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Diels-Alder Reactions of A Cage-Annulated Cyclohexa-1,3-diene. Synthesis and Crystal Structure of A Doubly-Caged Sterically-Congested Tetraol.‡

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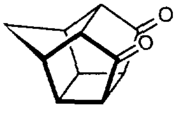
Abstract: The cage-annulated cyclohexa-1,3-diene **4a** was synthesized form the Diels-Alder adduct of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (DTCP) and 1,4-naphthoquinone by a [6 + 2]photocycloaddition. The cyclohexadiene substructure in **4a** undergoes Diels-Alder cycloadditions with dienophiles, such as maleic anhydride, *p*-benzoquinone, 1,4-naphthoquinone and dimethyl acetylenedicarboxylate. The adduct **9** from the Diels-Alder reaction of **4a** with *p*-benzoquinone was further elaborated to a C_{2v} symmetric bis-caged tetraol **16** via oxidation of **9** with DDQ, followed subsequently by a [4+2]cycloaddition with DTCP, an intramolecular photoaddition, and dechlorination. Tetraol **16** displays strong intramolecular hydrogen bonding.

INTRODUCTION

The synthesis and chemistry of cage compounds involving pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCUD, **1/2**) framework have been the subjects of extensive study.[1-4] Because of the easy accessibility and the strain contained in the pentacyclic ring system, this carbon skeleton has attracted considerable interest not only in theory[1] but applications as a starting structure for the syntheses of natural and non-natural products,[2,3] and as a potential new class of energetic materials.[4] Interest has been recently extended to the chemistry of 1,3-cyclohexadiene systems **3** that are annulated by PCUD-**1**[5] and analogous caged frameworks,[6] with regard to particularly the study of π-facial selectivity in the Diels-Alder reactions.[5a,b,e,6] As part of a continuing program which is concerned with the synthesis and chemistry of polycyclic cage compounds,[7] we have undertaken the synthesis of a facially dissymmetric cyclohexa-1,3-diene **4a** which is annulated by PCUD-**2**. We anticipated that, due to the chlorine-substituents on the cyclobutane ring, the Diels-Alder reactions would proceed with the attack of dienophiles upon caged diene **4a** via the face *syn* to the carbonyl groups (*anti* to the



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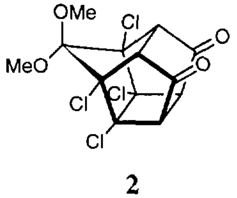

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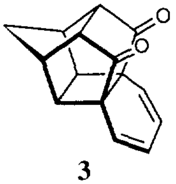

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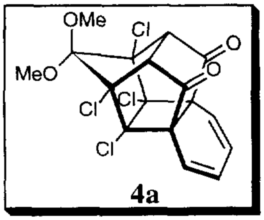

4a

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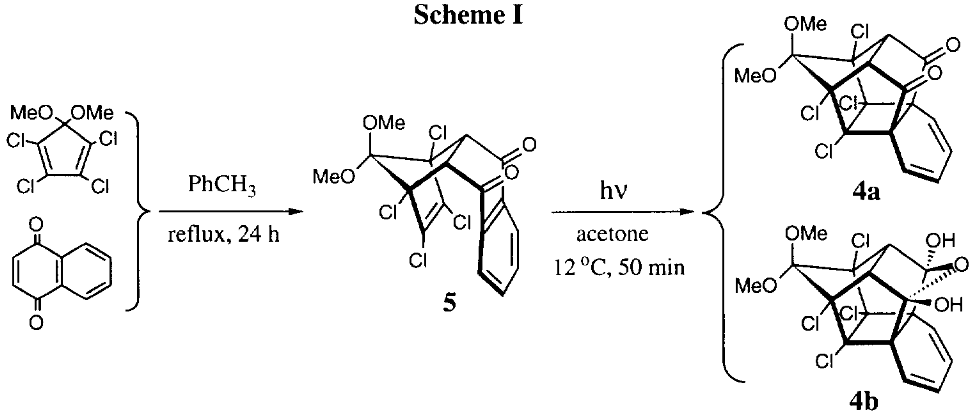
‡ This paper is dedicated to Professor Philip Eaton on the occasion of his 60th birthday.

cyclobutane ring). The cycloadducts which result might be further elaborated via another [4+2] and/or [2+2] cycloadditions to afford bis-caged polycyclic systems of novelty. Here we report the results of the Diels-Alder cycloadditions of **4a**, and the synthesis of a novel doubly-caged compound with C_{2v} character from the Diels-Alder adduct of **4a** and *p*-benzoquinone.[8]

RESULTS AND DISCUSSION

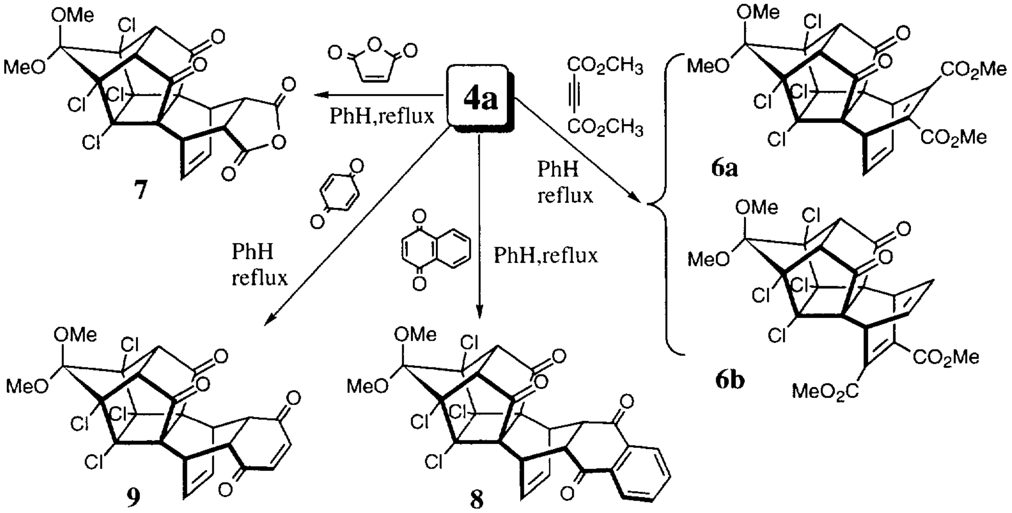
The synthesis of cage-annulated 1,3-cyclohexadiene **4a** followed the reported procedure used for the preparation of related cage compound **3**,[5j,k] starting from Diels-Alder adduct **5** of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and 1,4-naphthoquinone, followed by a [6+2]photocyclization (Scheme I). As noted in the preparation of **3**, we also found that photochemical closure of adduct **5** was fast but reversible, leading to a 35:1 mixture of caged diene **4a** and unchanged **5** (medium-pressure Hg lamp/acetone/12 °C/50 min). Caged diene **4a** contains hygroscopic carbonyl groups and could be obtained in pure form by sublimation. Elemental analysis and spectral data are consistent with the photoclosed structure. The carbonyl bands were observed at 1772 and 1746 cm^{-1} in the infrared spectrum. The ^1H NMR spectrum showed no absorption in the aromatic region, but displayed vinyl proton resonance equivalent to 4 hydrogen atoms at δ 6.21 and δ 5.26 as an A_2B_2 system.

