



Supporting Information

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Escape from a Nonporous Solid: Mechanically Coupled Biconcave Molecules**

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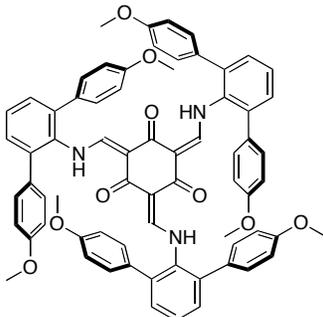
Experimental Section

General Considerations. All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Dichloromethane was saturated with nitrogen and purified by passage through activated Al₂O₃ columns under nitrogen (Innovative Technology SPS 400). The compounds 2,6-di(*p*-methoxyphenyl)aniline, 2,6-dimesitylaniline, and 1,3,5-triformylphloroglucinol (**3**) were synthesized according to literature procedures.^{S1-S4} All air-sensitive manipulations were carried out under nitrogen atmosphere by standard Schlenk-line techniques.

Physical measurements. ¹H-NMR and ¹³C-NMR spectra were recorded on a 300 MHz Varian Gemini 2000 NMR spectrometer. Chemical shifts were reported versus tetramethylsilane and referenced to the residual solvent peaks. High-resolution mass spectra were obtained on a Thermo Electron Corporation MAT 95XP-Trap. FT-IR spectra were recorded on a Nicolet 510P FT-IR Spectrometer with EZ OMNIC E.S.P. software. X-Ray diffraction data were collected on a Bruker platform X-Ray diffractometer having a SMART 6000 CCD detector, using Mo K α radiation from a sealed source.

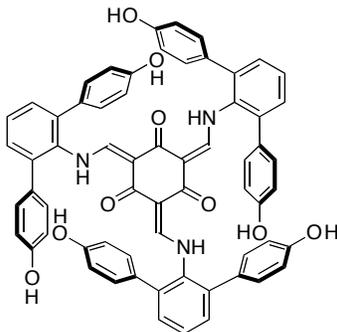
2,4,6-tris(2,6-di(4-methoxyphenyl)phenylaminomethylene)cyclohexane-1,3,5-trione (4). To a rapidly stirred anhydrous ethanol (10 mL) solution of **3** (100 mg, 0.47 mmol) at 95 °C was added a hot ethanol solution (10 mL) of 2,6-di(*p*-methoxyphenyl)aniline (712 mg, 2.33 mmol). The reaction was heated at reflux under nitrogen for 12 h to afford a heterogeneous mixture. The solid material was isolated by filtration, washed with boiling ethanol (10 mL x 3), and dried in vacuo to furnish **4** as a yellow powder (432 mg, 86%). Vapor diffusion of Et₂O to a CHCl₃ solution of this material at r.t. afforded yellow blocks, which were suitable for x-ray crystallography. mp 290 °C. ¹H NMR (300 MHz, CD₂Cl₂): δ 12.43 (d, *J* = 13 Hz, 3H), 7.53 (d, *J* = 13 Hz, 3H), 7.28 (m, 21H), 6.92 (m, 12H), 3.82 (s, 18H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 184.79, 159.46, 157.56, 137.06, 131.13, 130.89, 130.65, 127.04, 114.332, 55.60. IR (thin film on NaCl,

cm⁻¹) 2932 (w), 2834 (w), 1597 (s), 1577 (s), 1512 (m), 1292 (m), 1246 (m), 831 (m). HRESI calcd for C₆₉H₅₇N₃O₉Na [M + Na]⁺ 1094.3992, found = 1094.3987.



