CRYSTAL GROWTH & DESIGN

pubs.acs.org/crystal

Article

Total Syntheses Supramolecular Style: Solid-State Construction of [2.2]Cyclophanes with Modular Control of Stereochemistry

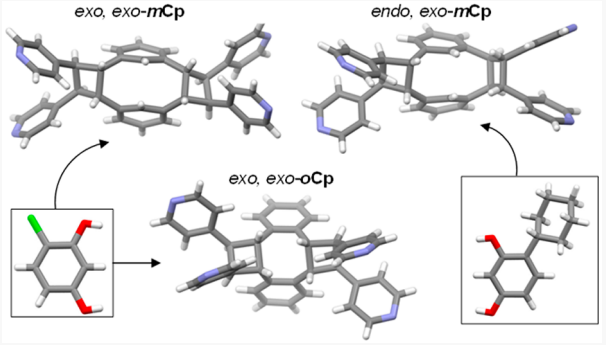
Tomislav Friščić, Elizabeth Elacqua,[⊥] Saikat Dutta,[⊥] Shalisa M. Oburn, and Leonard R. MacGillivray*

Cite This: *Cryst. Growth Des.* 2020, 20, 2584−2589

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: A series of templated solid-state reactions are used to construct the 'bent' isomer of the [2.2]cyclophane family of molecules. Small-molecule hydrogen-bond-donor templates based on resorcinol complete the supramolecular construction of ortho-, meta-, and para-[2.2]cyclophanes in the solid state. The family of *exo,exo*-dicyclobutyl-[2.2]cyclophanes forms regiospecifically in up to quantitative yields. The confines of the organic solid state and the modular nature of the template approach allow for the generation of a less stable *exo,endo*-[2.2]metacyclophane by simply changing the template to enforce a concomitant change in self-assembly. Our results demonstrate the first completed solid-state construction of each member of the family of [2.2]cyclophanes.



INTRODUCTION

The ability to form covalent bonds in the crystalline state has received widespread attention with implications in organic synthesis, green chemistry, optics, nanotechnology, and catalysis.[1−13] In this context, efforts to exploit principles of supramolecular chemistry to confront frustrating effects of crystal packing have been highly promising as a means to reliably direct the formation of covalent bonds in solids. Specifically, small-molecule hydrogen-bond-donor templates based on resorcinol (**res**) have provided stereocontrolled and high-yielding access to architecturally rich molecules such as [*n*]ladderanes[14] and [2.2]paracyclophanes (***p*Cp**).[15−19] Nevertheless, difficulties to exert control over the assembly and organization of molecules in solids continue to severely limit the scope of organic molecules that have been constructed in solids.

[2.2]Cyclophanes are tractable target molecules of [2+2] photodimerizations performed in solids.[20−23] Whereas [2.2]-cyclophanes were originally introduced over 50 years ago, the three fundamental isomers (i.e., linear ***p*Cp** and bent meta (***m*Cp**)- and ortho-[2.2]cyclophane (***o*Cp**)) continue to garner attention in synthetic chemistry and materials science.[24−32] Moreover, while the face-to-face π-stacked geometry inherent to a [2.2]cyclophane core is accessible through double photocycloadditions, there have been very limited reports on the syntheses of ***p*Cps**[16,25,33,34] and ***m*Cps** in organic solids,[24,35−37] with no reports of the ***o*Cp** isomer. All examples to date also lack a systematic synthetic approach, which is a hallmark of solution-phase organic synthesis. The syntheses of [2.2]cyclophanes in the organic solid state have thus lagged considerably in comparison to the liquid phase. Double photocycloadditions of dienes to form [2.2]cyclophanes in solution have been reported in classic work by Nishimura yet typically occur in exceptionally low yields (0.5−40%).[15,38]

Herein, we report the first completed, systematic total syntheses of [2.2]cyclophanes in the organic solid state. We utilize principles of supramolecular chemistry to show how a series of templated solid-state syntheses, or covalent captures,[39] provide stereocontrolled and quantitative access to bent isomers of the [2.2]cyclophane family of molecules (Scheme 1). Specifically, we report the solid-state construction of the ortho cyclophane ***o*Cp** and the two meta cyclophanes ***m*Cp-1** and ***m*Cp-2**. Both ***m*Cp-1** and ***o*Cp** have been constructed using 4-chloro-**res** (**4-Cl-res**) from the photoactive binary cocrystals 2(**4-Cl-res**)·2(***o*-bpeb**) and 2(**4-Cl-res**)·2(***m*-bpeb**), respectively (Scheme 2). The less sterically favored ***m*Cp-2** has been constructed using 4-cyclohexyl-**res** (**4-Cy-res**) from the cocrystal 2(**4-Cy-res**)·2(***m*-bpeb**). In constructing ***m*Cp-2**, we show how the stereochemical outcome of a [2.2]cyclophane synthesis can be advantageously manipulated[16] by modifying the pendant R group.