Scheme I



The Diels-Alder reactions of caged diene **4a** with dimethyl acetylenedicarboxylate, maleic anhydride, 1,4-naphthoquinone, and *p*-benzoquinone occured smoothly, albeit slowly, to afford the corresponding 1:1 adducts. The results of these cycloadditions are outlined in Scheme II. In these Diels-Alder reactions, trial experiments showed that the same products were obtained whether pure **4a** or its hydrated form **4b** was used as starting material. Reaction of diene **4a** with dimethyl acetylenedicarboxylate in refluxing benzene afforded two 1:1 adducts as a 85:15 mixture (by integration of ^1H NMR spectrum of crude product). Only the major adduct could be separated in pure form (in 66% yield) by repeated recrystallization from dichlomethane, and was suggested to have structure **6a** based on the consideration of the attack of dienophile upon diene **4a** preferentially from the sterically less-hindered carbonyl-bearing face (*anti*-addition, defined by the relationship to the chlorine-substituted cyclobutane ring). Its ^1H NMR spectrum displayed a characteristic doublet of doublet at δ 6.76 due to the vinyl protons of etheno-bridge in a bicyclo[2.2.2]octadiene system and a singlet of intensity equivalent to 6 hydrogen atoms at δ 3.82 due to the two equivalent methoxycarbonyl

Scheme II

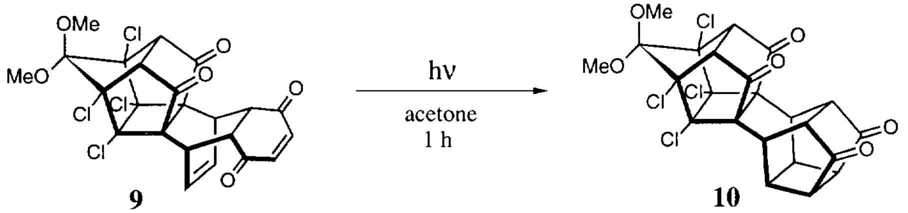


groups in the dimethyl maleate substructure, which was also indicated by an absorption band at 1726 cm^{-1} in the infrared spectrum (KBr).

Diene **4a** when treated with maleic anhydride in refluxing benzene for 36 h formed a crystalline adduct in 82% yield after recrystallization from acetone. The infrared spectrum of this adduct showed absorption bands at 1878/1855 and 1788 cm^{-1}; this doublet is characteristic of strained, cyclic acid anhydride.[9] The appearance of olefinic protons at δ 6.54 (dd, J = 4.3, 3.0 Hz) in its ^{1}H NMR spectrum established the presence of a bicyclo[2.2.2]octene system.[10,11] Again, the assignment of structure **7** as depicted in Scheme II to this adduct was based on the expectation of the dienophile to approach diene **4a** from the less-hindered carbonyl-bearing face and an endo-type addition in accordance with the Alder rule.

Heating caged diene **4a** with 1,4-naphthoquinone in benzene under reflux led to the formation of a 1:1 adduct as the sole detectable product in 86% isolated yield. This cycloadduct was assigned to have structure **8** based on the same expectation stated above, and was supported by elemental analysis and spectral data. The infrared spectrum of **8** displayed strong carbonyl absorption bands at 1769 and 1690 cm^{-1}, respectively indicating the presence of strained cyclopentanone and conjugated carbonyl groups in the molecule. An AA'BB' absorption pattern at δ 8.00 and δ 7.73 in its ^{1}H NMR spectrum confirmed the formation of adduct **8**.

The cycloaddition of diene **4a** with *p*-benzoquinone in refluxing benzene for 48 h produced a 1:1 adduct as the sole detectable product in 87% yield after recrystallization from dry benzene. The infrared spectrum of this adduct exhibited strong carbonyl absorption bands at 1767 and 1683 cm^{-1}, indicating respectively the presence of both strained cyclopentanone and conjugated enedione moieties. The characteristic absorptions at δ 6.43 (dd) and δ 6.71 (s) in the ^{1}H NMR spectrum and the corresponding absorptions at δ 132.9 (d) and δ 196.8 (s)/δ 142.1 (d) in the ^{13}C NMR spectrum further confirmed the presence of bicyclo[2.2.2]octene and 1,4-enedione substructures in this cycloadduct. Structure **9** assigned to this adduct as depicted was based on the same expectation stated above and the chemical transformations to be described later. Adduct **9** was capable of undergoing an intramolecular [2+2]photocylization (eq 1) to form a doubly-

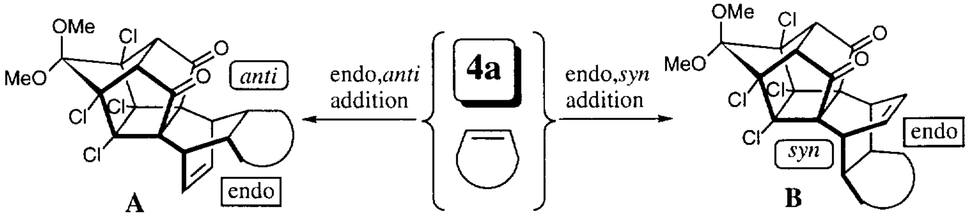


(1)

-caged compound **10**, suggesting that an endo-type addition in accordance with the Alder rule for the Diels-Alder reaction of diene **4a** with *p*-benzoquinone in particular, and with other substituted olefinic dienophiles in general, might be valid.

Cage-annulated diene **4a** can undergo Diels-Alder reaction with dienophile attacking on either the carbonyl-bearing face of the diene to produce **A** (endo,anti-addition), or on the opposite face to produce **B** (endo,syn-addition) (Scheme III). With substituted olefinic dienophiles, the corresponding anti-Alder adducts (via exo,anti addition and exo,syn addition) can be excluded, since the transition states leading to these adducts would be destablized by steric interactions between the substituents of the dienophile and either the carbonyl oxygens or the cyclobutane ring chlorine atoms. Although anti-Alder adducts are not uncommon,[12] the above reasoning is supported by the fact that Diels-Alder reaction of diene **4a** with *p*-benzoquinone produced only one adduct (type **A** or **B**) which could be induced to undergo an intramolecular [2+2]photocyclization (*vide supra*).