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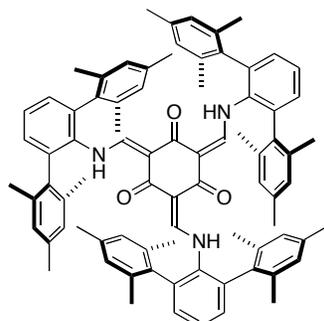
2,4,6-tris(2,6-di(4-hydroxyphenyl)phenylaminomethylene)cyclohexane-1,3,5-trione (5). An anhydrous CH₂Cl₂ solution of 4 (1.0 g, 0.93 mmol) was cooled to -78 °C under nitrogen. A portion of neat BBr₃ (1.0 mL, 10.6 mmol) was added via syringe over a period of 0.5 h. The reaction was warmed to r.t. and stirred under nitrogen for 12 h. The mixture was cooled to 0 °C and quenched by adding H₂O (50 mL). The resulting suspension was filtered to isolate a solid material, which was dissolved in aq NaOH (2 M, 20 mL). Insoluble fraction was filtered off and the solution acidified to pH = 3 (with aq HCl) to induce precipitation of 5 as a yellow powder. This material was isolated by filtration and dried in vacuo (yield = 643 mg; 70%). Yellow blocks suitable for X-ray crystallography were obtained by vapor diffusion of Et₂O into a DMF solution of this material at r.t. m.p. > 350 °C. ¹H NMR (300 MHz, DMSO-*d*₆: CD₂Cl₂ = 1:1 (v/v)): δ 12.24 (d, *J* = 13 Hz, 3H), 9.04 (s, 6H), 7.27 (d, *J* = 13 Hz, 3H), 7.15 (m, 3H), 7.06 (m, 6H), 6.94 (m, 12H), 6.62 (m, 12H). ¹³C NMR (100 MHz, DMSO: CD₂Cl₂ = 1:1 (v/v)): δ 183.56, 156.44, 136.36, 135.49, 129.96, 129.46, 128.52, 115.30. IR (thin film on NaCl, cm⁻¹) 3298 (b), 1602 (s), 1576 (s), 1535 (m), 1511 (m), 1337 (s), 1237 (s). HRESI calcd for C₆₃H₄₅N₃O₉Na [M + Na]⁺ 1010.3053, found = 1010.3048.



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2,4,6-tris(2,6-dimesitylphenylaminomethylene)cyclohexane-1,3,5-trione (6). This compound was prepared from 3 (90 mg, 0.42 mmol) and 2,6-dimesitylaniline (690 mg, 2.1 mmol) by a procedure analogous to that used to prepare 4 (yield = 312 mg; 65%). Vapor diffusion of pentanes into a CHCl₃ solution of this material at r.t. afforded yellow

blocks suitable for x-ray crystallography. mp = 302 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ 12.45 (d, $J = 12.73$ Hz, 3H), 7.51 (m, 3H), 7.47 (d, $J = 12.95$ Hz, 3H), 7.28 (m, 6H), 2.48 (s, 18H), 2.22 (s, 36H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 185.97, 157.12, 137.03, 135.98, 132.58, 129.79, 105.92, 20.97, 18.67. IR (thin film on NaCl, cm^{-1}) 2918 (m), 2855 (w), 1600 (s), 1575 (s), 1410 (s), 1288 (s), 848 (m). HRESI calcd for $\text{C}_{81}\text{H}_{81}\text{N}_3\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 1166.6175, found = 1166.6170.



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References

- (S1) Saednya, A.; Hart, H. *Synthesis* **1996**, 1455–1458.
- (S2) Sasaki, S.; Hatsushiba, H.; Yoshifuji, M. *Chem. Commun.* **1998**, 2221–2222.
- (S3) Gavenonis, J.; Tilley, T. D. *Organometallics* **2002**, 21, 5549–5563.
- (S4) Chong, J. H.; Sauer, M.; Patrick, B. O.; MacLachlan, M. J. *Org. Lett.* **2003**, 5, 3823–3826.

Comparative Geometry of 4–6

Planarity of the $\{C_6O_3(CNH)_3\}$ cores. Each unique molecule of each structure was examined by fitting a plane to the fifteen carbon, nitrogen, and oxygen atoms of its core, and determining the mean and maximum deviations. For **4**·0.5CHCl₃ and **4**, there are two unique molecules, each with crystallographic three-fold symmetry; in the other cases there is one unique molecule with no internal crystallographic symmetry. The results are summarized in Table S1.

