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Synthesis, Crystal Structure, and Rearrangements of *ortho*-Cyclophane Cyclotetraveratrylene (CTTV) Tetraketone

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Abstract:
Oxidation of cyclotetraveratrylene (CTTV) with potassium permanganate in pyridine under reflux gave the tetraketone (the [1]$_4$ketonand) **3** which exists as a previously unobserved barrel conformation with S$_4$ symmetry in the crystal structure, although the more familiar "boat" conformer was shown by semi-empirical AM1 calculations to be 3.03 kcal/mol lower in energy. In addition to the CTTV tetraketone **3**, an isomeric bis-spiro lactone **4** was isolated from the basic oxidation conditions, analogous to the product of trans-annular attack and rearrangement observed with CTV, whereas in acid at elevated temperatures, tetraketone **3** underwent a very efficient rearrangement and decarboxylation to afford the highly symmetric spirobi[anthracene]-10,10'-dione derivative **5**.
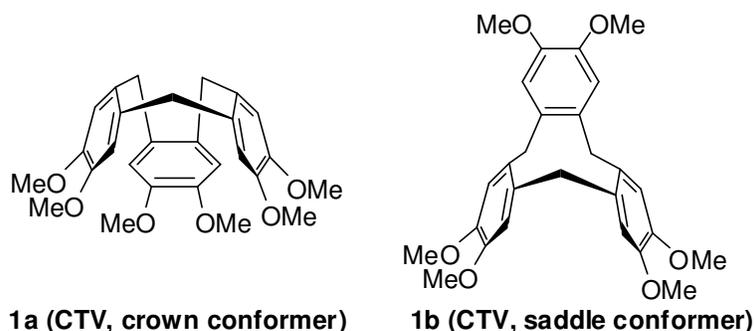
Introduction:
Supramolecular chemistry involves the study of complex molecular entities that have the capacity to participate in specific molecular recognition.[1; 2] The trimeric [1.1.1]orthocyclophane cyclotriveratrylene (CTV, **1**)[3] is a commonly-employed supramolecular scaffold that is readily prepared from the acid-catalyzed cyclotrimerization of veratryl alcohol.[4] CTV exists primarily in its rigid "crown" conformer (**1a**), useful for providing a concave face for host-guest interactions, and its saddle conformer **1b** was only recently isolated and characterized.[5] CTV has been extensively studied for its capability to bind small organic and organometallic guests within its bowl-shaped cleft. Many clathrates of CTV have been structurally characterized[6; 7] including with xenon,[8] lanthanides,[9] and anionic C70 dimers.[10] Elegant cryptophanes have been constructed by tethering CTV moieties in a face-to-face fashion employing linker chains attached to the peripheral phenolic oxygens,[11; 12] and Hardie has reported the self-assembly of ligand-bearing CTV derivatives into a star-like "stella" octangular supramolecular cagelike structure incorporating Pd(II).[13]

CTV is the best-known member of an oligomeric series of veratrylene orthocyclophanes. The tetrameric homolog, cyclotetraveratrylene (CTTV, **2**) is formed along with CTV in the acid-catalyzed oligomerization of veratryl alcohol,[14] and was originally separated and characterized by White and Gesner[15; 16] and may be conveniently prepared by condensation of 3,4-dimethoxybenzyl alcohol with trifluoroacetic acid followed by selective crystallization as described by Al-Farhan,[17] The parent hydrocarbon lacking the eight methoxy groups was thereafter synthesized by Lee[18] in a multistep sequence. White and Gesner studied the conformational dynamics of CTTV with variable temperature NMR and found that the "sofa" conformers of CTTV with C$_{2h}$ symmetry (**2b**) interconvert with an activation energy of 10.9 ±0.2 kcal/mole[16] and suggested based on a large negative entropy of activation for the interconversion