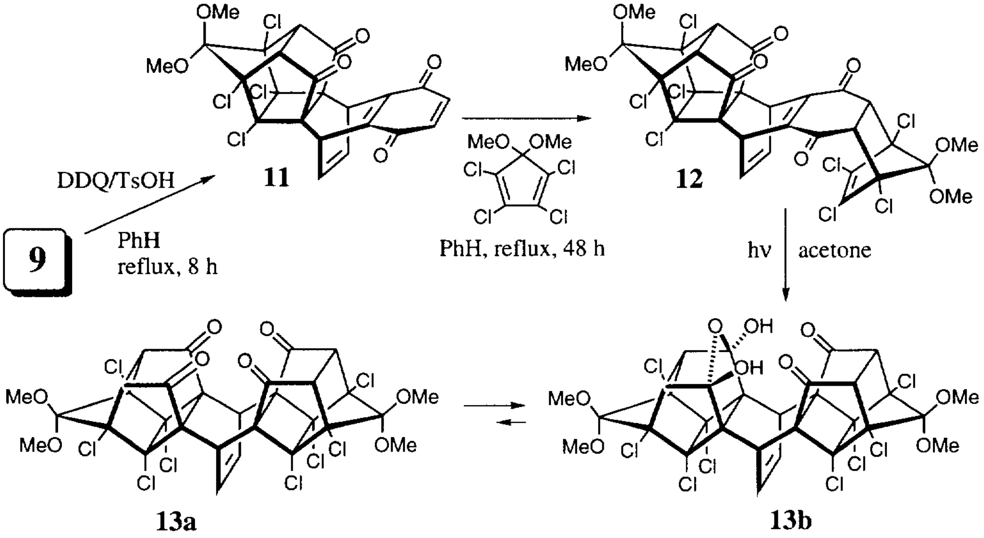
Scheme III



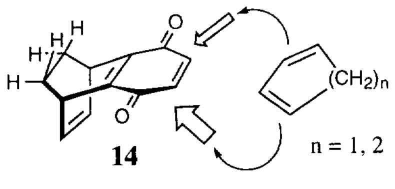
It is also reasonable to expect that diene **4a** exhibits very similar π-facial selectivity as diene **3**,[5b,c] which reacted with maleic anhydride, *p*-benzoquinone, and 1,4-naphthoquinone stereospecifically to produce a single adduct resulting from addition of dienophile to the carbonyl-bearing face of the diene (i. e., endo,anti addition). With dimethyl acetylenedicarboxylate, however, the Diels-Alder reaction of **3** gave a 55:45 mixture of two possible stereoisomers.[5e] The origin of the observed π-facial selectivity of diene **3** in Diels-Alder reaction has been considered as a result of cooperative influences of secondary carbonyl orbital interactions and steric factors of cyclobutane hydrogens.[5b] In the present case, due to the severe steric hindrance by the chlorine-substituents on the cyclobutane ring, the [4+2]cycloadditions of diene **4a** would be expected to display even stronger preference for the attack of dienophiles upon diene **4a** via the face *anti* to the cyclobutane ring to afford adducts having the structure of type **A** shown in Scheme III.

In order to gain evidence to support our stereochemical speculation of the reaction course, we carried out chemical transformations of cycloadduct **9** to a symmetric bicyclo[2.2.2]octene **13a** which is doubly-caged by PCUD-**2** as shown in Scheme IV. To this end, cyclohexenedione **9** was first converted to ring-fused*p*-benzoquinone **11** in 70% yield by oxidation in benzene with DDQ in the presence of *p*-toluenesulfonic acid.[13] The *p*-benzoquinone substructure in **11** was secured by an absorption band at 1673 cm^{-1} in the

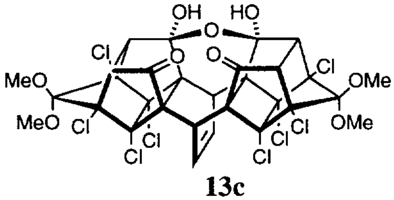
Scheme IV



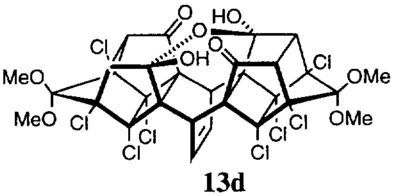
infrared spectrum, a singlet at δ 6.72 (s) in the ^{1}H NMR spectrum, and absorptions at δ 182.3 (s), δ 149.1(s), and δ 136.5 (d) in the ^{13}C NMR spectrum. The ring-fused *p*-benzoquinone **11** underwent Diels-Alder cycloaddition with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene in refluxing benzene to afford, in 80% yield, a hygroscopic product which was purified by recrystallization from dry benzene to furnish **12**. That 1:1 nature of a [4+2]cycloadduct was established by elemental and mass spectral analyses, and was further supported by IR and NMR spectra. However, the stereochemical outcome of cycloaddition leading to the endo-adduct having the depicted stereostructure **12** as a result of the addition of diene to the face *syn* to the etheno-brigdge of **11** could not be ascertained by NMR spectral data. It was suggested by our recent study of the Diels-Alder reactions of 5,8-ethano-5,8-dihydro-1,4-naphthoquinone (**14**) with cyclohexadiene and cyclopentadiene,[14] in which addition of cyclic dienes to **14** occurred preferentially at the face *syn* to the etheno-bridge to produce the corresponding endo adducts.



The endo-adduct **12**, in which the dichlorinated C=C double bond lies in close proximity to the enedione C=C double bond, could be induced to undergo an intramolecular and intercyclic [2+2]photocyclization (medium-pressure Hg lamp/acetone/1.5 h),[3d] thereby producing quantitatively a bis-pentacylo-undecadione-fused bicyclo[2.2.2]octene **13a** in its monohydrated form **13b**. The structure of **13b** was suggested by the infrared spectrum which exhibited absorption bands at 3326 (broad) and 1761 cm^{-1} (strong), consistent with the presence of both hydroxyl and strained cyclopentanone moieties in the molecule, and was supported by elemental analysis and mass spectral data [CI, *m/z* 815/813/811/809/807 (M^++1); 797/795/793 (100)/791/789 (M^+- H_2O + 1)]. Formation of monohydrate, but not dihydrate, can be attributed to the fact that four carbonyl groups in tetraketone **13a** are confined within a sterically crowded environment. The inherent mirror plane symmetry was indicated by the ^{1}H NMR spectrum which displayed an eight-group absorptions; four of which are due to four nonequivalent methoxy groups. This NMR data reveals that hydration of **13a** occurs in intra-cage fashion to form **13b**, and thereby excluding structures **13c** and **13d** which would be formed by inter-cage manners.

