Synthesis of Dibenzopyrenes and Pyrenes via Photolytic Sulfur Extrusion and Intramolecular Cross-Coupling Reactions of Dithia[3.3](1,3)naphthalenophanes and Dithia[3.3]metacyclophanes

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The syntheses of several substituted dithia[3.3]metacyclophanes and dithia[3.3](1,3)naphthalenophanes are reported and their photolyses in triethyl or trimethyl phosphite are described. Under these conditions, the corresponding tetrahydrodibenzopyrenes and tetrahydropyrenes are produced in a one-pot procedure when the precursor dithianaphthalenophanes and dithiacyclophanes possess at least one intraannular methoxyl group. A mechanism with supporting evidence is proposed to account for these results. Structural determinations of the four isomeric 11,22-dimethoxy-2,13-dithia[3.3](1,3)naphthalenophanes by NMR and X-ray single-crystal diffraction studies are also described. The syntheses of the novel *anti-transoid*- and *anti-cisoid*-[2.2](1,3)naphthalenophanes are also described.

In connection with our ongoing research into the chemistry of the calixnaphthalenes[1,2] and their analogues,[3] we were interested in the synthesis of tetrahomocalix[4]naphthalene (**1**) and its structural isomers. The synthetic approach which we employed was similar to that used for the synthesis of (1,3)dihomocalix[4]naphthalenes.[3] The latter compounds, which are the first [1.2.1.2](1,3)naphthalenophanes to be reported, were obtained via a final photolytic sulfur extrusion reaction in triethyl phosphite. Such photolytic sulfur extrusion reactions have also been used by others to synthesize cyclophanes.[4,5] During attempts to produce the tetrathia[3.3.3.3](1,3)naphthalenophane (**2**), which is the potential precursor to **1**, the four isomeric 11,22-dimethoxy-2,13-dithia[3.3](1,3)naphthalenophanes (**3**−**6**) were obtained. These products are analogous to the corresponding 11,22-dimethyl- and 11,22-unsubstituted-2,13-dithia-[3.3](1,3)naphthalenophanes (**13**−**16**) reported by Mitchell *et al.*[6] However, when each of the compounds **3**−**6** was photolyzed in triethyl or trimethyl phosphite, tetrahydro-3,4:8,9-dibenzopyrene (**7**) or tetrahydro-3,4:9,10-dibenzopyrene (**8**) was obtained instead of the expected corresponding naphthalenophane. Facile oxidation of these tetrahydro compounds produced dibenzopyrenes **9** and **10**, respectively. In this paper we report that this type of sulfur extrusion with concomitant transannular cyclization appears to be a general one which could offer some advantages for the synthesis of dibenzopyrenes and pyrenes. A mechanism is proposed to account for the observed results. We also describe the structural determinations of the isomeric dithianaphthalenophanes **3**−**6** and the novel [2.2](1,3)naphthalenophanes **41** and **42**.

Results and Discussion

Base-mediated coupling of bis(bromomethyl)methoxynaphthalene **11** with bis(mercaptomethyl)methoxynaphthalene **12** produced a mixture which, after preparative layer chromatographic (PLC) separation, afforded four isomeric 11,22-dimethoxy-2,13-dithia[3.3](1,3)naphthalenophanes (**3**−**6**) in 10%, 18%, 34% and 19% yields, respectively (Scheme 1). Isomer **3** was the least polar, followed by **4**, **5**, and **6** being increasing more polar. A fifth fraction was also isolated (17%) whose spectral properties (NMR and FAB MS) were distinctly different from those of any of the compounds **3**−**6**. This fraction, which is homogeneous on TLC, appears to be a mixture of possibly all four isomeric tetrathia[3.3.3.3](1,3)naphthalenophanes. Work is presently ongoing on this fraction with results to be published in a forthcoming paper.

The ^{1}H NMR spectrum of **3** has well-resolved signals with simple splitting patterns (as do, to varying degrees, the spectra of each of the other isomers **4**−**6**) that are consistent with a *transoid-anti* structure.[6] Support for the NMR assignments (of this and the other isomers, Figure 1) is based upon 2-D and NOED experiments and by comparison with arguments presented by Mitchell *et al.*[6] for their closely related compounds **13**−**16**. The methoxyl groups of **3** at $\delta = 2.93$ are shielded by 0.64 ppm relative to those of its *syn* isomer **5**. The bridging methylene protons of **3** are diasteretopic and appear as two sets of AB quartets, one which is poorly resolved and is centered at $\delta = 3.26$. Since H-5 (H-16) is the only naphthalene-ring singlet, it was used as the reference signal together with NOED determinations to unequivocally assign the remaining naphthalene-ring protons H-6 to H-9 (H-16 to H-20) and also the remainder of the protons. The AB quartet at $\delta = 3.26$ is attributed to the H-3 (and H-14) protons since irradiation of this system produces a 5.6% NOED enhancement of the H-5 (and H-16) singlet and also a 2.4% NOED enhancement of the doublet at $\delta = 8.18$ which is due to H-20 (and H-9). Molecular models indicate that H-20 and H-9 can only

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(1) Georghiou, P. E.; Li, Z. *Tetrahedron Lett.* **1993**, *34*, 2887.
(2) Georghiou, P. E.; Ashram, M.; Li, Z.; Chaulk, S. G. *J. Org.Chem.* **1995**, *60*, 7284.
(3) Georghiou, P. E.; Li, Z.; Ashram, M.; Miller, D. O. *J. Org.Chem.* **1996**, *61*, 3865.
(4) Boekelheide, V.; Reingold, I. D.; Tuttle, M. *J. Chem. Soc. Chem. Commun.* **1973**, 406.
(5) Yamato, T.; Miyazawa, A.; Tashiro, M. *Chem. Ber.* **1993**, *126*, 2505.
(6) Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2560; see also Mitchell, R. H. In *Cyclophanes*; Academic Press, New York, 1983; Vol. 1.