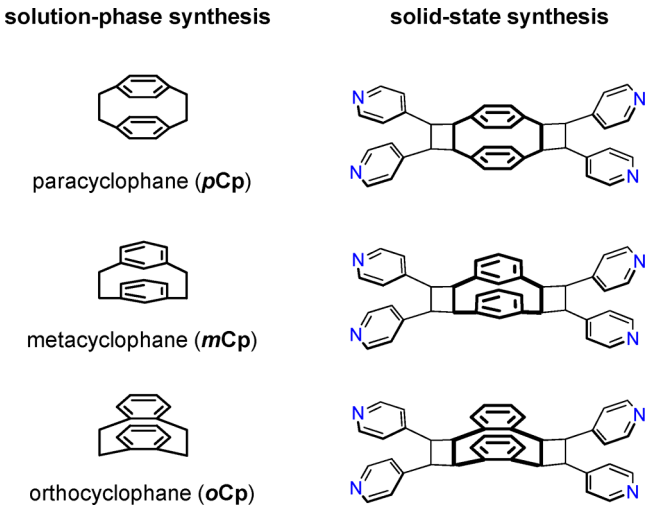
RESULTS AND DISCUSSION

The first [2.2]cyclophane formed in the solid state was a ***p*Cp** in pioneering work of Hasegawa.[18,40] Since the original report, there have been very limited examples of [2.2]cyclophanes forming in solids. A major obstacle to generate a [2.2]-

Received: December 24, 2019
Revised: January 27, 2020
Published: January 30, 2020

https://dx.doi.org/10.1021/acs.cgd.9b01712
Cryst. Growth Des. 2020, 20, 2584−2589

Scheme 1. Para-, Meta-, and Orthocyclophanes Generated in Solution and in the Solid State

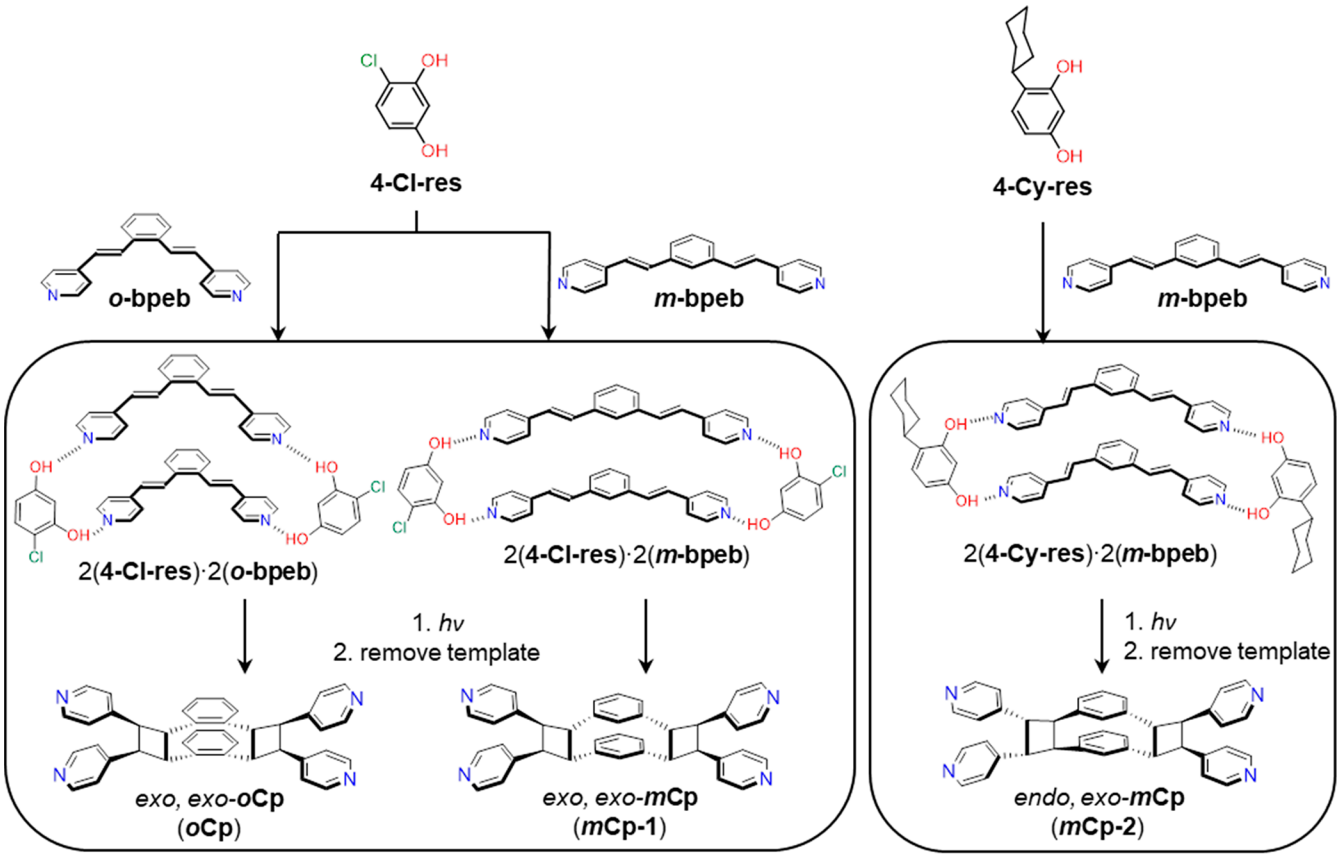


cyclophane in a solid relates to both achieving and maintaining the stacked geometry during cyclobutane generation. The problem of cyclobutane ring formation can be confronted using small-molecule templates to direct the reactivity in binary cocrystals. Our first demonstration was the directed synthesis of a ***p*Cp** (Scheme 1). To date, however, there still remains no report of a solid-state synthesis of an ***o*Cp**. We expected that cocrystallization of **res** with *o*-**bpeb** would allow us to generate a binary cocrystal wherein the dienes are preorganized by O−H···N hydrogen bonds for a double photocycloaddition to give the *exo,exo*-orthocyclophane ***o*Cp** (Scheme 2, left). The related *exo,exo*-metacyclophane ***m*Cp-1** has been very recently reported to form in a coordination network that exhibits fluorescence switching (Scheme 1, center). A synthesis of the *endo,exo* isomer ***m*Cp-2**, however, has not been reported (Scheme 2, right). We describe the solid-state construction of ***m*Cp-2** here by identifying a template that influences the solid-state packing and resulting stereochemical outcome of the conformation of ***m*-bpeb**. Collectively, our work provides the first completed and systematic total syntheses—akin to total syntheses practiced in solution—of [2.2]cyclophanes in solids. Our efforts to achieve the total syntheses are made possible by principles of supramolecular chemistry.