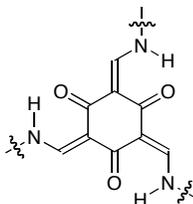


Table S1. Molecular Core Planarity

Compound	Mean deviation, Å	Maximum deviation, Å
4	0.041, 0.173	0.060, 0.289
4 ·0.5CHCl ₃	0.072, 0.122	0.103, 0.197
5	0.090	0.148
6	0.064	0.165

Molecular Fitting. Structures **4**·0.5CHCl₃ and **4** represent the *same crystal*, before and after the lattice solvent was allowed to evaporate, respectively. The two structures have the same space group type (*P31c*), and very similar structures. Each contains two unique molecules having crystallographic three-fold symmetry, but in each case the two unique molecules' positions are distinguished by having different relationships to the other symmetry elements in the space group: one is on the intersection of three glide planes, and the other is between glide planes. As part of an effort to evaluate the structural differences, the unique molecules of the former were fitted to those of the latter by a least-squares minimization procedure. The molecules disposed equivalently with respect to the space group symmetry fit best, and those results are reported here. In both these cases, the rigid molecular cores fit each other perfectly (maximum deviation less than 0.05 Å), as would be expected. In fact, the second molecules (**4b**, represented by C(28) through C(54) of each structure) fit very well overall, with an RMS deviation of 0.250 Å for all atoms, and a maximum deviation of 0.481 Å at the methoxy carbon on the open side of the molecule (C(52)). Like the second molecules, the first molecules, **4a**, fit quite well on their closed sides, with a maximum deviation of only 0.270 Å. The fit for the first molecules worsens in the central phenyl ring of the terphenyl group, however, and it is at best approximate on the open side of the molecule. The terminal terphenyl phenyl ring at this position in the solvated structure is

disordered, accommodating a nearby CHCl_3 molecule about 13% of the time. The corresponding phenyl ring of the major (87%) disorder component lies in about the same plane as that of the solvent-vacated structure (10° interplanar angle), but it is rotated in that plane by roughly 15° about an axis passing through atom C(19). The largest linear deviation is 1.873 Å between the corresponding methoxy carbon atoms. The plane of the phenyl ring of the minor disorder component, on the other hand, is rotated by about 54° relative to that of the phenyl ring of the unsolvated structure (64° relative to the major disorder component), yet its methoxy group fits that of the unsolvated structure very well, with the larger of the two deviations being 0.144 Å between the oxygen positions.

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- Figure S2.** ORTEP diagram of **5** with thermal ellipsoids at 50% probability: left, top view; right, side view.
- Figure S3.** ORTEP diagram of **6** with thermal ellipsoids at 50% probability: left, top view; right, side view.
- Figure S4.** ORTEP diagram of $\text{4}\cdot\text{0.5CHCl}_3$ with thermal ellipsoids at 50% probability showing two chemically identical but crystallographically unique molecules: left, molecule **4a**; right, molecule **4b**. Hydrogen atoms were omitted for clarity.
- Figure S5.** ORTEP diagram of **4** with thermal ellipsoids at 50% probability showing two chemically identical but crystallographically unique molecules: left, molecule **4a**; right, molecule **4b**. Hydrogen atoms were omitted for clarity.