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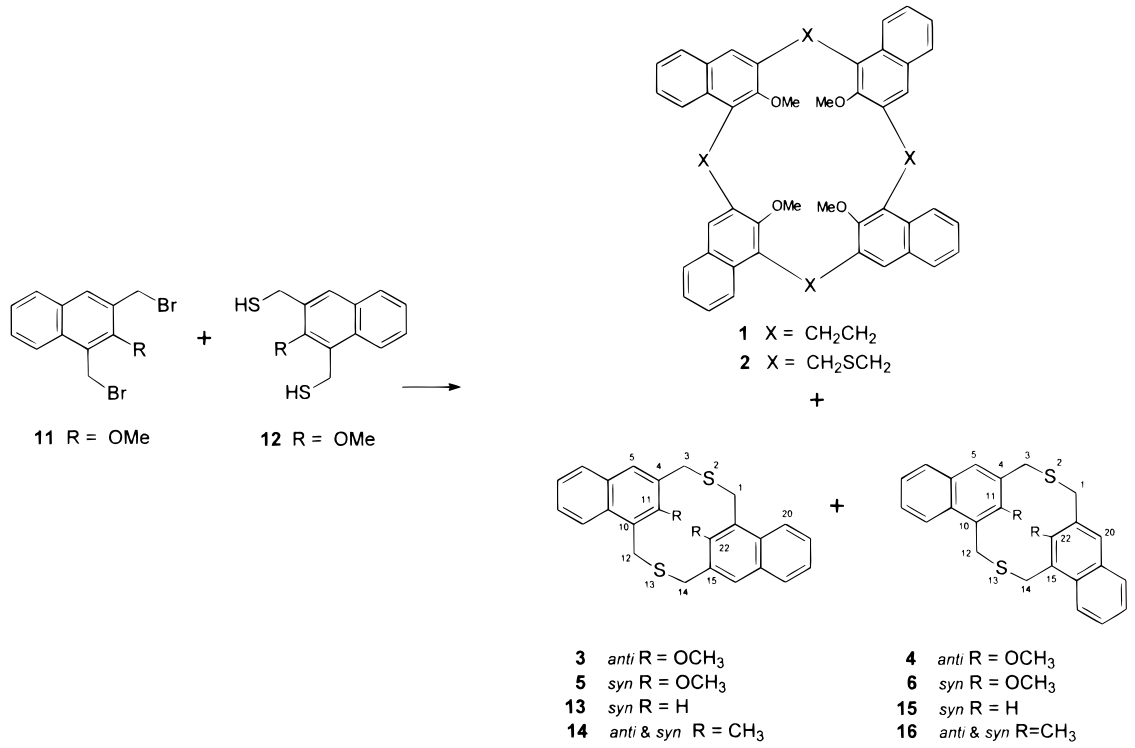
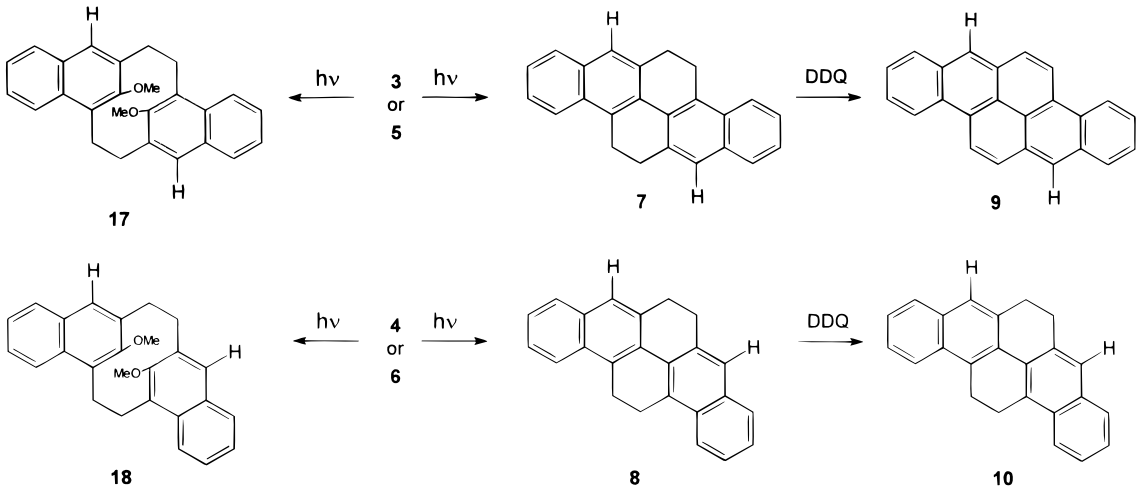
Scheme 1



Scheme 2



be in close proximity to H-3x and H-14x, respectively, when the intraannular 12-membered dithia ring is in a conformation with S-2 pointing down and S-13 pointing up, as indicated in Figure 1. This is in agreement with the conformation proposed by Mitchell *et al.*[6] for the analogous compound *anti*-**14**. The other AB quartet has two clearly defined doublets; one centered at $\delta = 4.00$ ($J = 11.7$ Hz; H-1y and H-12y; pseudo-equatorial[7]) which is NOED-enhanced by 6.2% when H-9 is irradiated, and the other at $\delta = 4.33$ ($J = 11.7$ Hz; H-1x and H-12x; pseudo-axial[7]), which is not. A single crystal X-ray diffraction analysis on **3** (Figure 2) confirms the structural assignments and indicates that the preferred conformation in the solid state is the same as that in solution. Molecular modeling calculations[8] are also consistent with the conformational assignment depicted in Figure 1.