that the transitional conformer is more rigid, consistent with the CTTV crown conformer **2a** with C_{4v} symmetry as shown, or more likely a C_{2v} conformer formed by inward movement of a pair of benzene rings, and an outward movement of the opposite pair, though no signals due to this structure were observed in 1H NMR experiments, even at low temperatures.[19] Nevertheless, the bowl-shaped crown conformer (**2c**) is highly desirable for host-guest chemistry as it presents a concave surface for potential guest molecules including fullerenes, based on the ball-and-socket type complexes of CTV with C_{60}[20] and CTV with anionic C_{70} dimers.[10] Hardie succeeded in coaxing a CTTV derivative bearing ligating pyridine substituents around the periphery to adopt a new "distorted-cup" conformer when complexed with palladium.[21] Synthesis of the CTTV diketone was shown to exist as the sofa in solution based on NMR, and crystallized as the boat conformer as well.[19]

We are interested in apex modified CTV and CTTV derivatives, including the oxidized apical ketones that are useful intermediates for other cyclophanes, and should be reversibly reduced to anion radicals (ketyls) that are of interest to us with applications in redox switchable host-guest interactions. Since an understanding of the conformational dynamics is critical for host-guest interactions we studied the isolation and the saddle/crown interconversion of CTV oxime,[22; 23] and we utilized CTV oxime in the nanoscale attachment of CTV to gold surfaces with its concave bowl-shaped cavity directed away from the surface enabling host-guest attachment of the fullerene C60.[24] Although CTV monoketone[25] and CTV diketone (5,10-dione),[25; 26] have been prepared and are both known to exist as the saddle conformers, attempts to prepare the elusive CTV triketone have been thwarted by rearrangement to a spiro isomeric compound.[27; 28] The Seoul National University group has synthesized a number of ketonic crowns, coined "ketonands"[29] of significant interest since they can coordinate cations,[30] including [1]$_4$ketonand,[31] the tetraketone of [1$_4$] cyclophane (1,4,7,11-tribenzocyclododecatetraene) and higher odd-numbered ketonands including [1$_5$]-,[1$_7$]-, and [1$_9$] ketonands.[29] We now wish to report the synthesis of CTTV tetraketone, a 12-membered ring containing all sp^2 hybridized atoms, along with the isolation of the rearranged bis-spiro derivative **4**, and the efficient production of symmetric spirobi[anthracene]dione **5**.

1a (CTV, crown conformer)   **1b (CTV, saddle conformer)**

MeO   OMe

MeO   OMe
MeO   OMe

OMe
OMe

MeO
MeO   OMe
OMe

MeO   OMe
MeO   OMe

MeO
MeO   OMe

MeO   OMe

2a (CTTV, sofa conformer)   2b (CTTV, boat conformer)   2c (CTTV, crown/bowl conformer)
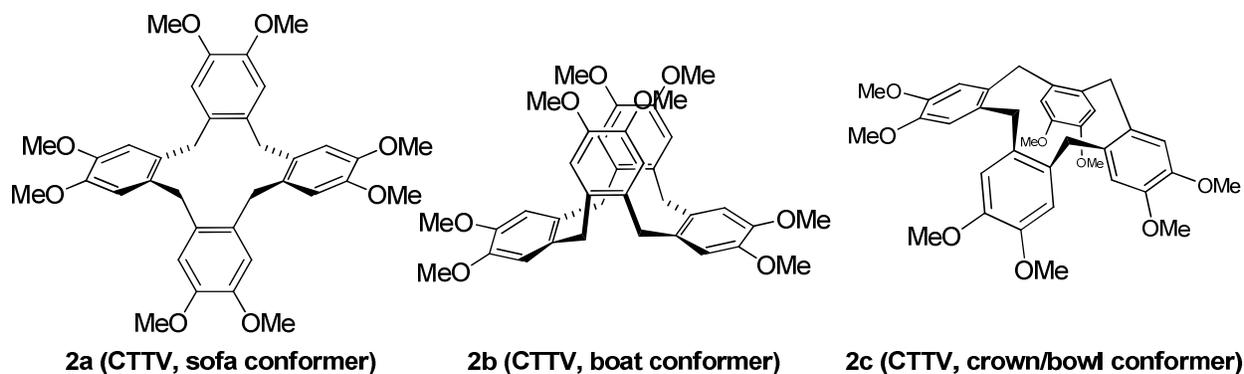
Figure 1. Conformers of CTV and CTTV