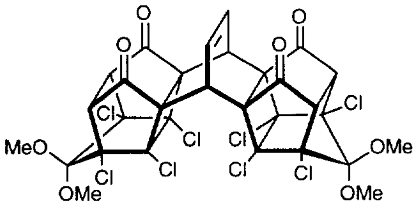


13c



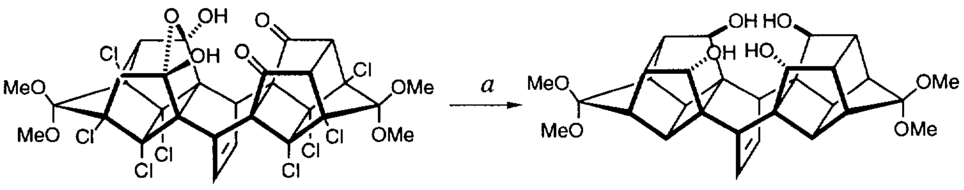
13d

Bis-PCUD-2 fused compound **13a** could be obtained by sublimation (120 °C/5 mTorr/4 days), and showed high melting point (> 300 °C), highly hygroscopic nature, and low solubility in the common organic solvents, resulting in difficulty to record its ^{13}C NMR spectrum. The relatively simple ^{1}H NMR spectrum of freshly attained **13a**, which exhibited only five groups of signals with relative intensities of 1:3:3:1:2, confirmed the existence of C_{2v} symmetry. However, this spectral data could not allow a distinction to be made between **13a** and its stereoisomeric doubly-caged compound **15**; both have C_{2v} character. Compound **15** would have formed from diene **4a**, if two Diels-Alder reactions (**4** → **9**, Scheme II; **11** → **12**, Scheme IV) had occurred with opposite π-facial selectivities (i.e. endo,syn addition for the first Diels-Alder reaction and endo,anti addition for the second one).



15

We expected the distinction between stereostructures **13a** and **15** could be achieved by establishing the relative stereochemistry of the etheno-bridge double bond with respect to the cyclobutane rings (or carbonyl groups) via NOE experiment. Thus, the doubly-caged **13b** was subjected to dechlorination with lithium/*tert*-butyl alcohol in NH$_3$-THF at -33 °C, yielding a doubly-caged tetraol **16** in 40% yield, as a result of concomitant reduction of carbonyl groups (eq 2).[3c] Tetraol **16** displayed strong absorption bands at



(2)

13b ^{a} Li/*t*-BuOH/NH$_3$ - THF/-33 °C **16**

3087 cm^{-1} in the infrared spectrum. The inherent C_{2v} symmetry expected for **16** was obviously demonstrated by a ^{1}H NMR spectrum containing eight groups of absorptions (two groups of hydrogens have similar chemical shifts to display a non-resolvable multiplet at δ 2.41) and a ten-line ^{13}C NMR spectrum. One feature in the ^{1}H NMR spectrum of **16** which merits additional comment is the appearance of a very broad absorption at unusual low-field (δ 8.13) which shows little dependence on the concentration of the NMR sample, suggesting the existence of strong intramolecular hydrogen bonding between four sterically congested hydroxyl groups. The resonances for all carbons and hydrogens in **16** were unequivocally assigned using chemical shift, DEPT, ^{1}H-^{1}H COSY, and HETCOR experiments. Assignments are presented in Figure 1. Irradiation of vinyl hydrogens (δ 6.60) gave rise to an enhancement of all hydrogens (δ 2.41) that are at allylic and cyclobutane bridgehead carbons, and no effect on all other protons. Particularly, NOE was not observed for those hydrogens at carbons bearing hydroxyl groups (δ 3.78) and the hydroxyl hydrogens (δ 8.13), indicating that dechlorination product was not formed from the doubly-caged tetraone **15**.

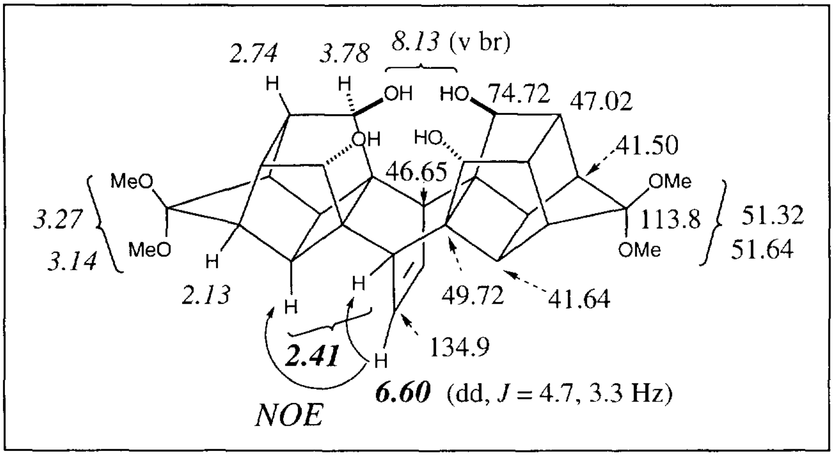


Figure 1. Carbon-13 and proton NMR chemical shifts and the NOE experimental results for **16**.

To confirm the structure of tetraol **16** unambiguously, and thereby the doubly-caged tetraone **13a**, an X-ray single-crystal structure of **16** was determined and is shown in Figure 2. One of the interesting features in the structure of **16** is displayed by the four "inward-oriented" hydroxyl groups. The four oxygens atoms of these hydroxyl groups lie in the same plan within short O·····O distances ($d_{O\cdots O} < 2.65$ Å); a very unusual and quite unique arrangement in crystal structures. It is known that for "non-ionic " O-H·····O hydrogen bonds the O·····O distances are rigidly limited to values $d_{O\cdots O} > 2.65$ Å, and the H·····O distances to values $d_{H\cdots O} > 1.68$ Å.[15,16] Therefore, the short O·····O distances, O(1)-O(2) = 2.608(5), O(1)-O(4) = 2.573(5), O(2)-O(3) = 2.576(5) and O(3)-O(4) = 2.623(5) Å, suggest the existence of strong asymmetric hydrogen bonds[17] between hydroxyl groups in the structure of **16**. Such strong intramolecular hydrogen bonding is consistent with the appearance of a very broad absorption due to hydroxyl protons at unusual low-field (δ 8.13) in the ^{1}H NMR spectrum of **16**.