Unequivocal chemical proof of the *transoid* structure of **3** (and of **5** and also of the *cisoid* structures of isomers **4** and **6**; see below) was obtained unexpectedly from its photolysis in triethyl phosphite,[4] which produced, instead of the anticipated naphthalenophane **17**, a product whose NMR spectra showed it to be highly symmetrical and lacking the methoxyl groups. Mass spectral data indicated, and single crystal X-ray crystallography (Figure 3) confirmed, it to be 1,2,6,7-tetrahydro-3,4:8,9-dibenzopyrene (**7**). DDQ oxidation easily converted **7** to 3,4:8,9-dibenzopyrene (**9**).[9]

The methoxyl groups in the ^{1}H NMR spectrum of the *syn* isomer **5** are at $\delta = 3.57$, which is more typical for an unshielded 2-naphthyl methoxyl group ($\delta = 3.92$ in

(7) In this paper, "pseudo-axial" protons refer to bridging methylene group protons which are in, or are directed toward, the planes of the naphthalene rings; "pseudo-equatorial" protons refer to bridging methylene group protons which are out of, or are directed out of, the planes of the rings.

(8) SPARTAN, version 4.1, Wavefunction, Inc., Irvine, CA.

(9) Clar, E. *Polycyclic Hydrocarbons*, Academic Press, London, 1964; Vol. II.

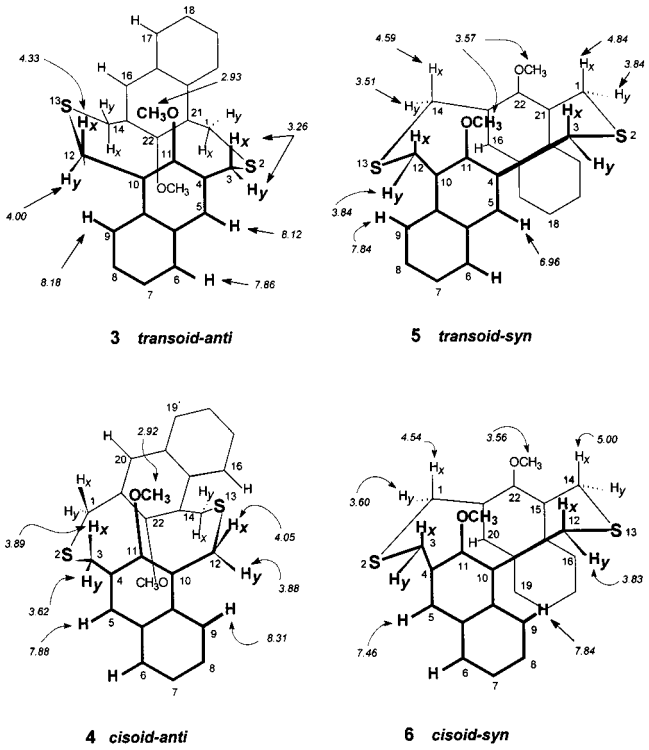


Figure 1. Selected ^{1}H δ values and preferred conformations of compounds **3**−**6**.

2-methoxynaphthalene, and $\delta = 3.86$ in bis(2-methoxy-1-naphthyl)methane). The bridging methylene protons are diasteretopic and appear as two sets of AB quartets each having a pair of clearly defined doublets. One AB quartet has a doublet centered at $\delta = 4.84$ ($J = 13.5$ Hz) assigned to H-1x and H-12x which is coupled to the doublet centered at $\delta = 3.84$ assigned to hydrogens H-1y and H-12y. The other AB quartet, assigned to the H-3x (and H-14x) protons, has a doublet centered at $\delta = 4.59$ ($J = 16.4$ Hz) which is coupled to the doublet at $\delta = 3.51$ (H-3y; H-14y). The *transoid* hydrogens H-5 and H-16 are eclipsed by the opposing naphthalene rings and thus appear as a singlet at $\delta = 6.96$ which is shielded by 1.16 ppm compared to the corresponding signal in **3**. The conformational assignment shown is further supported by NOED determinations and molecular modeling calculations. For example, there is NOED enhancement of H-1x (H-12x) by H-3x (H-14x) and *vice versa*. Photolysis of **5** under the conditions employed for **3** also produced **7**, but no **17**.

The ^{1}H NMR spectrum of **4** is consistent with its *cisoid-anti* structure. The methoxyl groups of **4** are at $\delta = 2.92$ indicating shielding by 0.64 ppm relative to those of its *cisoid-syn* isomer **6**. The bridging methylene protons appear as two overlapping sets of AB quartets whose respective pairs of coupled doublets are centered at $\delta =$ 4.05 ($J = 13.8$ Hz; H-12x, H-14x) and $\delta = 3.88$ (H-12y, H-14y); and at $\delta = 3.89$ ($J = 13.8$ Hz, H-1x, H-3x) and δ = 3.62 (H-1y, H-3y). The singlet at $\delta = 7.88$ due to the *cisoid* hydrogens H-5 and H-20 is deshielded relative to the corresponding signal (at $\delta = 7.46$) for **6**. NOED experiments on **4** reveal that irradiation of *either* H-3x (H-1x) *or* H-3y (H-1y) enhances H-5 (H-20) by 1.9% and 1.4%, respectively. However, irradiation of *only* H-12y (H-14y) enhances H-9 (H-16) by 7.7%. Irradiation of H-12x (H-14x) does not enhance H-9 (H-16). To account for these NMR observations, the preferred conformation appears to be one in which there is, on average, a skewing of the C-1−S-2−C-3 bridge which would place the S-2−C-3−C-4 bonds in a nearly coplanar arrangement with the C-4−C-11 naphthalene ring (in dynamic equilibrium with the conformation which places S-2−C-1−C-21 bonds in a nearly coplanar arrangement with the C-21−C-22 naphthalene ring). Since only H-9 (H-16) is NOED enhanced when H-12y (H-14y) is irradiated, the other (C-12−S-13−C-14) bridge cannot be similarly skewed. This is also in general agreement with the interpretations made without any such NOED data, by Mitchell *et al.* for the ^{1}H-NMR spectra of their analogous *anti*-**16**.