CTTV was oxidized in the presence of a large excess of potassium permanganate and activated manganese dioxide to afford the CTTV tetraketone (Scheme 1). We specifically wanted to avoid acid-catalyzed processes so we employed pyridine as the solvent subjected the reaction to heating under reflux for 35 h. Filtration through Celite followed by column chromatography eluting with EA/DCM gave the CTTV tetraketone in a very modest 8-12% yield. Treatment of CTTV with ceric ammonium nitrate in acetonitrile according to the method employed by Hwang[31] for the oxidation of the *nor*-methoxy cyclophane parent to the corresponding [1]$_4$ketonand afforded a complex mixture which contained only traces of the desired tetraketone.
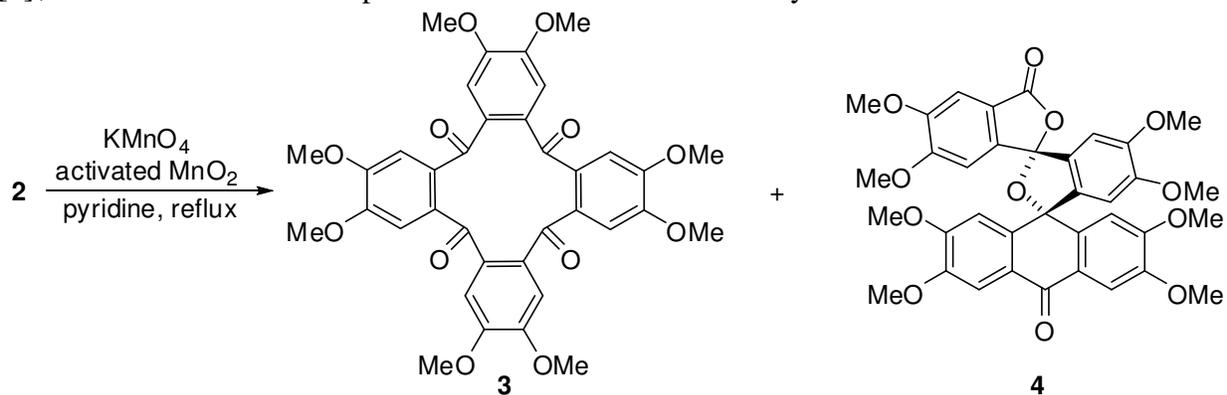
Scheme 1. Synthesis of CTTV tetraketone **3** from CTTV with bis-spiro keto-lactone **4**

The tetraketone, mp 339-341°C, exhibits an extremely broad peak centered at 6.91 ppm for the 8 aryl protons consistent with slow conformational interconversions, shifted downfield from the rather broad singlet at 6.60 for the parent CTTV[14], along with a sharp singlet at 3.92 for all eight methoxy groups, in the appropriate ratio of 3:1. In the ^{13}C NMR, a single carbonyl resonance was observed at 192.3 ppm and one larger peak is observed at 111.14 ppm for the H-bearing carbons of the aryl rings, but the quaternary carbons appear as four separate, broadened resonances at 152.4, 149.9, 137.7, 128.6 ppm, indicating a lack of symmetry induced by conformational restriction. The UV spectrum of the tetraketone exhibits two maxima in dichloromethane (c = 3.7 X 10^{-5}M), at 389 nm (e = 3.81 X 10^{-4}M) and 320 nm (e = 3.15 X 10^{-4} M), tailing out to nearly 430 nm, consistent with the pale yellow color exhibited by the crystalline compound.