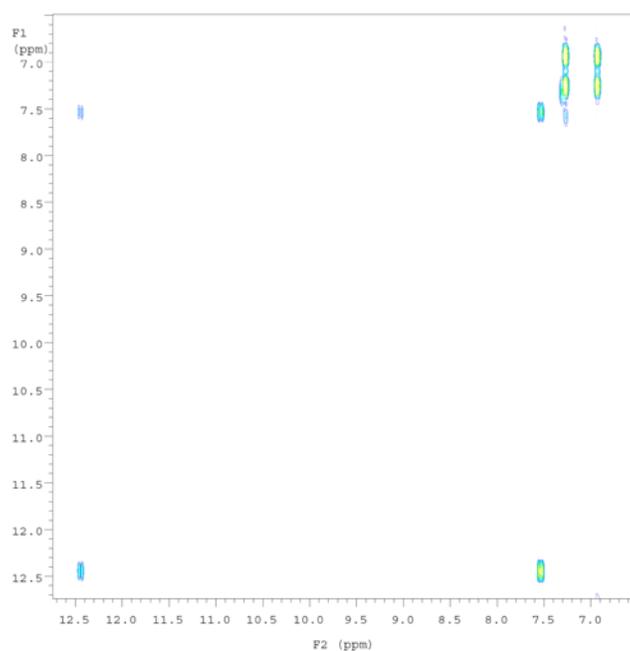
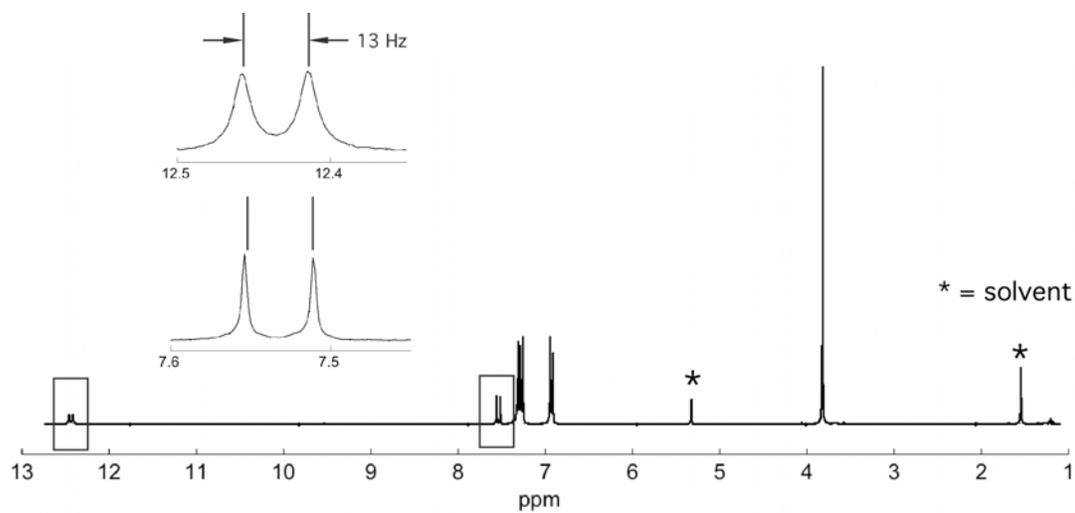
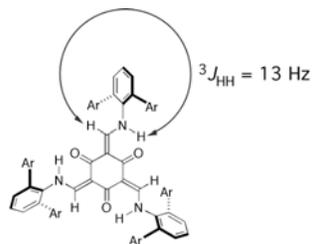


Figure S1. ^1H NMR spectrum (top) and ^1H - ^1H COSY NMR spectrum (bottom) of **4** in CD_2Cl_2 showing the coupling ($J = 13$ Hz) between N-H and C-H protons.