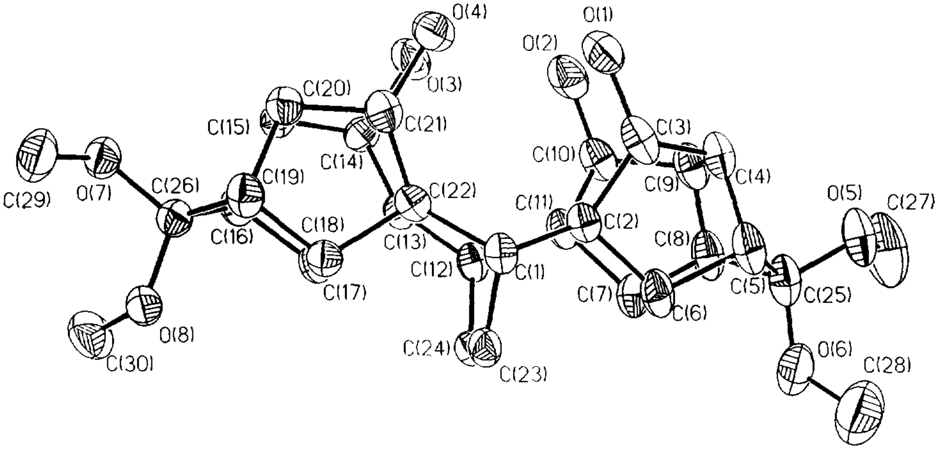


Figure 2. X-ray Structure of Doubly-Caged Tetraol **16**.

Experimental Section

All solvents were dried and distilled by standard procedures. Melting points were determined with an capillary melting point apparatus (Thomas-Hoover) and are uncorrected. Infrared (IR) spectra were recorded with a Perkin-Elmer 682 or Bio-RAD FTs 40 spectrometer. NMR spectra were recorded with a Varian Unity-300 or Varian Gemini 200 spectrometer and were obtained using $CDCl_3$ as solvent (unless otherwise specified) and tetramethylsilane (for ^1H NMR), $CDCl_3$ (for ^{13}C NMR) as internal references. The multiplicity of ^{13}C NMR signals taken from DEPT analysis refers to the number of attached H's (i.e., s = C, d = CH, t = CH_2, q = CH_3). Mass spectra were obtained on a VG Trio-2000 GC/MS or Joel JMS-SX/SX 102A mass spectrometer at 70 eV in the EI mode unless otherwise indicated. Elemental microanalyses were performed by Analytical Center operated by the Cheng-Kung University, Tainan, Taiwan.

Most of the cycloadducts prepared in this study are hygroscopic. Recrystallization from dry benzene was done via azeotropic distillation off benzene-water using Dean-Stark apparatus.

(1α,4α,4aβ,9aβ)-1,2,3,4-Tetrachloro-1,4,4a,9a-tetrahydro-1,4-dimethoxymethano-9,10-anthraquinone (5). A mixture of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (73.2 g, 0.28 mol) and 1,4-naphthoquinone (47.4 g, 0.30 mol) in toluene (250 ml) was heated under reflux for 24 h. The color of solution changed from light green to dark brown accompanied with formation of precipitates. The reaction mixture was cooled to room temperature and the precipitate was collected by filtration. The filtrate was concentrated under reduced pressure to leave additional product which was washed with a small amount of dichloromethane. The solid crude products thus obtained were combined and recrystallized from chloroform to furnish adduct **5** (83 g, 71%) as colorless plates: mp 235-236 °C; IR (KBr) 2963, 1688 (vs), 1612, 1586, 1459, 1264 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (dd, J = 6.0, 3.3 Hz, 2H), 7.73 (dd, J = 6.0, 3.3 Hz, 2H), 3.86 (s, 2H), 3.69 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 190.8 (s), 135.8 (s), 134.6 (d), 129.4 (s), 127.0 (d), 111.4 (s), 77.95 (s), 55.67 (d), 53.10 (q), 52.15 (q); MS (EI) *m/z* (relative intensity) 422 (M^+, w), 389 (57), 387 (100), 385 (100), 351 (4), 349 (6), 337 (10), 335 (12), 303 (10), 291 (7), 257 (11), 255 (31), 253 (32), 209 (23), 207 (24), 104 (59), 76 (73), 59 (48). Anal. Calcd for $C_{17}H_{12}Cl_4O_4$: C, 48.37; H, 2.87; Cl, 33.60. Found: C, 48.35; H, 2.88; Cl, 33.44.

10,12,13,14-Tetrachloro-11,11-dimethoxyhexacyclo[7.5.1.$0^{1,6}$.$0^{6,13}$.$0^{8,12}$.$0^{10,14}$]pentadeca-2,4-diene-7,15-dione (4a). A solution of adduct **5** (8.0 g, 0.02 mol) in purified acetone (200 ml) was cooled at 12 °C under nitrogen atmosphere and irradiated with a 450 W medium-pressure mercury lamp (Pyrex filter) for 50 min. Removal of solvent under reduced pressure left a solid residue which was indicated by ^{1}H NMR spectral analysis to contain caged diene **4a** and unchanged adduct **5** in a ratio 35:1. Longer irradiation resulted in only the disappearance of photoadduct **4a**. The residue thereby obtained was washed with a small amount of acetone, followed by sublimation, to give **4a** as colorless powders (6.5 g, 81%): mp 212-214 °C; IR (KBr) 2960, 1772 (vs), 1746 (vs), 1462, 1227 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.21 (dd, J = 7.0, 2.4 Hz, 2H), 5.26 (dd, J = 7.0, 2.4 Hz, 2H), 3.71 (2 s, Δν = 1.0 Hz, 3H x 2), 3.43 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 199.9 (s), 127.5 (d), 115.9 (d), 103.1 (s), 82.10 (s), 74.73 (s), 58.57 (s), 58.01 (d), 52.10 (q), 51.10 (q); MS (EI) *m/z* (relative intensity) 424 (3), 422 (8) 420 (M$^+$, 6), 389 (77), 387 (100), 385 (100), 349 (11), 341 (11), 335 (10), 311 (9), 291 (5), 257 (13), 255 (37), 253 (38), 222 (19), 220 (30), 209 (15), 207 (17), 185 (11), 150 (20), 109 (10), 104 (39), 76 (24), 59 (32). Anal. Calcd for $C_{17}H_{12}Cl_4O_4$: C, 48.37; H, 2.87; Cl, 33.60. Found: C, 48.37; H, 2.89; Cl, 33.37.

The washing solution was either recycled or concentrated to leave a mixture of **4b** and **5**, which was separated by column chromatography to afford caged diene **4b** (1.2 g, 15%): 202-204 °C, (dec.); IR (KBr) 3436 (br), 2960, 1463, 1218, 1029 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (dd, J = 7.0, 2.4 Hz, 2H), 5.46 (dd, J = 7.0, 2.4 Hz, 2H), 3.66 (s, 3H), 3.60 (s, 3H), 3.43 (br s, 2H, -OH), 3.37 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 128.2 (d), 116.1 (d), 111.2 (s), 77.65 (s), 75.98 (s), 60.01 (s), 59.72(d), 51.78 (q), 51.41 (q); Anal. Calcd for $C_{17}H_{12}Cl_4O_4 \cdot H_2O$: C, 46.40; H, 3.21; O, 18.17. Found: C, 46.61; H, 3.22; O, 18.12.