The structure of tetraketone **3** was obtained by single-crystal X-ray crystallography (Figure 2) and exhibits a previously unobserved "barrel" conformation when viewed down the molecular (C2) axis and possesses S_4 symmetry, rather than the previously observed sofa or boat conformations of CTTV derivatives, or the bowl-shaped crown conformer. Each carbonyl group overlaps directly with the π–electron cloud of an electron-rich dimethoxy aryl ring which may stabilize the conformer, although no evidence of charge-transfer bands were seen in the visible portion of the electronic spectrum. Even though the structure appears as a barrel, space-filling views reveal that van der Waals contact is maintained from side to side. The crystal structure is consistent with the calculated MNDO-optimized structure of the parent hydrocarbon [1]₄ketonand,[31] the tetraketone of [1₄] cyclophane, which predicted the pair-wise distance between the oxygen atoms to be between 3.2-4.6Å. CTTV-tetraketone **3** adopts this conformation in the crystal, but in solution the equilibrium may include other aforementioned conformations. To explore the possible accessibility of the crown conformer, we employed semi-empirical AM1 calculations and initiated minimization from a crown (bowl-shaped) conformer which ultimately led to the minimized boat conformer shown in Figure 3, analogous to the boat conformer typically observed for CTTV and its derivatives. Two of the veratrole rings are π-stacked, and all four carbonyls are oriented away from the π-stacked pair, leading to a substantial calculated dipole moment of 7.40 Debye.
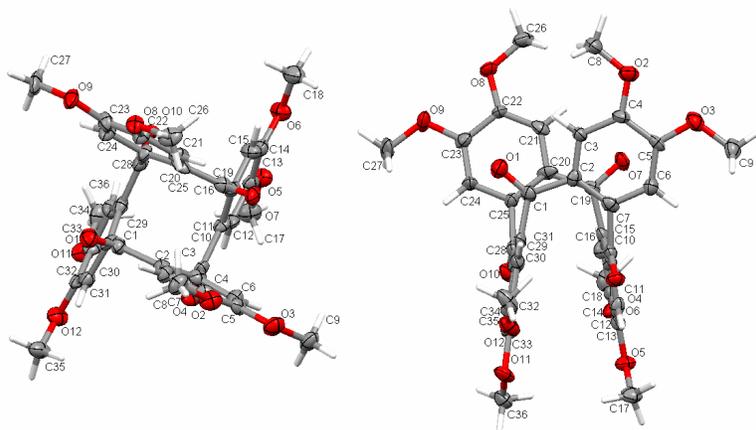

Figure 2. Single crystal X-ray structure of CTTV tetraketone **3** (50 % thermal probability level), view down and perpendicular to the molecular axis.

In a separate computational experiment, the X-ray coordinates were used as the starting point for semi-empirical AM1 minimization and the minimized S_4 conformer derived from the crystal structure has almost no dipole moment (0.06 Debye) as expected, but is calculated to be 3.03 kcal/mole higher in energy than the minimized boat geometry of Figure 3.

Attempts to co-crystallize the CTTV tetraketone **3** with C_{60} in a ball-and-socket arrangement as accomplished by Steed and Atwood with CTV[29] were unsuccessful, leading only to distinctly separate crystals of tetraketone **3** and C_{60}, perhaps due to the greater stability of the folded conformers, although we were hoping that favorable π-stacking interactions between the tetraketone and the fullerene C_{60} would overcome the intramolecular interactions favoring the boat or S_4 barrel conformers.
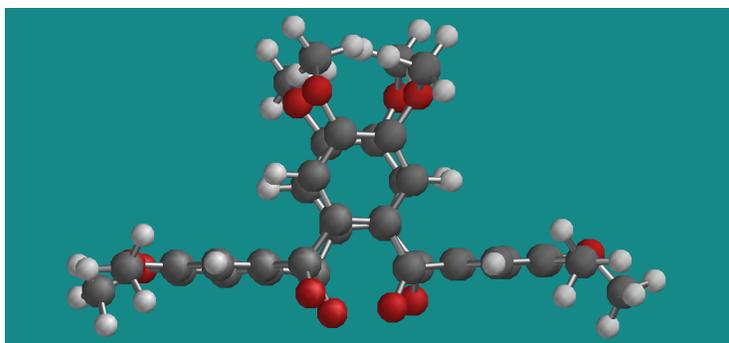
Figure 3. "Boat" conformation of CTTV Tetraketone **3**, minimized from an initial open crown (bowl) conformer