The line shapes and chemical shifts for the bridging methylene protons in the *cisoid-syn* compound **6** are similar to those observed in the *transoid-syn* isomer **5**. In **6**, one AB quartet has a doublet centered at $\delta = 5.00$ ($J = 14.7$ Hz) assigned to H-12x (and H-14x), which is coupled to the doublet centered at $\delta = 3.83$ (H-12y, H-14y). The other AB quartet due to the protons on C-1 (and C-3) has a doublet centered at $\delta = 4.54$ ($J = 15.0$ Hz) assigned to H-1x (and H-3x) and its coupled doublet at $\delta = 3.60$ assigned to H-1y (and H-3y). Mitchell *et al.* assigned a preferred conformation to the analogous compound *syn*-**16** in which they postulated that, in order to minimize the *peri* interactions between the methylene bridge protons and the protons on the A-rings (H-5 and H-20 in **6**), the C-1−S-2−C-3 bridge should be pointing up and the C-12−S-13−C-14 bridge pointing down in a boat−chair type of conformation. NOED determinations did not permit distinguishing unequivocally between such a boat−chair type of conformation and one in which both bridges are pointing down in a chair−chair type of conformation. Molecular modeling calculations however clearly indicate that the latter is energetically favored (by 6.35 kcal/mol). Also, the optimized geometries of the two conformations reveal that the distance between H-3y and H-5 (the *peri* interaction referred to above) is only 2.40 Å in the boat−chair but 2.71 Å in the chair−chair conformation.

Photolysis of either **4** or **6**, under the same conditions employed for **3**, and **5** produced only 1,2,6,7-tetrahydro-3,4:9,10-dibenzopyrene (**8**) and no 10,20-dimethoxy(1,3)-naphthalenophane (**18**). DDQ oxidation of **8** afforded 3,4:9,10-dibenzopyrene (**10**). Both of the isomeric benzopyrenes **9** and **10** had identical physical properties with those previously reported.[9]

We are unaware of any other reports of similar one-pot sulfur extrusion/transannular cyclizations from 2,13-dithia[3.3]naphthalenophanes or 2,11-dithia-[3.3]cyclophanes leading to either tetrahydrodibenzopyrenes or tetrahydropyrenes, respectively. Boekelheide *et al.*[4] first reported the photochemical transformation in trimethyl phosphite of 6-methyl- and 9-methyl-2,11-dithia[3.3]cyclophane to the corresponding [2.2]metacyclophanes but did not report the formation of any of the corresponding pyrenes. Earlier, Mitchell and Boekelheide[10] had reported the transformation of 9,18-dimethyl-2,11-dithia-[3.3]metacyclophanes into the corresponding 15,16-dimethyldihydropyrene, but the sequence involved several steps including a Stevens rearrangement and an elimination step. On the other hand, there are many examples that have been reported in which halogen-induced[11−13] and photolytically induced[14] transannular

(10) Mitchell, R. H.; Boekelheide, V. *Tetrahedron Lett.* **1970**, 1197; Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.
(11) Sato, T.; Nishiyama, K.; Murai, A. *J. Chem. Soc. Chem. Commun.* **1972**, 163.

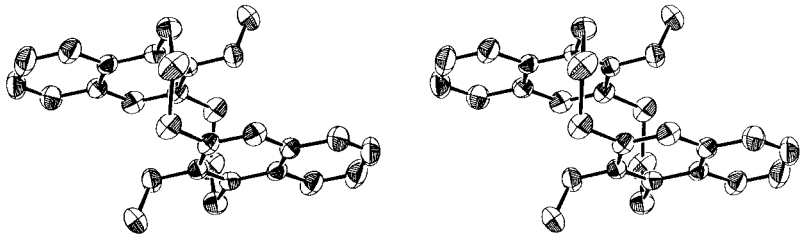


Figure 2. Stereoview of **3**.

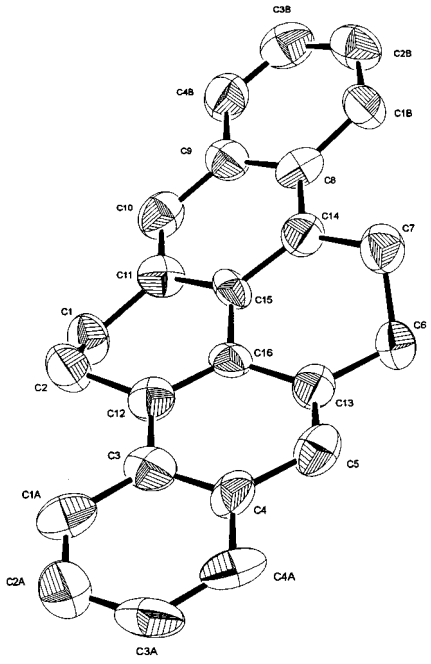


Figure 3. ORTEP diagram of X-ray structure of **7**.

cyclization of various [2.2]metacyclophanes produce the corresponding tetrahydropyrenes. However, all of these instances involve prior formation of the cyclophanes from the precursor dithiaphanes, a process which usually requires two separate steps involving oxidation of the disulfides to the bissulfones, followed by a vacuum pyrolysis.

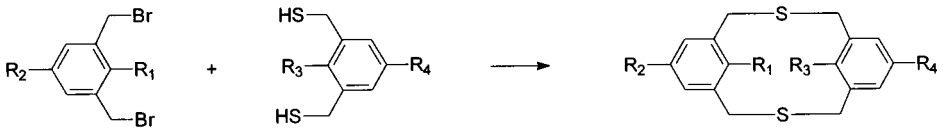
In order to ascertain whether our observation on the photolyses of compounds **3**−**6** was a general one, we examined the reactions leading to the dithia[3.3]metacyclophane precursors **26**−**30** of the tetrahydropyrenes **33**−**36**, respectively, as summarized in Scheme 3. Boekelheide *et al.*[4] had not observed any cyclization during the photolytic sulfur elimination reaction of dithiacyclophane **31**, in which only hydrogen atoms are present at both the 9- and 18-positions, or **32**, in which a methyl group and a hydrogen atom are present at the 9- and 18-positions, respectively. The reactions of dithia[3.3]-metacyclophanes **26**−**30**, in which at least one methoxyl group was present at these intraannular positions, were therefore examined. Intermediate compounds **20**−**25** were all synthesized and coupled by standard procedures to give the corresponding dithiacyclophanes **26**−**30** in good yields. Photolytic sulfur elimination/intraannular cyclization occurred in all cases, except with **30**, to produce the tetrahydropyrenes **33**−**35**. At least one intraannular methoxyl group therefore appears to be necessary to allow for the *in situ* transannular cyclization step. The presence of an electron-withdrawing group at the 6- or 15-position, e.g. bromine in the case of **30**, however, appears to inhibit the sulfur elimination/intrannular cyclization. It can be noted that Yamato and co-workers[13] have reported the cyclization of various substituted 8-methoxy[2.2]metacyclophanes themselves to the corresponding tetrahydropyrenes using benzyltrimethyl ammonium tribromide (BTMA-Br_3). However, in agreement with our findings with **30**, they too were unable to effect cyclization when a bromine atom or other electron-withdrawing groups were present in the *para*-positions (R_2 or R_4, in Scheme 4). DDQ oxidation easily converted **33**−**35** into the corresponding pyrenes.