Dimethyl (1α,2β,5β,9α)-10,12,13,14-Tetrachloro-11,11-dimethoxy-7,15-dioxoheptacyclo[7.5.1.-$2^{2,5}$.$0^{1,6}$.$0^{6,13}$.$0^{8,12}$.$0^{10,14}$]heptadeca-3,16-diene-3,4-dicarboxylate (6a). A solution of diene **4a** (0.5 g, 1.2 mmol) and dimethyl acetylenedicarboxylate (1.7 g, 12 mmol) in benzene (10 ml) was heated under gentle reflux for 60 h. Removal of solvent under reduced pressure left a solid residue which was indicated by ^{1}H NMR spectral analysis to contain two adducts **6a** and **6b** in a ratio 85:15. The mixture was recrystallized from dichlomethane several times followed by sublimation to furnish a pure sample of **6a** (0.45 g, 66%) : mp 206-208 °C; IR (KBr) 3007, 2963, 1787 (vs), 1726 (vs), 1635, 1604, 1444, 1343, 1294 (vs), 1215 (vs), 1138 (vs), 1069 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (dd, J = 4.4, 3.2 Hz, 2H), 4.28 (dd, J = 4.4, 3.2 Hz, 2H), 3.82 (s, 6H), 3.68 (s, 2H), 3.67 (s, 3H), 3.26 (s, 2H); ^{13}C NMR (75.4 MHz, acetone-d_6) δ 200.8 (s), 164.8 (s), 145.1 (s), 135.3 (d), 106.0 (s), 75.80 (s), 69.57 (s), 60.23 (s), 57.92 (d), 52.19 (q), 51.76 (q), 51.64 (q), 39.17 (d); MS (EI) *m/z* (relative intensity) 566 (50), 564 (100), 562 (M$^+$, 74), 533 (27), 531 (47), 529 (88), 527 (87), 503 (21), 501 (49), 499 (47), 257 (11), 255 (33), 253 (31), 163 (42), 157 (21), 109 (5), 59 (24). Anal. Calcd for $C_{23}H_{18}Cl_4O_8$: C, 48.96; H, 3.22; O, 22.69. Found: C, 48.73; H, 3.22; O, 22.96.

(1α,2β,3β,4β,5β,9α)-10,12,13,14-tetrachloro-11,11-dimethoxy-7,15-dioxoheptacyclo[7.5.1.$2^{2,5}$.-$0^{1,6}$. $0^{6,13}$.$0^{8,12}$.$0^{10,14}$]heptadeca-3,16-diene-3,4-dicarboxylic anhydride (7). A solution of diene **4a** (0.5 g, 1.2 mmol) and maleic anhydride (1.2 g, 12 mmol) in benzene (10 ml) was heated under gentle reflux for 36 h. Removal of solvent under reduced pressure left a solid residue which was subjected to sublimation to remove unchanged maleic anhydride. The product (0.6 g) thereby obtained was indicated by ^{1}H NMR spectral analysis to contain only one adduct. Recrystallization from acetone gave pure adduct **7** (0.5 g, 82%): mp 259-261 °C; IR (KBr) 2967, 1878 (s), 1855 (s), 1788 (vs), 1769 (vs), 1444, 1224, 836 cm^{-1}; ^{1}H NMR (300 MHz,CDCl$_3$) δ 6.54 (dd, *J* = 4.3, 3.0 Hz, 2H), 3.83 (br s, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.55 (m, 2H), 3.40 (s, 2H); ^{13}C NMR (75.4 MHz, acetone-d$_6$) δ 202.3 (s), 172.3 (s), 132.2 (d), 105.4 (s), 77.55 (s), 75.33 (s), 63.36 (s), 59.60 (d), 51.91 (q), 51.82 (q), 40.84 (d), 31.96 (d); MS (EI) *m/z* (relative intensity) 522 (3), 520 (10) 518 (M$^+$, 6), 487 (70), 485 (100), 483 (100), 459 (24), 457 (73), 455 (74), 389 (27), 387 (76), 385 (77), 255 (10), 253 (9), 220 (6), 176 (5), 109 (10), 76 (18), 59 (22). Anal. Calcd for $C_{21}H_{14}Cl_4O_7$: C, 48.49; H, 2.71; O, 21.53. Found: C, 48.28; H, 2.78; O, 21.88.

(1α,2α,4α,5β,6α,7α,8β,9α,11α,12α,13α,22α)-5,6,7,8-Tetrachloro-25,25-dimethoxynonacyclo-$[10.10.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,22}.0^{15,20}]$pentacosa-15,17,19,23-tetraene-3,10,14,21-tetraone (8). A solution of diene **4a** (0.3 g, 0.7 mmol) and freshly sublimed 1,4-naphthoquinone (1.1 g, 7.0 mmol) in benzene (25 ml) was heated under gentle reflux for 48 h. Removal of solvent under reduced pressure left a solid residue which was subjected to sublimation to remove unchanged 1,4-naphthoquinone. The white powder (0.37 g) thereby obtained was indicated by ^{1}H NMR spectral analysis to contain only one adduct. Recrystallization from acetone gave pure adduct **8** (0.35 g, 86%): mp 284-285 °C; IR (KBr) 2955, 1769 (vs), 1690 (vs), 1589, 1471, 1283, 1225, 1130 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.00 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.73 (dd, *J* = 5.7, 3.3 Hz, 2H), 6.45 (dd, *J* = 4.2, 3.0 Hz, 2H), 3.91 - 3.86 (m, 4H), 3.70 (s, 3H), 3.68 (s, 3H), 3.39 (s, 2H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 202.1 (s), 195.0 (s), 135.5 (s), 134.3 (d), 132.8 (d), 126.9 (d), 104.6 (s), 74.55 (s), 63.19 (s), 59.05 (d), 51.83 (q), 51.46 (q), 44.58 (d), 32.90 (d); MS (EI) *m/z* (relative intensity) 582 (51), 580 (100), 578 (M$^+$, 76), 387 (5), 385 (5), 255 (8), 253 (5), 210 (11), 104 (10), 76 (5), 59 (5). Anal. Calcd for $C_{27}H_{18}Cl_4O_6$: C, 55.90; H, 3.13. Found: C, 55.61; H, 3.15.