In addition to CTTV tetraketone **3**, a very small amount (1.2%) of another isomeric product was isolated. Eight unique methoxy peaks and eight unique aryl protons revealed a complete loss of symmetry. Single crystal X-ray crystallography confirmed the structure to be the bis-spiro compound **4**, an isomer of the tetraketone. Apparently the tetraketone **3** has undergone a trans-annular electrophilic aromatic addition, sequential nucleophilic acyl attacks, followed by carbon-carbon bond cleavage to regenerate aromaticity and the formation of the lactone moiety (proposed mechanism in Supplemental Scheme S1). *bis*-Spirolactone **4** is a chiral molecule containing two stereogenic carbon atoms, and is structurally analogous to the spirocycle produced by attempted oxidation of the trimeric lower homolog CTV to its corresponding triketone. [23, 24]

Figure 4. Single-crystal X-ray structure of bis-spiro lactone **4** (50 % thermal probability level)
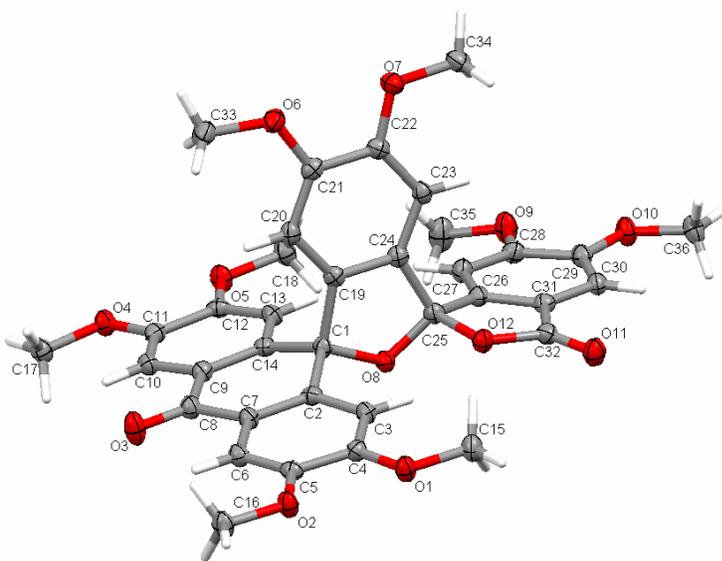
The initial electrophilic addition is apparently enhanced by the close proximity of each carbonyl carbon with a corresponding electron-rich veratrole carbon (2.87-2.90Å). Resubjection of tetraketone **3** to the oxidation conditions gave rise to very slow conversion to small amounts the bis-spirocyclic product

as judged by TLC and proton NMR. In contrast, exposure of tetraketone **3** to aqueous acetic acid under reflux with a catalytic amount of sulfuric acid afforded a new product which was shown to be the highly symmetric 10H,10'H-9,9'-spirobi[anthracene]-10,10'-dione **5** as the major product in 96% isolated yield (Scheme 2). The proton NMR features only two unique aryl protons (7.85 and 6.06 ppm), and two unique methoxyls (4.01 and 3.55 ppm), and the loss of CO_2 was apparent from the high resolution mass spectrum. Formation of spirobi[anthracene] **5** at elevated temperatures under acidic conditions apparently proceeds initially in a similar manner to the formation of spirocycle **4**, but may suffer cleavage and reclosure enabling the loss of CO_2 (proposed mechanism in Supplemental Data, Scheme S2). The production of spirobi[anthracene] **5**, which possesses S_{2n} symmetry, is a very efficient and high-yielding process, and oligomeric molecules related to **5** have been patented[32] for use in electroluminescent devices and is reminescent of fullerene spiro dimers of interest in nanomaterials research.[33]
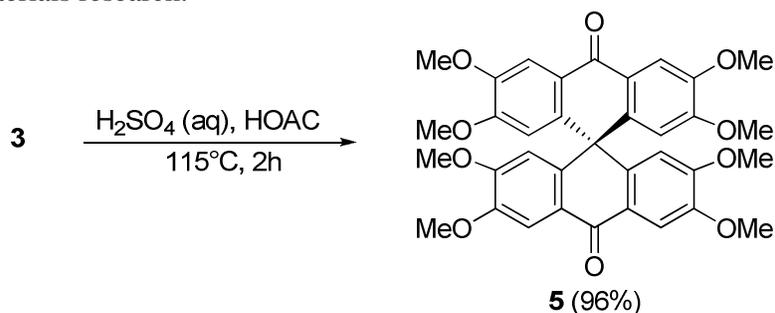
Scheme 2. Formation of 10H,10'H-9,9'-spirobi[anthracene]-10,10'-dione **5** from CTTV Tetraketone **3**