To further support our findings, dithia[3.3](1,3)naphthalenophanes **37** and **38**, in which the methoxyl groups are situated at the 5- and 16- positions and the 5- and 20-positions, respectively, were synthesized and subjected to the same photolytic conditions. Synthesis of **37** and **38** was achieved by the base-mediated coupling of **39** and **40** (Scheme 4). It was possible by repeated PLC separation to obtain small amounts of the less polar *transoid-anti*-dithianaphthalenophane **37** in a pure enough state to enable it to be unambiguously characterized. *Cisoid-anti*-**38** however, was always contaminated with small amounts of **37**. That **37** and **38** are conformationally more mobile than **3**−**6** is evident by the fact that the bridging methylene protons appear as sharp singlets in their respective ambient temperature ^{1}H NMR spectra. Photolysis of PLC-purified fractions which contained a mixture of **37** and **38** afforded two easily separable products whose spectral properties are consistent with the novel *transoid-anti* and *cisoid-anti*-[2.2](1,3)naphthalenophane structures **41** and **42**, respectively. These are the first [2.2](1,3)naphthalenophanes to be reported. In light of the previous discussions, **37** is most likely the precursor of **41**, and **38** the precursor of **42**. That both compounds are *anti* is evident by the fact that the intraannular protons appear upfield at $\delta = 4.51$ in both cases. Although the chemical shifts for the ethano bridge protons in both compounds are nearly identical, their line shapes are dramatically different. In **42** they appear as two distinct AX systems, centered at $\delta = 3.97$ and 2.01 ($J = 10.1$ Hz) and at $\delta = 3.72$ and 2.16 ($J = 9.0$ Hz), whereas in **41** they appear as two AMPX multiplets, one set of signals consisting of a doublet of triplets centered at $\delta = 3.95$ which is coupled to a triplet of doublets centered at $\delta = 2.24$ and the second set consisting of a doublet of triplets centered at $\delta = 3.72$ which is coupled to a triplet of doublets centered at $\delta = 2.00$. No transannular cyclized products were detected from the photolyses.

The mechanism depicted in Scheme 5 is consistent with the results found for a typical example in which

(12) Sato, T.; Wakabayashi, M.; Okamura, T.; Amada, T.; Hata, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2363.
(13) Yamato, T.; Ide, S.; Tokuhisa, K.; Tashiro, M. *J. Org. Chem.* **1992**, *57*, 271 and references cited therein.
(14) Sato, T.; Wakabayashi, M.; Hayashi, S.; Hata, K. *Chem. Soc. Jpn.* **1969**, *42*, 773.

Scheme 3



20 $R_1 = OCH_3$; R_2 = *tert*-Bu
21 $R_1 = OCH_3$; R_2 = H
21 $R_1 = OCH_3$; R_2 = H
22 R_1 = H ; R_2 = H
23 R_1 = H ; R_2 = Br

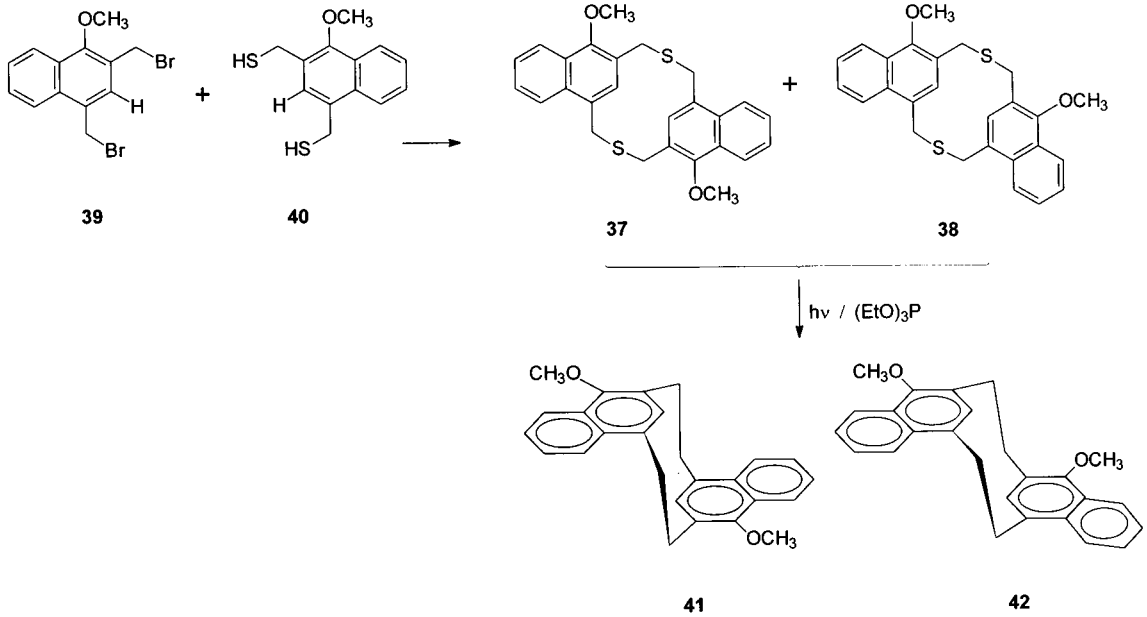
24 $R_3 = OCH_3$; R_4 = *tert*-Bu
24 $R_3 = OCH_3$; R_4 = *tert*-Bu
25 $R_3 = OCH_3$; R_4 = H
24 $R_3 = OCH_3$; R_4 = *tert*-Bu
24 $R_3 = OCH_3$; R_4 = *tert*-Bu