Reactive 2:2 Cocrystal To Form *o*Cp. Single crystals of 2(**4-Cl-res**)·2(*o*-**bpeb**) were formed by combining warm solutions of ***o*-bpeb** (200 mg, 0.77 mmol) with equimolar **4-Cl-res** (112 mg, 0.77 mmol) dissolved in nitromethane (15 mL). Cooling to ambient temperature generated colorless platelike crystals suitable for single-crystal X-ray diffraction.

The components of 2(**4-Cl-res**)·2(*o*-**bpeb**) crystallize in the triclinic space group $P\bar{1}$ (Figure 1) as discrete four-component hydrogen-bonded assemblies of 2(**4-Cl-res**)·2(*o*-**bpeb**) sustained by four O−H···N hydrogen bonds (distances (Å): O51···N1a 2.61(1)/O51···N1b 2.79(1), O52···N20 2.71(1), O59···N52 2.74(1), O45···N23 2.73(1)) (Figure 1a). The diolefins stack in a face-to-face geometry, with one C═C bond disordered over two sites (occupancies: 0.56:0.44) (Figure 1b). Nearly half of the assemblies contain a pair of C═C bonds that lie criss-crossed (centroid separations: 4.32 Å), while the remaining half contains pairs of C═C bonds at the

Scheme 2. Generation of Ortho- and Meta-[2.2]cyclophanes Using Cocrystals Based on res Templates



https://dx.doi.org/10.1021/acs.cgd.9b01712
Cryst. Growth Des. 2020, 20, 2584−2589

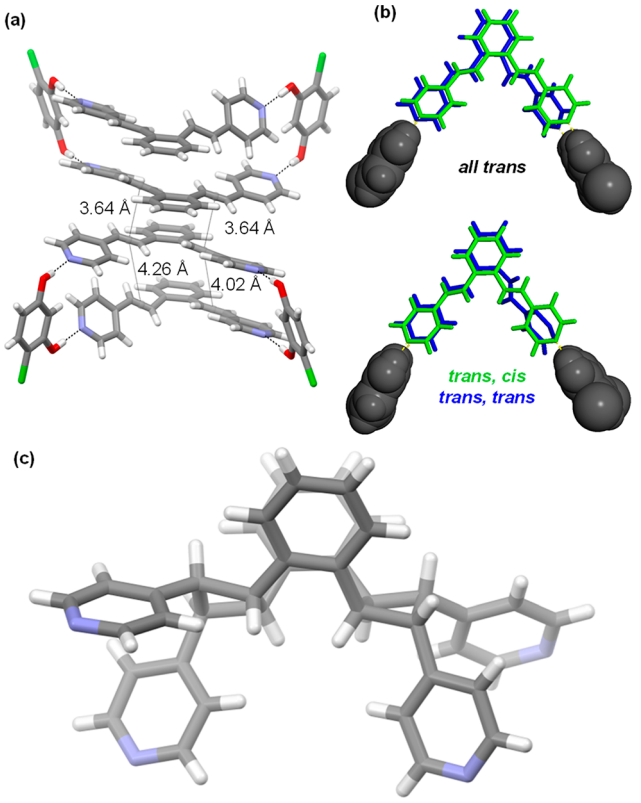


Figure 1. X-ray structures: 2(**4-Cl-res**)·2(***o*-bpeb**) showing (a) C═C distances and (b) C═C disorder of all trans (top) and trans,cis (green) with trans,trans (blue, bottom) conformations and ***o*Cp**·$2H_2O$ showing (c) isolated orthocyclophane.

upper limit for a [2+2] photodimerization (centroid separations: 4.26 and 4.02 Å).[41] The assemblies stack in columns perpendicular to the *a* axis in a head-to-tail fashion with nearest-neighbor C═C bonds separated by 3.64 Å. The latter C═C bonds are significantly displaced (28.1/26.1°), which contrasts with the stacked C═C bonds within the hydrogen-bonded assemblies (8.4/19.9°).[42,43]

When a finely ground crystalline sample of 2(**4-Cl-res**)·2(***o*-bpeb**) was exposed to UV light for 75 h, ^{1}H NMR spectroscopy revealed ***o*Cp** to form stereospecifically in quantitative yield. The generation of ***o*Cp** was evidenced by the disappearance of olefinic signals (7.97 and 7.13 ppm) and the appearance of cyclobutane protons (4.87 and 4.62 ppm). We attribute the quantitative formation of ***o*Cp**[41] to the C═C bonds undergoing a pedal-like motion.[44,45]

To confirm the stereochemistry of ***o*Cp**, single crystals in the form of colorless plates following basic extraction from **4-Cl-res** were obtained by recrystallization from nitromethane. The orthocyclophane crystallizes as the dihydrate ***o*Cp**·$2H_2O$ in the triclinic space group $P\bar{1}$ (Figure 1c). ***o*Cp** and the water molecules assemble by O−H···N hydrogen bonds to form discrete assemblies (see the Supporting Information). The stereocontrolled and quantitative generation of ***o*Cp** from 2(**4-Cl-res**)·2(*o*-**bpeb**) is the first example of an ortho[2.2]-cyclophane generated in a solid.