(1α,2α,4α,5β,6α,7α,8β,9α,11α,12α,13α,18α)-5,6,7,8-Tetrachloro-21,21-dimethoxyoctacyclo-$[10.6.2.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,18}]$heneicosa-15,19-diene-3,10,14,17-tetraone (9). A solution of diene **4a** (1.1 g, 2.6 mmol) and freshly sublimed *p*-benzoquinone (2.8 g, 26.0 mmol) in dry benzene (25 ml) was heated under gentle reflux using a Dean-Stark apparatus for 48 h. About one-third of solvent was removed by distillation and residual solution was set aside to allow formation of precipitate which was collected and washed with a small amount of methanol to remove unchanged *p*-benzoquinone. The pale yellow powder (1.3 g) thereby obtained was indicated by ^{1}H NMR spectral analysis to contain only one adduct. Recrystallization from dry benzene gave pure adduct **9** (1.2 g, 87%): mp 274-276 °C; IR (KBr) 2959, 1767 (vs), 1683 (vs), 1609, 1471, 1237 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.71 (s, 2H), 6.43 (dd, *J* = 4.2, 3.0 Hz, 2H), 3.71 - 3.66 (m + 2 s at δ 3.69 and δ 3.66, 10 H), 3.38 (s, 2H); ^{13}C NMR (75.4 MHz, acetone-d$_6$) δ 202.7 (s), 196.8 (s), 142.1 (d), 132.9 (d), 105.3 (s), 77.91 (s), 75.33 (s), 63.52 (s), 59.59 (d), 51.79 (q), 51.69 (q), 40.00 (d), 33.69 (d); MS (EI) *m/z* (relative intensity) 532 (52), 530 (100), 528 (M$^+$, 78), 387 (58), 385 (59), 255 (8), 253 (8), 160 (5), 104 (5), 76 (6), 69 (11). Anal. Calcd for $C_{23}H_{16}Cl_4O_6$: C, 52.11; H, 3.04; O, 18.11. Found: C, 52.14; H, 3.15; O, 18.36.

Intramolecular Photocyclization of 9 to Doubly-caged Tetraone 10. A solution of adduct **9** (0.2 g, 0.4 mmol) in purified acetone (20 ml) was cooled at 12 °C under nitrogen atmosphere and irradiated with a 450 W medium-pressure mercury lamp (Pyrex filter) for 1 h. Removal of solvent under reduced pressure left a solid residue which was recrystallized from dichloromethane, followed by sublimation to furnish photocyclized product **10** as colorless crystals (180 mg, 90%): mp 300-302 °C; IR (KBr) 2960, 1776 (vs), 1465, 1239 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.06 (m, 2H), 3.72 (2 s, Δν = 1.0 Hz, 3H x 2), 3.41 (s, 2H), 3.00 (m, 2H), 2.96

(m, 2H), 2.50 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 208.0 (s), 200.5 (s), 104.7 (s), 78.34 (s), 74.95 (s), 58.28 (d), 54.46 (s), 51.97 (q), 51.58 (q), 44.79 (d), 44.11 (d), 31.41 (d), 31.04 (d); MS (EI) *m/z* (relative intensity) 532 (48), 530 (100), 528 (M^+, 78), 495 (14), 493 (14), 387 (6), 385 (6), 337 (12), 335 (12), 255 (2), 187 (11), 59 (2). Anal. Calcd for $C_{23}H_{16}Cl_4O_6$: C, 52.11; H, 3.04; O, 18.11. Found: C, 52.22; H, 3.10; O, 18.40.

(1α,2α,4α,5β,6α,7α,8β,9α,11α,12α)-5,6,7,8-Tetrachloro-21,21-dimethoxyoctacyclo[10.6.2.1^{5,8}.-0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,18}]heneicosa-13(18),15,19-triene-3,10,14,17-tetraone (11). A solution of *p*-toluenesulfonic acid (0.4 g, 1.9 mmol) in dry benzene (20 ml) was refluxed using a Dean-Stark apparatus for 1 h, and into the solution were then added compound **9** (1.0 g, 1.9 mmol) and 2,3-dichloro-5,6-dicyano-benzoquinone (0.5 g, 1.9 mmol). The mixture was heated under gentle reflux for 16 h, cooled to room temperature, and diluted with dichloromethane (30 ml). The reaction mixture was filtered and the filtrate was successively washed with saturated sodium bicarbonate solution (20 ml), water (20 ml), and brine (20 ml). The organic layer was dried ($MgSO_4$), filtered, and concentrated to leave a solid residue which was purified by flash column chromatography (SiO_2) using ethyl acetate/hexane (1:5) as eluent to afford light yellowish solids of **11** (0.7 g, 70 %). Recrystallization from dry benzene gave pure, pale yellowish prisms of **11**: mp 284-285 °C; IR (KBr) 2958, 1779 (vs), 1673 (vs), 1595, 1465, 1323, 1226, 1130 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.72 (dd, *J* = 4.3, 3.2 Hz, 2H), 6.70 (s, 2H), 4.51 (dd, *J* = 4.3, 3.2 Hz, 2H), 3.67 (s, 3H), 3.66 (s, 2H), 3.24 (s, 3H); ^{13}C NMR (50 MHz,$CDCl_3$) δ 201.5 (s), 182.3 (s), 149.1 (s), 136.5 (d), 135.0 (d), 105.9 (s), 75.80 (s), 75.56 (s), 70.97 (s), 58.20 (d), 52.55 (q), 52.17 (q), 34.13 (d); MS (EI) *m/z* (relative intensity) 532 (4), 530 (13), 528 (23), 526 (M^+, 17), 495 (37), 493 (100), 491 (97), 467 (21), 465 (42), 463 (36), 257 (13), 255 (45), 253 (42), 231 (11), 209 (17), 207 (20), 200 (16), 174 (19), 109 (19), 87 (11), 59 (50). Anal. Calcd for $C_{23}H_{14}Cl_4O_6$: C, 52.30; H, 2.67; Cl, 26.85. Found: C, 52.02; H, 2.75; Cl, 26.70.