In summary, oxidation of cyclotetraveratrylene (CTTV) **2** with potassium permanganate in pyridine under reflux afforded CTTV tetraketone **3**, and single-crystal X-ray reveals that tetraketone **3** adopts a barrel-shaped S_4 conformation in the crystal, whereas semi-empirical AM1 calculations suggest the open crown ("bowl") conformation would be higher in energy than the S_4 barrel or the boat conformer (Figure 3), which appears to be the global minimum. The isomeric bis-spiro lactone **4** was also isolated and the structure confirmed by X-ray, which echoes a similar trans-annular attack and rearrangement that has been observed with the higher ketone oxidation products of the trimeric homolog cyclotriveratrylene (CTV). Aqueous acid treatment of tetraketone **3** efficiently produces the highly symmetric and potentially useful spiro bi[anthracene] **5** in 96% isolated yield. Thus, the tetraketone **3** at higher temperatures under acidic or basic conditions may undergo transannular attack and rearrangement as has been observed for more highly oxidized CTV derivatives.

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Experimental Section

All solvents and reagents were used without further purification unless otherwise noted. Reactions were performed under an atmosphere of nitrogen. Merck silica gel 60 (230-400 mesh) was used for flash chromatography. Merck Kieselgel 60 F254 DC-Fertigplatten (0.25 mm, Art. 5719) were used for TLC. ^{1}H NMR spectra were obtained from either a Varian INOVA 300 or Varian Gemini 2000 300 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. Noise-decoupled and ^{13}C NMR spectra were recorded at 75 MHz on either the Varian INOVA 300 or Varian Gemini 2000 spectrometer. IR spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR using an Alfa Aesar NaCl crystal polished optic disc, (25mm x 4mm). Mass spectra were run on a Thermo Finnigan LCQ Advantage instrument. UV-Vis spectra were obtained from an Agilent 8452 Value Analysis UV-Vis Spectrometer and using Agilent UV-Vis Chemstation version 8.2 software. Melting points were obtained using an Electrothermal Mel-Temp®. Single crystal X-ray structures were collected on a Bruker Smart Apex diffractometer at 100 K.

Cyclotetraveratrylene (CTTV, 2)
CTTV was prepared according to the method of Al-Farhan,[15] providing 4.07 g (38%) of **2** as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.60 (very broad singlet, 8H), 3.78 (very broad singlet, 32H).

CTTV Tetraketone 3 and Bis-Spiro Lactone 4
A mixture of KMnO$_4$ (26.2 g, 166 mmol) and activated MnO$_2$ (10.4 g, 120 mmol) were combined and ground to a fine uniform powder using a mortar and pestle. CTTV (1.0 eq, 1.00 g, 1.66 mmol), the KMnO$_4$/ MnO$_2$ mixture, and 60 mL of pyridine were combined and heated under for 35 hours, cooled to 80°C and filtered over a bed of Celite®. The Celite® bed was rinsed with DCM (3 x 50 mL). The filtrate was concentrated under reduced pressure and dried in vacuo at 100°C for 1 hour to afford 360 mg of crude solids. Purification by column chromatography eluting with a gradient system (10/90 to 50/50, EA/DCM) afforded CTTV Tetraketone **3** as a pale yellow solid (90.7 mg, 8.3%), mp 339-341°C. IR 2917, 2848, 1652, 1584 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.91 (8H, very broad singlet), 3.92 (24H, s). ^{13}C NMR of **3** (75 MHz, CDCl$_3$): δ 192.9, 152.4, 149.9, 137.7, 128.5, 111.1, 56.5. A single-crystal X-ray structure ultimately confirmed the structure of tetraketone **3**.

