

Supplementary Materials

Cubane-forming cyclic dienes that exhibit orthogonal reactivities in the solid state

Changan Li,^a Michael A. Sinnwell,^a Dale C. Swenson^a and Leonard R. MacGillivray^{*a}

^a*Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA*

e-mail: len-macgillivray@uiowa.edu

Supplementary Information:

- S1) Experimental section
- S2) Single crystal X-ray diffraction data
- S3) ¹H NMR spectroscopy data
- S4) Powder X-ray diffraction data
- S5) References

S1. Experimental section

A) Materials

2,6-Dimethyl-4*H*-pyran-4-one (**DMP**) was purchased from Sigma-Aldrich. 4-Oxo-4*H*-pyran-2,6-dicarboxylic acid (**CA**) was purchased from Honeywell Research Chemicals. Solvents were purchased from Fisher Scientific. All reagents and solvents were used without further purification.

B) Synthesis

1) Preparation of single crystals of **CA·THF**

CA powder (55 mg, 0.3 mmol) was dissolved in 5 mL THF. Single crystals as colorless irregular prisms were obtained after slow evaporation of 2 days. **CA·THF** quickly lost THF molecules and generated the non-solvated form of **CA** within periods of minutes. Powder X-ray diffraction (PXRD) showed the resulting powder to be the same phase as the solid obtained commercially (Honeywell Research Chemicals).

2) Preparation of cocrystals of **CA·DMP·2H₂O**

CA (50 mg, 0.27 mmol) and **DMP** (33.7 mg, 0.27mmol; 1:1 molar ratio) were dissolved in 5 mL warm MeOH/H₂O (1:1). Single crystals of **CA·DMP·2H₂O** as transparent plates were obtained by slow evaporation over a period of 3 days. The purity of **CA·DMP·2H₂O** is confirmed by PXRD. Compositions of **CA·DMP·2H₂O** were determined by ¹H NMR spectroscopy and single crystal X-ray diffraction.

C) Photodimerization

All photodimerization reactions were carried out in an ACE Glass photochemistry cabinet using a 450 W Hanovia medium-pressure mercury lamp with a broad wavelength distribution. Approximately 40-48% of total energy radiated lies in the UV range of the spectrum, 40-43% in the visible, and the balance in the IR. Cocrystals of **CA·DMP·2H₂O** were finely ground using a mortar and pestle before being placed between a pair of Pyrex glass plates. Samples were irradiated in 10 h intervals to ensure uniform irradiation. The progress of the photodimerization reaction was monitored using ¹H NMR spectroscopy.

S2. Single-crystal X-ray diffraction data

Single-crystal X-ray diffraction data of **CA·THF**, **CA·DMP·2H₂O** and **CG1-H** were collected on a Bruker D8 Venture Duo diffractometer using MoK α radiation ($\lambda=0.71073$ Å) with APEX II detector. Single-crystal X-ray diffraction data of **CG2** were collected on a Nonius APEX II Kappa diffractometer using MoK α radiation ($\lambda=0.71073$ Å). Crystals were mounted in paratone oil on a Mitegen magnetic mount. Lorentz and polarization corrections with programs from the APEXII package were used for data reduction. Structure solution and refinement were completed using SHELXT¹ and SHELXL², respectively within the Olex²³ graphical user interface. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined using a riding model.

Table S1. Crystallographic parameters for **CA·DMP·2H₂O** and **CG1-H·6H₂O**.

Compound name	CA·DMP·2H₂O	CG1-H·6H₂O
CCDC deposition number	2082537	2082538
Empirical formula	C ₁₄ H ₁₆ O ₁₀	C _{14.6} H _{24.6} O _{19.4} *
Formula weight	344.27	510.51
Temperature/K	298.15	150.15
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	8.2125(17)	7.7763(19)
<i>b</i> /Å	9.891(2)	8.1868(17)
<i>c</i> /Å	11.508(3)	8.683(2)
α /°	64.766(10)	82.568(7)
β /°	85.376(8)	82.756(8)
γ /°	74.390(10)	65.804(6)
Volume/Å ³	813.7(3)	498.4(2)
<i>Z</i>	2	1
ρ_{calc} /cm ³	1.405	1.701
μ /mm ⁻¹	0.122	0.163
<i>F</i> (000)	360.0	267.0
Crystal size/mm ³	0.125 × 0.12 × 0.07	0.105 × 0.095 × 0.02
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/°	4.69 to 52.764	4.746 to 50.04
Index ranges	-10 ≤ <i>h</i> ≤ 10, -12 ≤ <i>k</i> ≤ 12, -14 ≤ <i>l</i> ≤ 14	-9 ≤ <i>h</i> ≤ 9, -9 ≤ <i>k</i> ≤ 9, 0 ≤ <i>l</i> ≤ 10
Reflections collected	20353	1743
Independent reflections	3320 [<i>R</i> _{int} = 0.0276, <i>R</i> _{sigma} = 0.0214]	1743 [<i>R</i> _{int} = 0.0279, <i>R</i> _{sigma} = 0.0767]
Data/restraints/parameters	3320/0/227	1743/1/186
Goodness-of-fit on <i>F</i> ²	1.066	1.068
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0415, <i>wR</i> ₂ = 0.1215	<i>R</i> ₁ = 0.0605, <i>wR</i> ₂ = 0.1220
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0568, <i>wR</i> ₂ = 0.1333	<i>R</i> ₁ = 0.1004, <i>wR</i> ₂ = 0.1424
Largest diff. peak/hole / e Å ⁻³	0.20/-0.20	0.34/-0.36

*Non-integral number of atoms in unit cell from substitutional disorder at O2 position: 2/3 C-O-H; 1/3 C-O-CH₃.

Table S2. Crystallographic parameters for **CA·THF** and **CG2**.

Compound name	CA·THF	CG2
CCDC deposition number	2082539	2082540
Empirical formula	C ₁₁ H ₁₂ O ₇	C ₁₄ H ₁₆ O ₄
Formula weight	256.21	248.27
Temperature/K	150.15	298.15
Crystal system	monoclinic	orthorhombic
Space group	<i>P2₁/c</i>	<i>Cmce</i>
a/Å	9.6261(10)	12.4105(12)
b/Å	11.4586(11)	7.2547(7)
c/Å	11.0733(11)	13.7901(14)
α/°	90	90
β/°	111.621(5)	90
γ/°	90	90
Volume/Å ³	1135.5(2)	1241.6(2)
Z	4	4
ρ _{calc} /cm ³	1.499	1.328
μ/mm ⁻¹	0.127	0.097
F(000)	536.0	528.0
Crystal size/mm ³	0.14 × 0.085 × 0.055	0.34 × 0.16 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.552 to 52.778	8.792 to 50.696
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -12 ≤ l ≤ 13	-14 ≤ h ≤ 14, -7 ≤ k ≤ 8, -16 ≤ l ≤ 15
Reflections collected	25641	3393
Independent reflections	2319 [R _{int} = 0.0281, R _{sigma} = 0.0145]	598 [R _{int} = 0.0659, R _{sigma} = 0.0315]
Data/restraints/parameters	2319/0/165	598/0/49
Goodness-of-fit on F ²	1.099	1.052
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0319, wR ₂ = 0.0818	R ₁ = 0.0439, wR ₂ = 0.1102
Final R indexes [all data]	R ₁ = 0.0362, wR ₂ = 0.0847	R ₁ = 0.0527, wR ₂ = 0.1167
Largest diff. peak/hole / e Å ⁻³	0.24/-0.21	0.19/-0.12

S3. NMR spectral data

^1H NMR spectra were collected at ambient temperature using a Bruker AVANCE 400 MHz NMR spectrometer. $\text{DMSO-}d_6$, CDCl_3 and D_2O were used as NMR solvents. All NMR data were processed with MestreNova software suite.

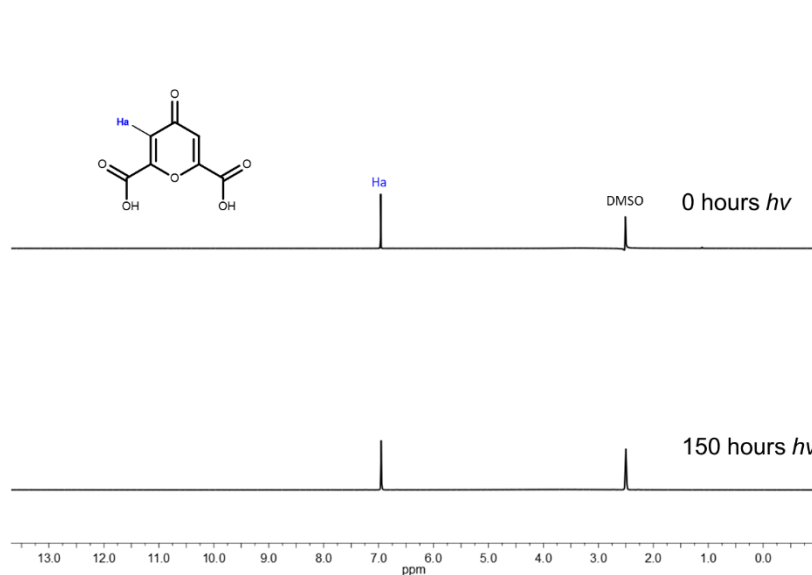


Fig. S1. ^1H NMR spectra showing photostability of **CA** after UV irradiation (150 h) (400 MHz, $\text{DMSO-}d_6$).

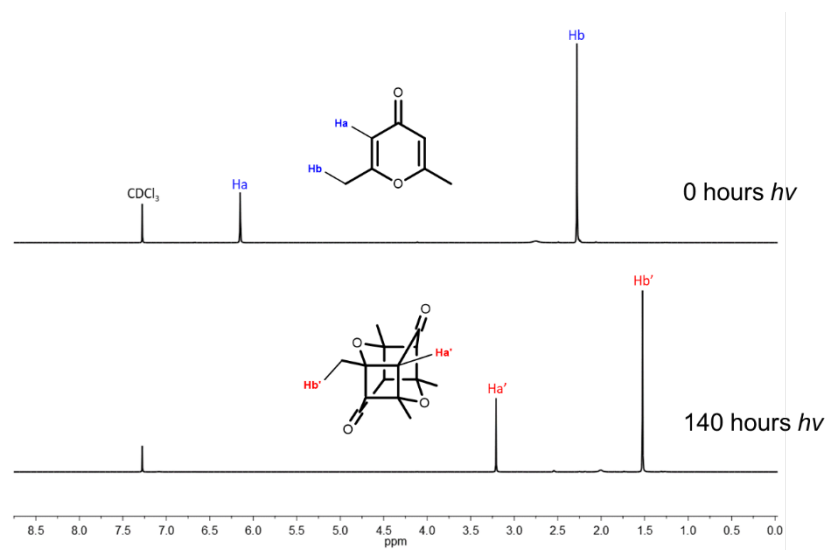


Fig. S2. ¹H NMR spectra of **DMP** before (top) and after (bottom) UV irradiation for 140 h (400 MHz, CDCl₃).

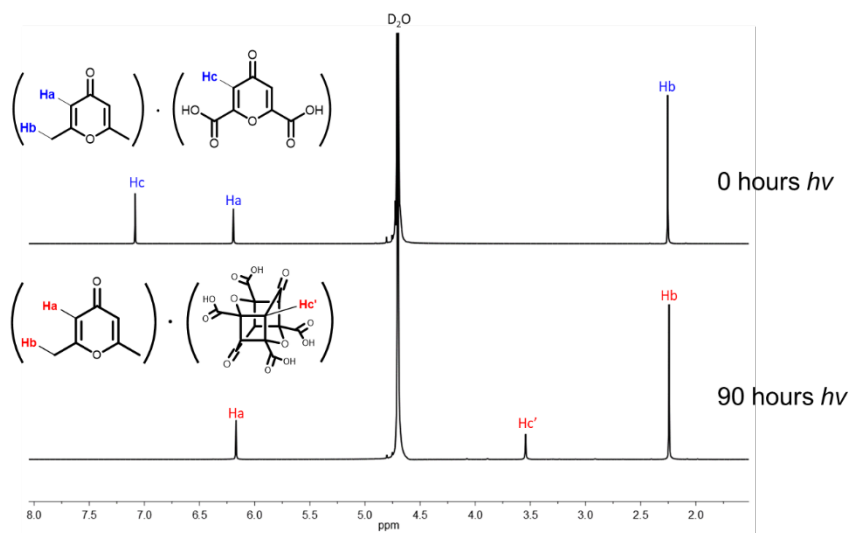


Fig. S3. ¹H NMR spectra of **CA·DMP·2H₂O** before (top) and after (bottom) UV irradiation for 90 h (400 MHz, D₂O).

S4. Powder X-ray diffraction data

Powder X-ray diffraction data were collected using a Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) typically in the range of $5\text{--}35^\circ$ two-theta (scan type: locked coupled; scan mode: continuous; step size: 0.02°). Samples were ground and mounted on glass slides. The equipment was operated at 40 kV and 30 mA.

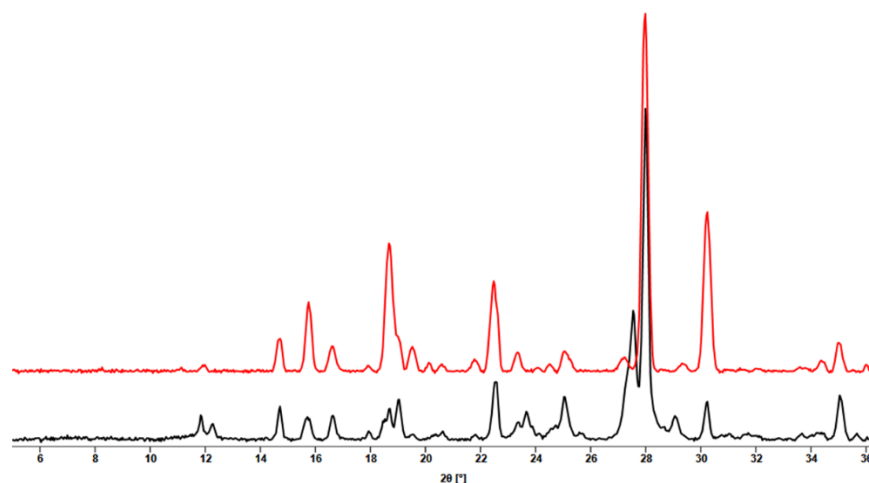


Fig. S4. PXRD patterns from commercial sample of **CA** (red) and desolvated **CA·THF** (black).

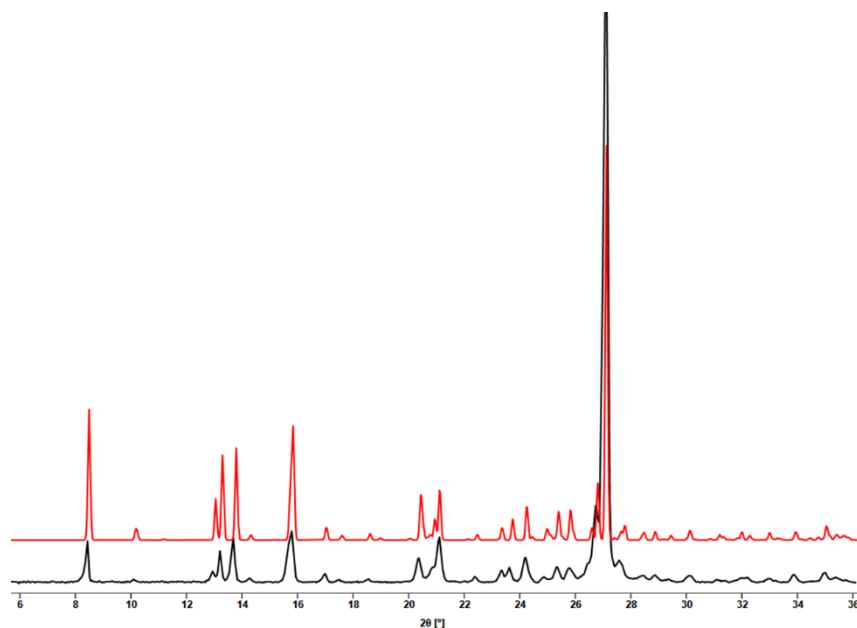


Fig. S5. PXRD patterns of **CA·DMP·2H₂O**: simulated pattern from single crystal X-ray diffraction data (red); experimental pattern from powder sample (black).

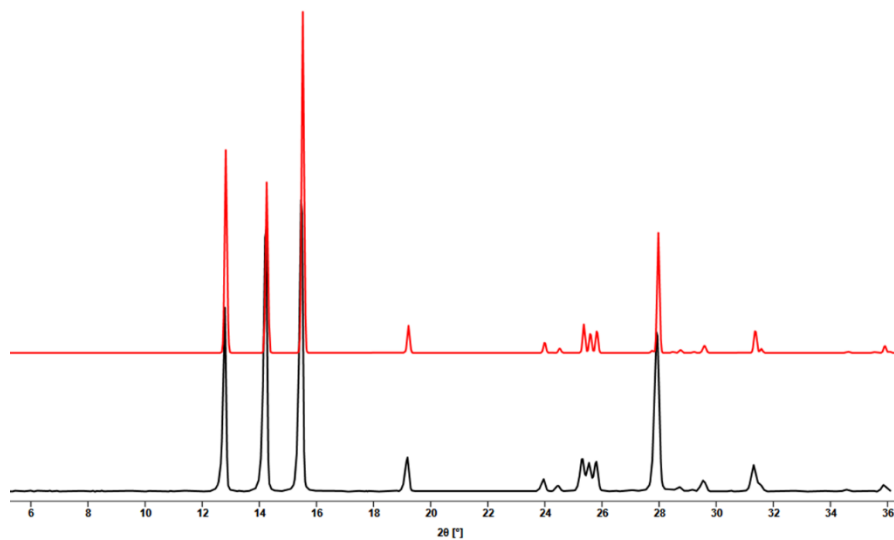


Fig. S6. PXRD patterns of **CG2**: simulated pattern from single crystal X-ray diffraction data (red); experimental pattern from powder sample (black).

S5. References

1. G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3-8.
2. G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.