26 $R_1 = R_3 = OCH_3$; $R_2 = R_4$ = *tert*-Bu
27a *anti*-$R_1 = R_3 = OCH_3$; R_2 = H ; R_4 = *tert*-Bu
27b *syn*-$R_1 = R_3 = OCH_3$; R_2 = H ; R_4 = *tert*-Bu
28a *anti*-$R_1 = R_3 = OCH_3$; $R_2 = R_4$ = H
28b *syn*-$R_1 = R_3 = OCH_3$; $R_2 = R_4$ = H
29 $R_1 = R_2$ = H ; $R_3 = OCH_3$; R_4 = *tert*-Bu
30 R_1 = H ; R_2 = Br ; $R_3 = OCH_3$; R_4 = *tert*-Bu
31 $R_1 = R_3$ = H ; $R_2 = R_4 = CH_3$
32 $R_1 = CH_3$; $R_2 = R_3 = R_4$ = H

26 - 29

33 $R_2 = R_4$ = *tert*-Bu
34 R_2 = H ; R_4 = *tert*-Bu
35 $R_2 = R_4$ = H
36 R_2 = Br ; R_4 = *tert*-Bu

Scheme 4



39 **40** **37** **38** **41** **42**

photolytic sulfur elimination/intrannular cyclization reaction did occur. Thus, when the photolysis of **5** was interrupted after 7 h, three new products in addition to **7** were isolated and characterized. These were, in order of increasing polarity, **7** and the three intermediate compounds *anti*-dimethoxy[2.2](1,3)naphthalenophane (**17a**), monothia compound **43**, and the *syn*-dimethoxy-[2.2](1,3)naphthalenophane (**17b**), which convert to **7** upon further photolysis.

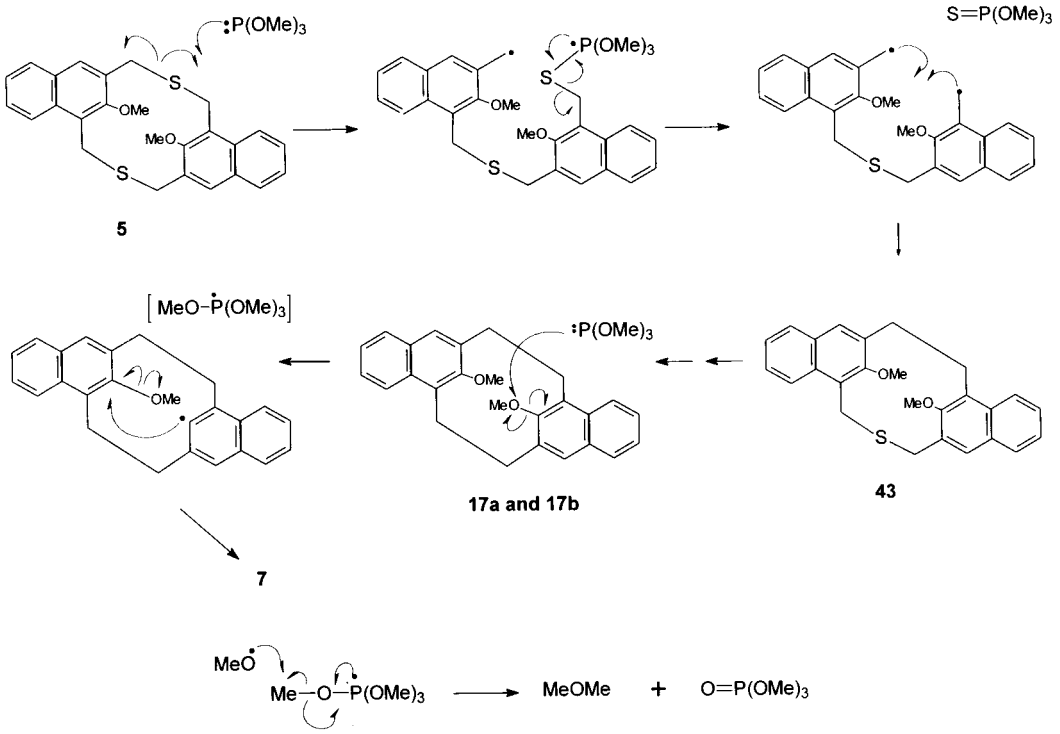
In conclusion, we have observed that the photolysis in trimethyl or triethyl phosphite solution of various substituted dithiacyclophanes which possess either one or two intraannular methoxyl groups can produce, in a single step, the corresponding tetrahydropyrenes. Similarly, the photolysis of similar intraannularly substituted methoxydithia[3.3](1,3)naphthalenophanes produced, in a single step, the corresponding tetrahydrodibenzopyrenes. Photolysis of 5,16-dimethoxy and 5,20-dimethoxy-2,13-dithia[3.3](1,3)naphthalenophanes (**37** and **38**) afforded the anticipated 4,14-dimethoxy- and 4,18-dimethoxy[2.2]naphalenophanes **41** and **42**, respectively.

Experimental Section

General Methods. For general experimental data, see ref 2. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 300 and 75.47 M Hz, respectively in $CDCl_3$ unless otherwise noted. All photochemical reactions were conducted in a Rayonet photochemical reactor. Where compounds have been reported by others, only the spectral data which have not previously been reported are presented here.