Further elution afforded spiro-lactone **4** (13.6 mg, 1.25%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.85 (1H, s), 7.67 (1H,s), 7.49 (1H, s), 7.41 (1H, s), 6.94 (1H,s), 6.89 (1H, s), 6.50 (1H, s), 6.30 (1H, s), 4.03 (3H, s), 4.02 (3H, s), 4.01 (3H, s), 3.98 (3H, s), 3.92 (3H, s), 3.89 (3H, s), 3.82 (3H, s), 3.72 (3H, s). A single-crystal X-ray structure ultimately confirmed the structure of bis-lactone **4**.

In a separate experiment, CTTV (4.00 g, 6.66 mmol) was heated under reflux with KMnO$_4$ (105 g, 6.6 mol) in pyridine (180 mL) for 13 h and worked up as above yielding CTTV tetraketone **3** (506 mg, 11.6%) as a pale yellow solid.

2,2',3,3',6,6',7,7'-octamethoxy-10H,10'H-9,9'-spirobi[anthracene]-10,10'-dione (5):
To a vial was added CTTV Tetraketone **3** (20.0 mg, 0.0305 mmol), 2 mL of glacial acetic acid, and 10 drops of 25% aqueous H$_2$SO$_4$ (v/v). The reaction mixture was heated to 115°C for 2 hours and poured into 10 mL of deionized water. The pH of the aqueous layer was adjusted to 8-

9 with aqueous sodium bicarbonate and extracted with DCM (3 x 3 mL). The combined DCM layers were successively washed with brine and dried over sodium sulfate. Concentration under reduced pressure afforded 2,2',3,3',6,6',7,7'-octamethoxy-10H,10'H-9,9'-spirobi[anthracene]-10,10'-dione **5** as a light pink solid (18 mg, 96%), mp 298-300°C. IR 2932, 2849, 1719, 1634, 1598, 1492 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.86 (s, 4H), 6.06 (s, 4H), 4.01 (s, 12H), 3.54 (s, 12H); ^{13}C (75 MHz, CDCl$_3$) δ 181.80, 153.90, 148.65, 141.97, 123.79, 110,54, 107.84, 56.14, 48.95. HRMS MH$^+$ calcd for C$_{35}$H$_{33}$O$_{10}$ 613.2068, found 613.2053; calc for C$_{35}$H$_{32}$O$_{10}$·Na 635.1888, found 635.1892.

Single crystal X-ray structure determinations of CTTV tetraketone **3** and bis-spiro lactone **4:** Diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer at 100 K using monochromatic Mo Kα radiation with the omega scan technique. Data for **3** and **4** were collected, their unit cells determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs.[A] The structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL.[B] Structure and refinement details are given in Table S1 in the supporting material, bond lengths and angles in Table S2. Complete structural details in cif format for structures **3** and **4** were deposited with the Cambridge Structural Data Cebtre as CCDC 882887 and CCDC 882888, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The structure of **3** exhibits large voids filled with ill defined solvent with a volume of 578.2 Å^3 per unit cell (29% of the unit cell volume). The solvate molecules within this void were initially refined as six (two times three) molecules of dichloromethane (one of the solvents of crystallization), but even after inclusion of disorder for all three independent molecules over two sites no completely satisfying model was achieved. ADPs were unreasonable even with more than modest re- and constraints and one large electron density peak remained without inclusion of disorder over more than three sites for some of the solvate molecules. The R1 value achieved that way was around 12-13%. The solvate molecules were thus eventually ignored and their electron density was corrected for using the Squeeze procedure implemented in the program Platon. The electron density found and corrected for by Platon was 226.8 electrons, which is close to the theoretical value expected for three dichloromethane molecules (252 electrons).

A) Apex2 v2009.7-0 (2009) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA.
B) *SHELXTL* (Version 6.14) (2000-2003) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA.