Electronic Supplementary Information

RI-CC2/cc-pVDZ orbitals

Figure 1 and 2 show selected orbitals of PARA and the anti-syn conformer of GEM, respectively. The orbitals correspond to those of the anti-anti conformer of GEM shown in Figure 5 of the main manuscript.

**Figure 1:** RICC2/cc-pVDZ orbitals of pseudo-para-vinyldime[2.2]paracyclophane.
Synthetic procedures

**General Remarks**: Melting points: Büchi 530 melting point apparatus, uncorrected. Thin layer chromatography (TLC): Macherey–Nagel Polygram SilG/UV254. Column chromatography: Merck Kieselgel 60 (70–230 mesh). IR(ATR): Bruker Tensor 27 spectrometer, Diamant ATR technique. $^1$H and $^{13}$C NMR: Bruker AC 200.2 MHz ($^1$H) and 50.3 MHz ($^{13}$C); Bruker AV II-300: $^1$H NMR (300.1 MHz), $^{13}$C NMR (75.47 MHz); Bruker AV III-400: $^1$H NMR (400.1 MHz), $^{13}$C NMR (100.6 MHz) in CDCl$_3$, internal standards: TMS, $\delta = 0$ ppm for $^1$H, CDCl$_3$, $\delta = 77.05$ ppm for $^{13}$C spectroscopy. UV–vis: Varian Carry 100 Bio. MS: Finnigan MAT 8400-MSS I (EI, 70 eV). Elemental analyses were conducted at the Institute for Pharmaceutical Chemistry TU Braunschweig.

Methyltriphenylphosphonium bromide, potassium tert-butoxide, dimethyl sulfoxide, triethyl amine, dimethylformamide and lithium aluminum hydride were purchased from Across; $n$-BuLi solution in hexane (2.5M) and bromine were purchased from Sigma-Aldrich. Reagents were used without further purification. The solvents used for the reactions were of analytical grade; anhydrous THF was distilled from an LiAlH$_4$ dispersion with triphenylmethane as indicator, anhydrous dichloromethane was distilled from phosphorus pentoxide.
Synthesis of 4-vinyl-12-formyl[2.2]paracyclophane (PARA)

1: 4,12-dibromo [2.2]Paracyclophane

The synthesis of 1 was carried out according to literature.\textsuperscript{1}

![Chemical structure](image1)

2: 4-bromo-12-formyl [2.2]Paracyclophane

A dispersion of 1 (3.3 g, 9 mmol) in anhydrous THF (100 mL) was prepared in a flame-dried Schlenk flask under nitrogen flush and cooled down to -84°C (liq. nitrogen/ethyl acetate slush bath) and n-BuLi solution in hexanes (2.5 M, 3.9 ml, 9.9 mmol) was added dropwise and left to react for 1 hour at this temperature. Anhydrous DMF (3.46 ml, 3.289 g, 45 mmol) was added dropwise into this solution, and the bath was removed. The reaction was left to run overnight. After cooling down to 0°C (ice/water bath), aq. 3M HCl solution (30 mL) was added with vigorous stirring to hydrolyze semi-aminal intermediate, the mixture was stirred for 15 minutes and poured into a crushed ice (500 g) and left to melt. The precipitate was filtered through a glass frit with suction and washed with water. The filter cake was dissolved in chloroform on filter, the filtrate was dried over magnesium sulfate, filtered and concentrated to dryness under reduced pressure. The crude product was separated by column chromatography (400 ml flash-SiO\textsubscript{2}, dichloromethane) to give 2.02 g (6.41 mmol, 71%) of the expected product as white crystals, 258 mg (0.7 mmol, 8%) of starting material and 47 mg (0.18 mmol, 2%) of 4,12-bisformyl [2.2]paracyclophane as by-product.

3: 4-bromo-12-vinyl [2.2]Paracyclophane

\textsuperscript{1} Reich, H.J.; Cram, D.J.; *JACS*, 1969, 91, 13, 3527-3533.
The freshly prepared solution of potassium tert-butoxide (4.49 g, 40 mmol) in anhydrous THF (50 mL) was added dropwise into a cooled down (ice/water bath) dispersion of methyltriphenylphosphonium bromide (14.29 g, 40 mmol) in anhydrous THF (50 mL, flame-dried Schlenk flask, nitrogen flow). After 1 hour reaction time, the solution of 2 (1.60 g, 5 mmol) in anhydrous THF (50 mL) was added dropwise into the reaction mixture. After 2.5 h the mixture was poured into stirred mixture of conc. aq. HCl (150 mL) and water/crushed ice (450 mL), stirred until ice completely melted and the precipitate was filtered with suction on glass frit and filter cake was washed 3M aq. HCl (2x50 mL) and with water (2x50 mL). The precipitate was dissolved on the frit with dichloromethane, water drops were separated and the solution was dried over magnesium sulfate, filtered and concentrated under reduced pressure to give 1.57 g (5 mmol, 100%) of product as colorless solid, pure by NMR.

4: 4-formyl-12-vinyl [2.2]Paracyclophane

A dispersion of 3 (1.253 g, 4 mmol) in anhydrous THF (40 mL) was prepared using a flame-dried Schlenk flask and under nitrogen flush, cooled down to -78°C (solid CO2/acetone bath) and a solution of n-BuLi in hexanes (2.5M, 4.8 ml, 12 mmol) was added dropwise and left to react for 1 h. Anhydrous DMF (4.6 ml, 60 mmol) was added dropwise into the reaction mixture and left to react overnight, while warming up to RT. After cooling down to 0°C (ice/water bath), aq. 3M HCl (12 mL) was added with vigorous stirring to hydrolyze semi-aminal intermediate, the mixture was stirred for 15 minutes and poured into a crushed ice (250 g) and left to melt. The solid precipitate was filtered off through glass frit, filter cake was washed with water (3x30 mL, filtrate pH>6) and dissolved with chloroform. Water drops were separated, organic solution was dried over MgSO4, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography giving pure product (808 mg, 3.08 mmol, 77%) as colorless solid.