Reactive 2:2 Cocrystals To Form mCp Stereoisomers. The stereoisomers *m***Cp-1** and *m***Cp-2** were generated using **4-Cl-res** and **4-Cy-res**, respectively. Single crystals of 2(**4-Cl-res**)·2(***m*-bpeb**) and 2(**4-Cy-res**)·2(***m*-bpeb**) were obtained by combining warm solutions of ***m*-bpeb** (200 mg, 0.70 mmol) with equimolar **4-Cl-res** (112 mg, 0.77 mmol) and **4-Cy-res** (148 mg, 0.77 mmol) in nitromethane (15 mL). Cooling to ambient temperature generated colorless rods and prisms of 2(**4-Cl-res**)·2(***m*-bpeb**) and 2(**4-Cy-res**)·2(***m*-bpeb**), respectively, for single-crystal X-ray diffraction.

Generation of *m*Cp-1. The components of 2(**4-Cl-res**)·2(***m*-bpeb**) crystallize in the triclinic space group $P\bar{1}$ (Figure 2)

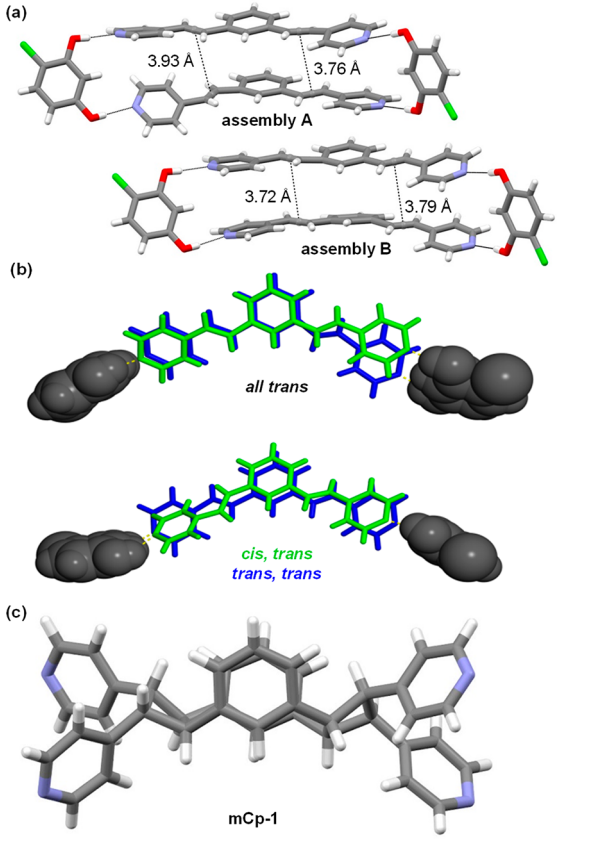


Figure 2. X-ray structures: for 2(**4-Cl-res**)·2(***m*-bpeb**) (a) distances separating reactive olefinic sites and (b) olefin disorder demonstrating all trans (top) and trans,cis (green) with trans,trans (blue, bottom) conformations and for (***m*Cp-1**)·4(**benzene**)·H_2O showing (c) *exo,exo-**m*Cp-1**.

as two crystallographically unique four-component hydrogen-bonded assemblies sustained by four O−H···N hydrogen bonds (distances (Å): assembly **A**, O9A···N10A 2.8565(3), O32A···N29A 2.7026(3), O33A···N41A 2.8961(3), O8A···N60A 2.7031(3); assembly **B**, O9B···N10B 2.7225(3), O32B···N29B 2.7376(3), O33B···N41B 2.7232(3), O8B···N60B 2.5435(3)) (Figure 2a). The diolefins adopt *trans,trans*[46] conformations and stack in nearly eclipsed geometries (Figure 2b). One C═C bond lies disordered in two positions (occupancies: 0.60:0.40). As a consequence of the assembly process, the diolefins stack with the C═C bonds in positions for [2+2] photodimerizations (centroid separations: 4.26 and 4.02 Å).[41] The assemblies stack in columns perpendicular to the *a* axis with nearest-neighbor C═C bonds separated by 3.64 Å.

Single-Crystal Reactivity. The cocrystal 2(**4-Cl-res**)·2(***m*-bpeb**) is highly photoreactive. The difference Fourier map from the X-ray data prior to exposing the solid to UV radiation shows diolefins of one assembly to partially react under ambient light in a single-crystal to single-crystal (SCSC)

https://dx.doi.org/10.1021/acs.cgd.9b01712
Cryst. Growth Des. 2020, 20, 2584−2589

transformation to form ***m*Cp-1** (occupancy reacted/unreacted: 0.40:0.60) (Figure 3).

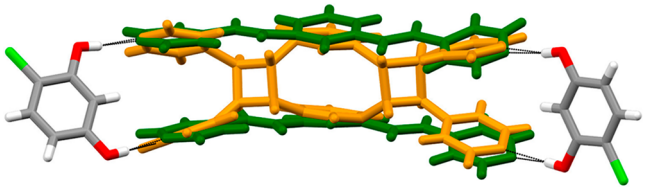


Figure 3. X-ray structure showing the partial SCSC reaction of 2(**4-Cl-res**)·2(***m*-bpeb**) to form ***m*Cp-1**.

