe, J. R.; Torimitsu, K.; Fujiki, M. *J. Am. Chem. Soc.* **2001**, *123*, 4847. (c) Hembury, G. A.; Borovkov, V. V.; Inoue, Y. *Chem. Rev.* **2008**, *108*, 1. (d) Dai, Z.; Lee, J.; Zhang, W. *Molecules* **2012**, *17*, 1247.