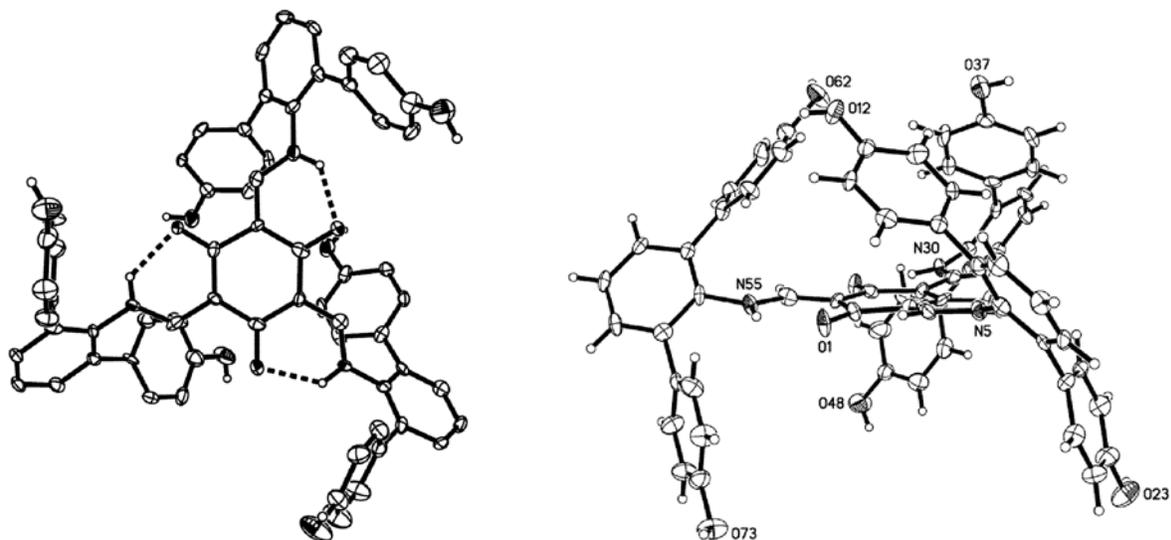


Figure S2. ORTEP diagram of 5 with thermal ellipsoids at 50% probability: left, top view; right, side view.

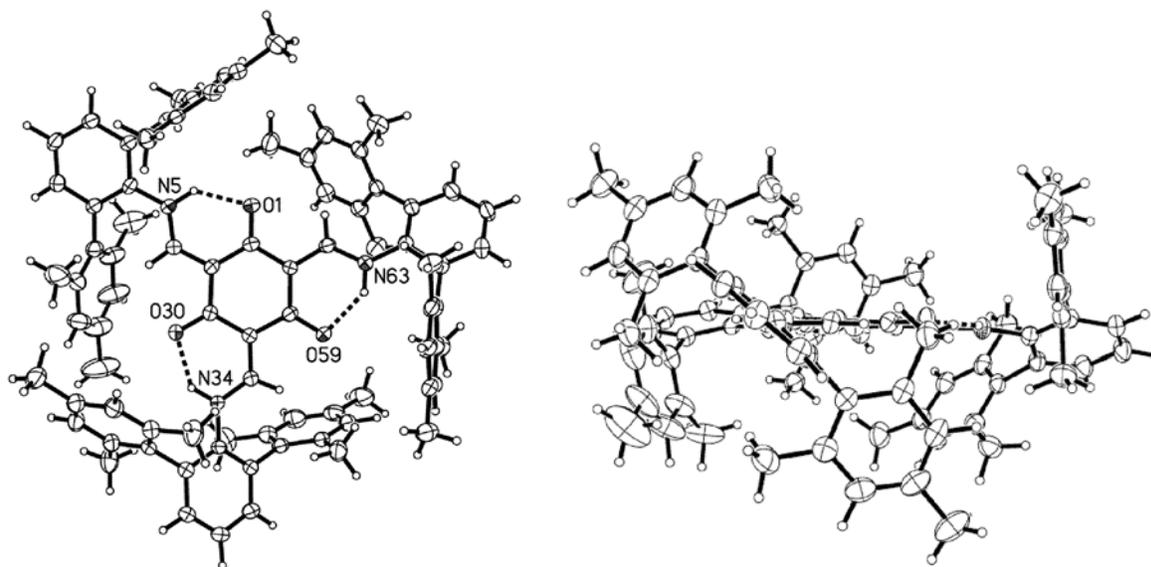


Figure S3. ORTEP diagram of 6 with thermal ellipsoids at 50% probability: left, top view; right, side view.