1,3-Bis(bromomethyl)-2-methoxynaphthalene (11). To a solution of 2-(hydroxymethyl)-3-methoxynaphthalene (14.1 g, 11.7 mmol) and paraformaldehyde (4.54 g, 150 mmol) in 200 mL of glacial acetic acid was added a 10% solution (200 mL) of HBr in glacial acetic acid. After stirring for 36 h, a precipitate formed which was filtered and washed several times with petroleum ether to afford 7.44 g of a colorless

Scheme 5



powder. The filtrate was diluted with CH_2Cl_2 (200 mL) and washed several times with water and finally with aqueous saturated $NaHCO_3$ solution until the washes were neutral. The organic layer was dried over $MgSO_4$ and the solvent evaporated on a rotary evaporator. The residue was washed with several portions of diethyl ether to give another 5.18 g of the crude product. The combined product (12.64 g; 49%), mp 114−116 °C, was used directly in subsequent steps, without further purification: ^{1}H-NMR δ 4.14 (s, 3H), 4.72 (s, 2H), 5.05 (s, 2H), 7.51−7.46 (m, 1H), 7.65−7.60 (m, 1H), 7.82 (d, J = 7.8 Hz 1H), 7.94 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H). ^{13}C-NMR δ 24.69, 28.23, 62.35, 123.48, 125.28, 125.79, 127.56, 127.69, 128.63, 130.92, 132.44, 132.70, 154.70; MS m/z (%) 344 (16), 342 (9), 266 (14), 265 (100), 264 (14.5), 263 (96.5), 235 (13), 233 (15), 183 (13), 169 (17.5), 156 (24), 155 (90), 154 (20), 153 (19.5), 152 (13), 141 (32); HRMS M^+ 341.9250, calcd for $C_{13}H_{12}Br_2O$ 341.9255.

1,3-Bis(mercaptomethyl)-2-methoxynaphthalene (12). A solution of **11** (0.41 g, 1.2 mmol) and thiourea (0.22 g, 2.9 mmol) in 25 mL of DMSO was stirred at room temperature under Ar for 5 h. The mixture was poured into 50 mL of aqueous 10% NaOH which was cooled in an ice bath. The reaction mixture was stirred for an additional 2 h at room temperature, under Ar, and then cooled in an ice bath, and aqueous 4 N HCl was added until the solution become acidic. The reaction mixture was extracted twice with 30-mL portions of CH_2Cl_2. The combined organic layer was washed with two 20-mL portions of H_2O and then with three 20-mL portions of aqueous saturated NaCl. After drying over anhydrous $MgSO_4$, filtering, and evaporating the solvent, the crude product was flash chromatographed using CH_2Cl_2:petroleum ether (50:50) to give 0.21 g (0.84 mmol, 70%) of **12** as an oil: ^{1}H-NMR δ 1.97 (t, 1H), 1.99 (t, 1H), 3.89 (d, J = 7.8 Hz, 2H), 3.99 (s, 3H), 4.22 (d, J = 6.9 Hz, 2H), 7.54−7.39 (m, 2H), 7.73 (s, 1H), 7.76 (d, J = 7.8 Hz 1H), 7.96 (d, J = 8.4 Hz 1H); ^{13}C-NMR δ 19.23, 24.13, 62.63, 123.30, 125.58, 126.58, 128.36, 128.48, 128.83, 131.26, 134.21; MS m/z (%) 250 (75, M^+), 218 (16), 217 (100), 172 (19), 171 (99), 143 (17.5), 141 (23); HRMS M^+ 250.0467, calcd for $C_{13}H_{14}S_2O$ 250.0485.

Base-Mediated Coupling of 11 with 12. To a solution of ethanolic KOH (481 mg in 170 mL 95% ethanol) was added a solution of **11** (397 mg, 1.16 mmol) and **12** (290 mg, 1.16 mmol) in 70 mL of benzene, dropwise over (24 h) under Ar at room temperature. The reaction was left stirring for an additional 24 h after which the reaction solvent was evaporated on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (50 mL) and the organic solution was washed with portions of aqueous 10% HCl until the aqueous layers become acidic. The organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was evaporated on a rotary evaporator. A portion of the crude product (250 mg) was chromatographed by PLC using CH_2Cl_2:petroleum ether (60:40) to give five fractions in the following order of increasing polarity:

***transoid-anti*-11,22-Dimethoxy-2,13-dithia-[3.3](1,3)-naphthalenophane (3)** was obtained as a colorless crystalline compound (from $CHCl_3$, chlorobenzene, or toluene) (25 mg): mp 268−270 °C; ^{1}H-NMR δ 2.93 (s, 6H), 3.26 (m, 4H), 4.0 (d, J = 11.7 Hz, 2H), 4.33 (d, J = 11.7 Hz, 2H), 7.44 (m, 2H), 7.54 (m, 2H), 7.86 (d, J = 7.8 Hz, 2H), 8.12 (s, 2H), 8.18 (d, J = 8.4 Hz, 2H); ^{13}C-NMR δ 22.89, 25.88, 61.10, 119.81, 123.1, 124.44, 126.10, 128.27, 131.11, 131.29, 131.48, 132.50, 156.68; MS m/z (%) 432 (6, M^+), 368 (11), 218 (10), 217 (17), 216 (14), 215 (12), 186 (45), 185 (100), 183 (14), 171 (19). 155 (54); HRMS M^+ 432.1193, calcd for $C_{26}H_{24}S_2O_2$ 432.1216.

***cisoid-anti*-11,22-Dimethoxy-2,13-dithia[3.3](1,3)-naphthalenophane (4)** was obtained as a colorless powder (37 mg): mp 123−125 °C; ^{1}H-NMR δ 2.93 (s, 6H), 3.62 (d, J = 13.8 Hz, 2H), 3.88 (d, J = 13.8 Hz, 2H), 3.89 (d, J = 13.8 Hz, 2H), 4.05 (d, J = 13.8 Hz, 2H), 7.43 (m, 2H), 7.53 (m, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.88 (s, 2H), 8.31 (d, J = 8.4 Hz, 2H) ; ^{13}C-NMR δ 24.05 , 26.6, 61.18, 121.98, 123.86, 124.33, 125.60, 128.02, 128.97, 131.57, 133.03, 156.37; MS m/z (%) 432 (100, M^+), 247 (29), 217 (18), 216 (61), 215 (58), 214 (39), 201 (17), 186 (28), 185 (47), 184 (17), 183 (17), 171 (20), 167 (22), 155 (37); HRMS M^+ 432.1213, calcd for $C_{26}H_{24}S_2O_2$ 432.1216.