When a finely ground sample of crystalline 2(**4-Cl-res**)·2(***m*-bpeb**) was exposed to UV irradiation for 75 h, ^{1}H NMR spectroscopy revealed the complete disappearance of diolefin resonances (7.38 and 7.57 ppm) and the appearance of three cyclobutane signals (4.78, 4.71, and 4.53 ppm) that correspond to ***m*Cp-1** (yield 78%) and ***m*Cp-2** (yield 22%).[15] The generation of the less symmetrical ***m*Cp-2** can be attributed to pedal-like rotation of C═C bonds.[44,45] The formation of each product is consistent with the photodimerizations occurring within each hydrogen-bonded structure.[16]

To confirm the *exo,exo* stereochemistry, single crystals of ***m*Cp-1** following removal from **4-Cl-res** using base were obtained as colorless prisms from benzene.[47] ***m*Cp-1** crystallizes in the monoclinic space group *C*2/*c* as (***m*Cp-1**)·4(**benzene**)·H_2O (Figure 2c). The metacyclophane and water molecules form 1D hydrogen-bonded chains. The chains propagate along the *a*-axis to generate cavities filled with disordered benzenes (Platon calculated void volume 661 Å^3). An additional benzene participates in edge to face $\pi\cdots\pi$ interactions with hydrogen-bonded chains along the *c* axis.

Generation of *m*Cp-2. The components of 2(**4-Cy-res**)·2(***m*-bpeb**), which react to afford *endo,exo*-***m*Cp**, crystallize in the triclinic space group $P\bar{1}$ (Figure 4) as a discrete hydrogen-bonded assembly sustained by four O−H···N bonds (distances (Å): O66···N1 2.77(1), O23···N20 2.78(1), O30···N37 2.77(1), O59···N56 2.78(1)) (Figure 4a). One diolefin adopts two *trans* conformations, while the second diolefin adopts a cis,trans conformation with disorder over two closely related positions (cis/trans occupancies: 0.16:0.84 and 0.84:0.16) (Figure 4b).[48] Each pair of olefins is aligned for a [2+2] photodimerization (pairs of C···C separations (Å): 4.18 and 4.32). Nearest-neighbor assemblies are stacked with C═C bonds lying crisscrossed and separated by 3.58 Å (Figure 4a).

A crystalline powder of 2(**4-Cy-res**)·2(***m*-bpeb**) was exposed to UV irradiation for 36 h. ^{1}H NMR spectroscopy showed the quantitative disappearance of the diolefin (7.49 and 7.38 ppm) and the emergence of cyclobutane signals consistent with the *endo,exo* isomer ***m*Cp-2** (4.78 and 4.51 ppm). That ***m*Cp-2** formed quantitatively can be attributed to pedal-like rotations of the C═C bonds.[44,45] Single crystals of ***m*Cp-2**, following removal from **4-Cy-res** using base, were obtained as colorless plates from acetonitrile. ***m*Cp-2** crystallized as (***m*Cp-2**)·(**CH_3CN**)·H_2O in the monoclinic space group $P2_1/c$. The structure determination confirmed the *endo,exo* stereochemistry (Figure 4c).

Exploiting Modularity. That **res** templates assemble ***m*-bpeb** to afford two stereoisomers of ***m*Cp** demonstrates the modularity of the template method. In combination with the dynamic nature of C═C units,[49] both high-yielding and stereoselective formations of the isomers were achieved. The

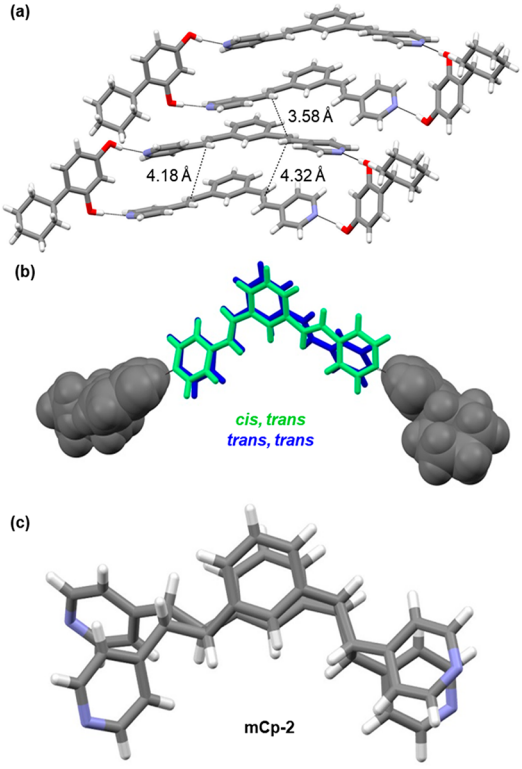


Figure 4. X-ray structures of 2(**4-Cy-res**)·2(***m*-bpeb**) with (a) distances separating reactive olefinic sites and (b) olefin disorder demonstrating trans,cis (green) with trans,trans (blue) conformations and (c) structure of ***m*Cp-2**.

ability to switch the template to afford either the *exo,exo* or less stable *endo,exo* isomer illustrates that the cocrystal method can be utilized to covalently capture[50−53] conformations of reactive molecules to form targeted products.

Structural and Optical Properties. ***m*Cp-1**, ***m*Cp-2**, and ***o*Cp** exhibit centroid-to-centroid stacked distances of 3.4 Å (***m*Cp1** and ***m*Cp-2**) and 4.2 Å (***o*Cp**) (see the Supporting Information). The corresponding distance for ***p*Cp** is 3.0 Å.[16] The rings of ***m*Cp-1** and ***m*Cp-2** (tilts: 38.4/36.2°) and ***o*Cp** (tilt: 61.5°) stack edge to face. Fluorescence data are in line with the cyclobutyl rings of ***m*Cp-1** and ***m*Cp-2** in comparison to that of ***o*Cp** being efficient through-bond electron donors.[9] ***m*Cp** exhibits a λ_{max} value (412 nm) comparable to that of ***p*Cp** despite greater tilting of the rings. ***o*Cp** displays a markedly broader fluorescence envelope and red-shifted λ_{max} value (456 nm) in the wake of the more tilted geometry.

CONCLUSIONS

In summary, we have used **res** templates to complete the total syntheses of [2.2]cyclophanes in the solid state. We have exploited the modularity of cocrystals to manipulate the stereochemical course of solid-state photodimerizations to control the generation of supramolecular and molecular isomers. We expect these principles to be used to generate more complex supramolecular assemblies and provide access to new complex targets in solids.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.9b01712.

https://dx.doi.org/10.1021/acs.cgd.9b01712
Cryst. Growth Des. 2020, 20, 2584−2589

Full experimental details including materials, methods, syntheses, and analyses along with characterization data from 1D spectroscopy and single-crystal X-ray diffraction (PDF)

Accession Codes

CCDC 1916583−1916588 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Leonard R. MacGillivray − *Department of Chemistry, University of Iowa, Iowa City, Iowa 52245-1297, United States;* orcid.org/0000-0003-0875-677X; Email: len-macgillivray@uiowa.edu

Authors

Tomislav Friščić − *Department of Chemistry, McGill University, H3A0B8 Montreal, Canada*

Elizabeth Elacqua − *Department of Chemistry and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, United States;* orcid.org/0000-0002-1239-9560

Saikat Dutta − *Department of Chemistry, National Institute of Technology Karnataka, Mangalore, Karnataka, India*

Shalisa M. Oburn − *Department of Chemistry, University of Iowa, Iowa City, Iowa 52245-1297, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.9b01712

Author Contributions

⊥E.E. and S.D. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation (L.R.M.: DMR-1708673) for funding.

REFERENCES

(1) Bhogala, B. R.; Captain, B.; Parthasarathy, A.; Ramamurthy, V. Thiourea as a Template for Photodimerization of Azastilbenes. *J. Am. Chem. Soc.* **2010**, *132*, 13434.

(2) MacGillivray, L. R.; Papaefstathiou, G. S.; Friščić, T.; Hamilton, T. D.; Bučar, D.-K.; Chu, Q.; Varshney, D. B.; Georgiev, I. G. Supramolecular Control of Reactivity in the Solid State: From Templates to Ladderanes to Metal−Organic Frameworks. *Acc. Chem. Res.* **2008**, *41*, 280.

(3) Santra, R.; Banerjee, K.; Biradha, K. Weak Ag···Ag and Ag···π interactions in templating regioselective single and double [2 + 2] reactions of *N,N′*-bis(3-(4-pyridyl)acryloyl)-hydrazine: synthesis of an unprecedented tricyclohexadecane ring system. *Chem. Commun.* **2011**, *47*, 10740.

(4) Zhao, Y.; Li, Z.; Liu, J.; Hu, C.; Zhang, H.; Qin, B.; Wu, Y. Intermolecular vibrational modes and H-bond interactions in crystalline urea investigated by terahertz spectroscopy and theoretical calculation. *Spectrochim. Acta, Part A* **2018**, *189*, 528.

(5) Chen, Z.; Li, Z.; Guo, H.; Zhang, J.; Ren, Z.; Yan, S.; Xie, P.; Zhang, R. Supramolecular Template-Directed Synthesis of Soluble Quadruple-Chain Ladder Polyphenylsiloxane (Ph-QCLP) with High Molecular Weight. *Chem. Mater.* **2012**, *24*, 1968.

(6) Oburn, S. M.; Swenson, D. C.; Mariappan, S. V. S.; MacGillivray, L. R. Supramolecular Construction of an Aldehyde−Cyclobutane via the Solid State: Combining Reversible Imine Formation and Metal−Organic Self-Assembly. *J. Am. Chem. Soc.* **2017**, *139*, 8452.

(7) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friscic, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. Mechanochemistry: opportunities for new and cleaner synthesis. *Chem. Soc. Rev.* **2012**, *41*, 413.

(8) Xu, H.; Gao, J.; Jiang, D. Stable, crystalline, porous, covalent organic frameworks as a platform for chiral organocatalysts. *Nat. Chem.* **2015**, *7*, 905.

(9) Elacqua, E.; Bučar, D.-K.; Skvortsova, Y.; Baltrusaitis, J.; Geng, M. L.; MacGillivray, L. R. Dramatic Red-Shifted Fluorescence of [2.2]Paracyclophanes with Peripheral Substituents Attached to the Saturated Bridges. *Org. Lett.* **2009**, *11*, 5106.

(10) Elacqua, E.; Jurgens, P. T.; Baltrusaitis, J.; MacGillivray, L. R. Organic nanocrystals of [2.2]paracyclophanes achieved via sonochemistry: enhanced and red-shifted emission involving edge-to-face chromophores. *CrystEngComm* **2012**, *14*, 7567.

(11) Bučar, D.-K.; MacGillivray, L. R. Preparation and Reactivity of Nanocrystalline Cocrystals Formed via Sonocrystallization. *J. Am. Chem. Soc.* **2007**, *129*, 32.