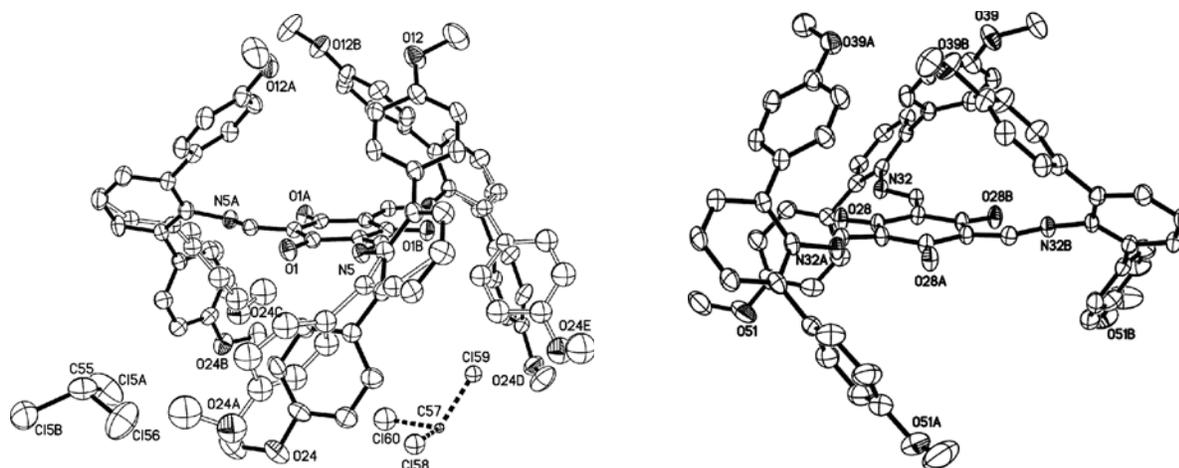


Figure S4. ORTEP diagram of $4 \cdot 0.5\text{CHCl}_3$, with thermal ellipsoids at 50% probability showing two chemically identical but crystallographically unique molecules: left, molecule **4a**; right, molecule **4b**. Hydrogen atoms were omitted for clarity.

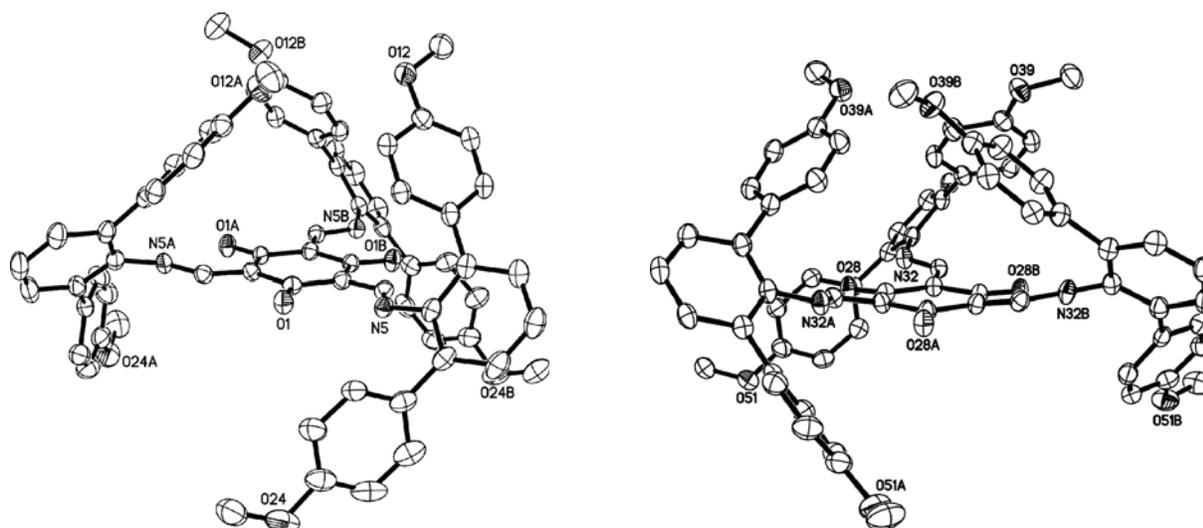


Figure S5. ORTEP diagram of **4** with thermal ellipsoids at 50% probability showing two chemically identical but crystallographically unique molecules: left, molecule **4a**; right, molecule **4b**. Hydrogen atoms were omitted for clarity.