(1α,2α,4α,5β,6α,7α,8β,9α,11α,12α,15α,16β,19β,20α)-5,6,7,8,16,17,18,19-Octachloro-25,25,26,26-tetramethoxydecacyclo[10.10.2.1^{5,8}.1^{16,19}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.-0^{13,22}.0^{15,20}]hexacosa-13(22),17,23-triene-3,10,14,21-tetraone (12). A mixture of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (7.5 g, 0.028 mol) and **11** (7.5 g, 0.014 mol) in dry benzene (150 ml) was heated under reflux using a Dean-Stark apparatus for 48 h. The reaction mixture was distilled to remove most of the solvent (*ca* . 130 ml) and then cooled to room temperature. The yellowish precipitate was collected by filtration and washed with methanol (20 ml) to furnish adduct **12** (8.9 g, 80%). Recrystallization from dry benzene provided pure **12** as colorless powders: mp 287-289 °C (decomp); IR (KBr) 2956, 1784 (vs), 1687, 1609, 1470, 1212, 1125, 987 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.67 (dd, *J* = 4.3, 3.3 Hz, 2H), 4.44 (dd, *J* = 4.3, 3.3 Hz, 2H), 3.73 (s, 2H), 3.65 (br s, 9H), 3.58 (s, 3H), 3.24 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.2(s), 186.2 (s), 155.2 (s), 135.1 (d), 129.9 (s), 111.5 (s), 105.8 (s), 78.32 (s), 75.71 (s), 70.43 (s), 58.24 (d), 55.70 (d), 55.10 (d), 53.81 (q), 52.84 (q), 52.53 (q), 52.17 (q), 34.64 (d); MS (EI) *m/z* (relative intensity) 761 (14), 759 (37), 757 (62), 755 (67), 753 (30, M^+ - Cl), 257 (33), 255 (76), 253 (74), 233 (23), 231 (23), 229 (14), 227 (16), 225 (10), 221 (13), 220 (13), 218 (16), 216 (17), 211 (19), 209 (67), 207 (67), 167 (10), 139 (14), 109 (22), 75 (15), 59 (100). Anal. Calcd for $C_{30}H_{20}Cl_8O_8$: C, 45.49; H, 2.55; Cl, 35.81. Found: C, 45.52; H, 2.58; Cl, 35.33.

Intramolecular Photocyclization of 12 to Doubly-caged Tetraone 13a. A solution of adduct **12** (100 mg, 0.13 mol) in purified acetone (150 ml) was irradiated under nitrogen atmosphere with a 450 W medium-pressure mercury lamp (Pyrex filter) for 1.5 h. Most of the solvent was recovered for use in other runs by distillation. The resulting precipitate was collected by filtration and washed with a small amount of chloroform to give photoclosed monohydrate **13b** as colorless powders (100 mg, 100%): IR (KBr) 3326 (vs), 1761 (vs), 1452, 1217, 1097, 863 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.79 (dd, *J* = 4.6, 3.0 Hz, 2H), 3.67 (s, 3H), 3.63 (s, 3H), 3.62 (s, 3H), 3.54 (s, 3H), 3.42 (s, 2H), 3.28 (dd, *J* = 4.6, 3.0 Hz, 2H), 3.42 (s, 2H); MS (CI) *m/z* (relative intensity) 815 (7), 813 (13), 811 (24), 809 (12), 807 (M$^+$ + 1, 7), 797 (26), 795 (67), 794 (30), 793 (100), 792 (26), 791 (85), 789 (M$^+$ + 1 - H$_2$O, 32). Anal. Calcd for $C_{30}H_{20}Cl_8O_8{\bullet}H_2O$: C, 44.48; H, 2.74. Found: C, 44.43; H, 2.83.

Monohydrate **13b** was sublimed at 120 °C (5mToor) for 4 days to give **13a** as colorless powders: mp > 300 °C; IR (KBr) 1765 cm^{-1} (vs); ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.74 (dd, *J* = 4.6, 3.0 Hz, 2H), 3.66 (s, 6H), 3.63 (s, 6H), 3.28 (dd, *J* = 4.6, 3.0 Hz, 2H), 3.42 (s, 4H); MS (CI) *m/z* (relative intensity) 799 (10), 797 (30), 796 (21), 795 (68), 794 (34), 793 (100), 792 (28), 791 (86), 790 (12), 789 (M$^+$+ 1, 37). Anal. Calcd for $C_{30}H_{20}Cl_8O_8$: C, 45.49; H, 2.55; Cl, 35.81. Found: C, 45.61; H, 2.57; Cl, 35.82.

Dechlorination of Doubly-caged Tetraone Monohydrate 13b to Tetraol 16. Into a 500-ml, three-necked reaction flask, fitted with a dry ice-acetone condenser, were placed tetraone monohydrate **13b** (500 mg, 0.62 mmol), tetrahydrofuran (100 ml), and *tert*-butyl alcohol (2.3 g, 31.2 mmol). The stirring suspension was cooled with a dry ice-acetone bath and charged with liquid ammonia (150 ml) under argon atmosphere. Lithium (200 mg, 42.9 g-atom) was added and the cooling bath was then removed. The resulting deep blue solution became milky-white after stirring for 24 h, and an additional portion of lithium (50 mg, 7.1 g-atom) was added. The deep blue solution was stirred for another 10 h, and was added ammonium chloride to quench the reaction. The resulting reaction mixture was allowed to warm-up gradually (overnight) to remove ammonia, and concentrated under reduced pressure. To the residue was added water (50 ml), and the mixture was extracted with chloroform (3 x 50 ml). The organic layers were combined, washed with brine (2 x 50 ml), dried (MgSO$_4$), filtered, and concentrated. The pale brown residue thereby obtained was purified via flash chromatography on silica gel (1:2 ethyl acetate-hexane as eluent) to afford tetraol **16** (130 mg, 40%). Recrystallization from chloroform-hexane provided pure **16** as colorless needle-like crystallines: mp 201-202 °C (decomp); IR (KBr) 3087, 1535, 1466, 1064 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) and ^{13}C NMR (50 MHz, CDCl$_3$) see Figure 1 in the text. MS (EI) *m/z* (relative intensity) 524 (1, M$^+$), 506 (3), 493 (11), 475 (26), 474 (100), 457 (27), 456 (92), 442(45), 424 (17), 380 (16), 362 (19), 155 (18), 151 (32), 139 (10), 127 (24), 125 (11), 121 (11), 101 (16), 97 (11), 95 (20), 75 (14). Anal. Calcd for $C_{30}H_{36}O_8$: C, 68.69; H, 6.92; Found: C, 68.57; H, 7.05;

Crystal Data for Tetraol 16. triclinic system, space group $P\bar{1}$; a = 6.716(1), b = 12.137(2), c = 15.257(3) Å, α = 77.77(3), β = 88.58(3), γ = 84.16(3)°; V = 1208.5(5) Å^3, Z = 2, F(000) = 552, D_{calc} = 1.430 Mgm^{-3}, μ = 0.103 mm^{-1}. Diffraction data were collected at 295 °K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated MO-K_α radiation, λ = 0.71069 Å. The unit cell parameters and orientation matrix were established from a least-squares fit of 25 reflections. Intensity data were collected in the ω-2θ scanning mode with three standard reflections monitored for intensity variation throughout the experiment. No significant variation in standards was observed. Of the 5548 reflections collected ($2\theta_{max}$ = 55 °), 2517 unique reflections were considered observed (I > 2σ (I)) after Lorentz polarization and empirical absorption corrections. The structure was solved by direct methods using NRCVAX[18] and refined by full-matrix least-squares (based on F^2) using SHELXL-93[19]. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were constrained to geometrically calculated positions. The reliability factors converged to R_1 = 0.066, wR_2 = 0.180 and GOF = 0.99. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at Cambridge Crystallographic Data Center.

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References and Notes

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