Supporting Information

Disentangling the Photochemistry of Benzocyclobutenedione

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1. Chemical synthesis of BCBD

All solvents were purified, dried, freshly distilled and stored under an atmosphere of N_2 in a Schlenk flask. Water and air-sensitive reactions were run under an atmosphere of N_2 and glassware was oven-dried overnight or flame-dried. ¹H NMR spectra were recorded using a *Bruker Avance III HD 400 (1H, 400 MHz)*.

Benzocyclobutene-1,2-dione was prepared in the following manner:

2-Carboxybenzenediazoium Chloride from Anthranilic Acid.

22.5 mL conc. HCl and 50.1 mL (43.6 g, 0.372 mol) isoamyl nitrite was added dropwise to an ice-cooled stirring solution of 30.0 g (0.219 mol) anthranilic acid in 330 mL absolute ethanol. After ten minutes in the ice bath, 1 L of ether was added to the dark brown solution. The solution was stirred for further five minutes. The resulting orange-yellow solid was filtrated, washed three times with portions of 30 mL ether and carefully dried; yield 39.9 g (0.216 mol, 99 %) of 2-carboxybenzenediazoium chloride.

Benzocyclobutenone from 2-Carboxybenzenediazoium Chloride.

39.9 g (0.216 mol) 2-carboxybenzenediazoium chloride, 137.3 mL (171.6 g, 1.77 mol) 1,1dichloroethylene and 30.3 mL (25.1 g, 0.430 mol) propylene oxid were diluted in 480 mL 1,2dichloroethane. The reaction mixture in the 2 L three-neck round bottom flask equipped with a reflux condenser, a nitrogen-inlet tube and a gas bubbler was heated under reflux. After the bubbler didn't show gas formation (CO_2 and N_2) anymore, the mixture was refluxed for further 5 h to complete the reaction. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to form the crude 1,1-dichlorobenzocyclobutenone as a dark brown oil.

¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.62 – 7.30 (m, 4 H, CH), 4.05 (s, 2 H, CH₂).

Crude 1,1-dichlorobenzocyclobutenone used without further purification was heated under reflux with 120 mL of 5% aqueous H_2SO_4 for 24 h. The solution was extracted four times with 40 mL of ether. The combined organic layers were washed with 40 mL of saturated NaHCO₃, dried with 15 g of Na₂SO₄ and the solvent was evaporated to yield the crude benzocyclobutenone. This oil, bp 40° C (2 mbar), was purified by vacuum distillation; yield 11.3 g (95.9 mmol, 44%) of colourless oil.

¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.50 – 7.33 (m, 4 H, CH), 3.99 (s, 2 H, CH₂).

Benzocyclobutenedione from Benzocyclobutenone.

11.2 g (94.8 mmol) benzocyclobutenone, 42.3 g (237.7 mmol) NBS and 1.3 g BPO were added to 600 mL tetrachloromethane in a 2 L three-neck round bottom flask fitted with a reflux condenser and a nitrogen inlet tube. After 72 h under N₂ and reflux the reaction mixture was cooled to room temperature. 1.0 L petroleum ether was added to the reaction mixture to precipitate succinimide as a white solid on the surface. Followed by filtration of the succinimide and evaporation of the solvent crude 2,2-dibromobenzocyclobutenone crystalized to white brown solid. In the next step the crude product was hydrolysed at 150° C with 250 mL H₂SO₄ (50 %) for 3 h. The reaction mixture was first cooled to rt and poured in 150 mL ice-water than extracted with portions of 50 mL DCM until the extracts were colourless. The combined organic layers were dried and condensed on a rotary evaporator to yield crude benzocyclobutene-1,2dione, a yellow brown solid. The crude solid was purified by column chromatography with SiO₂ as the solid phase and DCM as the liquid phase. After evaporation of the solvent, 4.49 g (34.0 mmol, 36%) of benzocyclobutene-1,2-dione could be obtained as a yellow solid.

¹H-NMR (400 MHz, CDCl₃, δ ppm): 8.06 – 8.02 (m, 2 H, CH), 7.82-7.77 (m, 2 H, CH).

2. Target analysis of transient UV/Vis spectra



Figure S1. Species-associated spectra (SAS) of five species contained in the sequential model for target analysis.



Figure S2. Time-dependent evolution of state populations obtained from target analysis of transient UV/Vis absorption spectra with sequential model containing five species.



Figure S3. Characteristic transient time traces from the UV/Vis spectral region and corresponding fitting by target analysis with sequential model containing five species.

3. The TDDFT calculated electronic absorption spectra of triplet oxacarbene



Figure S4. TDDFT calculated electronic absorption spectra of triplet oxacarbene.

4. The tautomer of oxacarbene B and its ring-opened quinonoid cumulenone



Figure S5. Possible reaction schemes for the formation of quinonoid cumulenone.

5. Oxacarbene dimers (biphthalyls) and TDDFT calculation



Figure S6. Illustrated structure of three possible oxacarbene dimers (biphthalyls).



Figure S7. TDDFT calculated electronic absorption spectra of three possible dimers of oxacarbene.