(12) Kim, T.; Zhu, L.; Mueller, L. J.; Bardeen, C. J. Dependence of the solid-state photomechanical response of 4-chlorocinnamic acid on crystal shape and size. *CrystEngComm* **2012**, *14*, 7792.

(13) Commins, P.; Natarajan, A.; Tsai, C.-K.; Khan, S. I.; Nath, N. K.; Naumov, P.; Garcia-Garibay, M. A. Structure−Reactivity Correlations and Mechanistic Understanding of the Photorearrangement and Photosalient Effect of α-Santonin and Its Derivatives in Solutions, Crystals, and Nanocrystalline Suspensions. *Cryst. Growth Des.* **2015**, *15*, 1983.

(14) Gao, X.; Friščić, T.; MacGillivray, L. R. Supramolecular Construction of Molecular Ladders in the Solid State. *Angew. Chem., Int. Ed.* **2004**, *43*, 232.

(15) Nishimura, J.; Horikoshi, Y.; Wada, Y.; Takahashi, H.; Sato, M. Intramolecular [2 + 2] photocycloaddition. 10. Conformationally stable syn-[2.2]metacyclophanes. *J. Am. Chem. Soc.* **1991**, *113*, 3485.

(16) Friščić, T.; MacGillivray, L. R. 'Template-switching': a supramolecular strategy for the quantitative, gram-scale construction of a molecular target in the solid state. *Chem. Commun.* **2003**, 1306.

(17) Elacqua, E.; Friščić, T.; MacGillivray, L. R. [2.2]Paracyclophane as a Target of the Organic Solid State: Emergent Properties via Supramolecular Construction. *Isr. J. Chem.* **2012**, *52*, 53.

(18) Maekawa, Y.; Kato, S.; Hasegawa, M. Quantitative formation of a highly strained tricyclic [2.2]paracyclophane derivative from a mixed crystal of ethyl and propyl.alpha.-cyano-4-[2-(4-pyridyl)ethenyl]-cinnamates through a topochemical reaction. *J. Am. Chem. Soc.* **1991**, *113*, 3867.

(19) Moorthy, J. N.; Venkatakrishnan, P. Double [2 + 2] Photocycloaddition: Topochemical Conversion of 4-Methyl-7-Styrylcoumarin Dimorphs into a Strained Cyclophane. *Cryst. Growth Des.* **2007**, *7*, 713.

(20) Cram, D. J.; Cram, J. M. Cyclophane chemistry: bent and battered benzene rings. *Acc. Chem. Res.* **1971**, *4*, 204.

(21) Cram, D. J.; Singler, R. E.; Helgeson, R. C. Solvolyses with retention of configuration and cis polar additions in the side-chain chemistry of [2.2]paracyclophane. *J. Am. Chem. Soc.* **1970**, *92*, 7625.

(22) Nugent, M. J. Steric and electronic effects in [2,2]-paracyclophane systems. *Chem. Commun. (London)* **1967**, 1160.

(23) Ron, A.; Schnepp, O. Electronic Spectrum of 2,2′-Paracyclophane. *J. Chem. Phys.* **1962**, *37*, 2540.

(24) Li, N.-Y.; Liu, D.; Ren, Z.-G.; Lollar, C.; Lang, J.-P.; Zhou, H.-C. Controllable Fluorescence Switching of a Coordination Chain Based on the Photoinduced Single-Crystal-to-Single-Crystal Reversible Transformation of a syn-[2.2]Metacyclophane. *Inorg. Chem.* **2018**, *57*, 849.

(25) Claassens, I. E.; Nikolayenko, V. I.; Haynes, D. A.; Barbour, L. J. Solvent-Mediated Synthesis of Cyclobutane Isomers in a Photo-

active Cadmium(II) Porous Coordination Polymer. *Angew. Chem., Int. Ed.* **2018**, *57*, 15563.
(26) Yu, C.-Y.; Turner, M. L. Soluble Poly(p-phenylenevinylene)s through Ring-Opening Metathesis Polymerization. *Angew. Chem., Int. Ed.* **2006**, *45*, 7797.
(27) Elacqua, E.; Geberth, G. T.; Vanden Bout, D. A.; Weck, M. Synthesis and folding behaviour of poly(p-phenylene vinylene)-based β-sheet polychromophores. *Chem. Sci.* **2019**, *10*, 2144.
(28) Elacqua, E.; Manning, K. B.; Lye, D. S.; Pomarico, S. K.; Morgia, F.; Weck, M. Supramolecular Multiblock Copolymers Featuring Complex Secondary Structures. *J. Am. Chem. Soc.* **2017**, *139*, 12240.
(29) Morisaki, Y.; Chujo, Y. Synthesis of Novel π-Conjugated Polymers Having [2.2]Paracyclophane Skeleton in the Main Chain. Extension of π-Conjugated Length via the Through-Space. *Macromolecules* **2002**, *35*, 587.
(30) Morisaki, Y.; Ishida, T.; Chujo, Y. Synthesis and Properties of Novel Through-Space π-Conjugated Polymers Based on Poly(p-phenylenevinylene)s Having a [2.2]Paracyclophane Skeleton in the Main Chain. *Macromolecules* **2002**, *35*, 7872.
(31) Bazan, G. C.; Oldham, W. J.; Lachicotte, R. J.; Tretiak, S.; Chernyak, V.; Mukamel, S. Stilbenoid Dimers: Dissection of a Paracyclophane Chromophore. *J. Am. Chem. Soc.* **1998**, *120*, 9188.
(32) Meier, C. A.-M. a. H. Cyclophanes obtained by photocyclodimerization reactions. *Trends Photochem. Photobio.* **2016**, *17*, 7.
(33) Park, I.-H.; Lee, S. S.; Vittal, J. J. Guest-Triggered Supramolecular Isomerism in a Pillared-Layer Structure with Unusual Isomers of Paddle-Wheel Secondary Building Units by Reversible Single-Crystal-to-Single-Crystal Transformation. *Chem. - Eur. J.* **2013**, *19*, 2695.
(34) MacGillivray, L. R.; Reid, J. L.; Ripmeester, J. A. Supramolecular Control of Reactivity in the Solid State Using Linear Molecular Templates. *J. Am. Chem. Soc.* **2000**, *122*, 7817.
(35) Yang, S.-Y.; Naumov, P.; Fukuzumi, S. Topochemical Limits for Solid-State Photoreactivity by Fine Tuning of the π−π Interactions. *J. Am. Chem. Soc.* **2009**, *131*, 7247.
(36) Li, W.-X.; Gu, J.-H.; Li, H.-X.; Dai, M.; Young, D. J.; Li, H.-Y.; Lang, J.-P. Post-synthetic Modification of a Two-Dimensional Metal−Organic Framework via Photodimerization Enables Highly Selective Luminescent Sensing of Aluminum(III). *Inorg. Chem.* **2018**, *57*, 13453.
(37) Mandal, R.; Biradha, K. Organic Polymers of an Angular Diene via Solid State [2 + 2] Polymerization: Coordination Polymers with Dicarboxylates as Templates. *Cryst. Growth Des.* **2019**, *19*, 3445.
(38) Nakamura, Y.; Tsuihiji, T.; Mita, T.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. Synthesis, Structure, and Electronic Properties of syn-[2.2]Phenanthrenophanes: First Observation of Their Excimer Fluorescence at High Temperature. *J. Am. Chem. Soc.* **1996**, *118*, 1006.
(39) Friščić, T.; MacGillivray, L. R., Template-controlled Solid-state Synthesis: Toward a General Form of Covalent Capture in Molecular Solids. In *Frontiers in Crystal Engineering*; Tiekink, E. R. T., Vittal, J. J., Eds.; Wiley-VCH: 2005; pp 53−68.
(40) Hasegawa, M.; Saigo, K.; Mori, T.; Uno, H.; Nohara, M.; Nakanishi, H. Topochemical double photocyclodimerization of the 1,4-dicinnamoylbenzene crystal. *J. Am. Chem. Soc.* **1985**, *107*, 2788.
(41) Schmidt, G. M. J. Photodimerization in the solid state. *Pure Appl. Chem.* **1971**, *27*, 647.
(42) Ramamurthy, V.; Venkatesan, K. Photochemical reactions of organic crystals. *Chem. Rev.* **1987**, *87*, 433.
(43) Grobelny, A. L.; Rath, N. P.; Groeneman, R. H. Varying the regiochemistry of a [2 + 2] cycloaddition reaction within isostructural hydrogen bonded cocrystals containing 4-stilbazole. *CrystEngComm* **2018**, *20*, 3951.
(44) Harada, J.; Ogawa, K. Invisible but Common Motion in Organic Crystals: A Pedal Motion in Stilbenes and Azobenzenes. *J. Am. Chem. Soc.* **2001**, *123*, 10884.
(45) Elacqua, E.; Kaushik, P.; Groeneman, R. H.; Sumrak, J. C.; Bučar, D.-K.; MacGillivray, L. R. A Supramolecular Protecting Group Strategy Introduced to the Organic Solid State: Enhanced Reactivity through Molecular Pedal Motion. *Angew. Chem., Int. Ed.* **2012**, *51*, 1037.
(46) The central aromatic rings of ***m*-bpeb** and ***o*-bpeb** can adopt three unique conformations with respect to the central phenyl ring: trans,trans, cis,trans, and cis,cis.
(47) Attempts to separate ***m*Cp-1** and ***m*Cp-2** using reported chromatographic methods as for the parent hydrocarbons were unsuccessful (see ref 5).
(48) Selby, T. M.; Meerts, W. L.; Zwier, T. S. Isomer-Specific Ultraviolet Spectroscopy of m- and p-Divinylbenzene. *J. Phys. Chem. A* **2007**, *111*, 3697.
(49) Ohba, H.; Hosomi, Y.; Ito, J. *J. Am. Chem. Soc.* **2001**, *123*, 6349.
(50) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. Dynamic Covalent Chemistry. *Angew. Chem., Int. Ed.* **2002**, *41*, 898.
(51) Badjić, J. D.; Cantrill, S. J.; Grubbs, R. H.; Guidry, E. N.; Orenes, R.; Stoddart, J. F. The Exclusivity of Multivalency in Dynamic Covalent Processes. *Angew. Chem., Int. Ed.* **2004**, *43*, 3273.
(52) Hartgerink, J. D. Covalent capture: a natural complement to self-assembly. *Curr. Opin. Chem. Biol.* **2004**, *8*, 604.
(53) Clark, T. D.; Ghadiri, M. R. Supramolecular Design by Covalent Capture. Design of a Peptide Cylinder via Hydrogen-Bond-Promoted Intermolecular Olefin Metathesis. *J. Am. Chem. Soc.* **1995**, *117*, 12364.

https://dx.doi.org/10.1021/acs.cgd.9b01712
Cryst. Growth Des. 2020, 20, 2584−2589