***Transoid-syn*-11,22-dimethoxy-2,13-dithia[3.3](1,3)-naphthalenophane (5)** was obtained as a colorless crystalline powder (52 mg): mp 208−209 °C; ^{1}H-NMR δ 3.51 (d, J = 16.4 Hz, 2H), 3.57 (s, 6H), 3.84 (d, J = 13.5 Hz, 2H), 4.59 (d, J = 16.4 Hz, 2H), 4.84 (d, J = 13.5 Hz, 2H), 6.75 (d, J = 7.8 Hz, 2H), 6.96 (s, 2H), 7.04 (m, 2H), 7.37 (m, 2H), 7.85 (d, J = 8.4 Hz, 2H); ^{13}C-NMR δ 27.59 , 28.94, 61.98, 121.95, 123.29, 124.13, 124.90, 127.90, 128.75, 130.37, 130.53, 130.87, 155.25; MS m/z (%) 432 (46, M^+), 247 (11), 217 (10), 215 (20), 186 (10), 185 (36), 184 (22), 183 (16), 169 (20), 155 (14); +FAB MS (matrix: 3-nitrobenzyl alcohol) m/z (%) 433 (19, $M^+ + 1$), 432 (41, M^+), 431 (6), 307 (10), 289 (10), 217 (14), 215 (44), 185 (61), 171 (26), 169 (30), 155 (43), 154 (100); HRMS M^+ 432.1231, calcd for $C_{26}H_{24}S_2O_2$ 432.1216.

***cisoid-syn*-11,22-dimethoxy-2,13-dithia[3.3](1,3)naphthalenophane (6)** was obtained as a colorless crystalline powder (48 mg): mp 238−240 °C; ^{1}H-NMR δ 3.56 (s, 6H), 3.60 (d, J = 15.0 Hz, 2H), 3.83 (d, J = 14.7 Hz, 2H), 4.54 (d, J = 15.0 Hz, 2H), 5.00 (d, J = 14.7 Hz, 2H), 7.00−6.88 (m, 4H), 7.22 (d, J = 8.1 Hz, 2H), 7.46 (s, 2H), 7.84 (d, J = 7.8 Hz, 2H); ^{13}C-NMR δ 27.43, 30.41, 62.44, 122.47, 123.95, 124.25, 124.34, 127.13, 130.29, 130.53, 130.67, 130.83, 155.09; MS m/z (%) 432 (88, M^+), 247 (44), 217 (28), 216 (58), 215 (100), 202 (10), 201 (32), 200 (18), 199 (5), 187 (13), 186 (52), 185 (10), 184 (87), 173 (10), 172 (18), 171 (35), 170 (15), 169 (35); HRMS M^+ 432.1185, calcd for $C_{26}H_{24}S_2O_2$ 432.1216.

A fifth fraction, which was the most polar one, was also isolated as an amorphous solid (42 mg) which decomposes at 138−140 °C. NMR spectral properties indicated this product to be a mixture which could not be resolved by TLC. +FAB MS revealed the presence of several pseudo-molecular ions, suggestive of tetrameric species such as **2** and/or its isomers.

X-ray Data for *transoid-anti*-11,22-Dimethoxy-2,13-dithia[3.3](1,3)naphthalenophane (3). Crystal (ex toluene) data for **3**: $C_{26}H_{24}S_2O_2$, triclinic, space group $P1$ (#2), a = 8.599(2) Å, b = 9.192(2) Å, c = 8.273(2)Å, α = 108.68 (2)°, β = 112.54 (2)°, γ = 103.00 (2)°, Z = 1, D_{calc} = 1.368 g/cm^3, crystal size = 0.400 × 0.350 × 0.250 mm. Intensity data were measured at 299 K on a Rigaku AFC6S diffractometer with Mo Kα (λ = 0.71069 Å) to $2\theta_{max}$ (deg) = 50.1°; 1853 unique reflections converged to a final R = 0.034, for 1587 reflections with $I > 2.00\sigma(I)$; R_w = 0.036, gof = 2.62. Atomic coordinates of the structure have been deposited with the Cambridge Crystallographic Data Centre. These coordinates are available, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EK, U.K.

1,2,6,7-Tetrahydro-3,4:8,9-dibenzopyrene (7) from 5. (a) Irradiation for 24 h. A solution of **5** (141 mg, 0.326 mmol) in 10 mL of trimethyl phosphite under Ar in a quartz tube was irradiated at 254 nm with stirring, for 24 h. The triethyl phosphite was removed by vacuum distillation and the yellow residue was dried under vacuum. Chromatography by PLC using CH_2Cl_2:hexane 40:60 gave **7** (33 mg 33%) as yellow crystals: mp 250−252 °C; ^{1}H-NMR δ 3.18 and 3.21 (dd, 4H), 3.32 and 3.35 (dd, 4H), 7.50−7.42 (m, 4H), 7.62 (s, 2H), 7.81−7.78 (m, 2H), 8.12−8.1 (m, 2H); ^{13}C-NMR δ 23.82, 29.25, 123.48, 124.06, 125.33, 125.56, 127.98, 129.18, 130.87, 131.68, 133.14, 134.16; MS m/z (%) 306 (100, M^+), 305 (33), 303 (15), 302 (18), 289 (12), 153 (13), 151 (17), 145 (22); HRMS M^+ 306.1413, calcd for $C_{24}H_{18}$ 306.1409. **(b) Irradiation for 7 h.** When a solution of **5** (100 mg, 0.231 mmol) in 6.0 mL of trimethyl phosphite under Ar in a quartz tube was irradiated at 254 nm with stirring for 7 h and worked up as before, chromatography by PLC using CH_2Cl_2:hexane (40:60) afforded the following in order of increasing polarity: **7** (6 mg, 9%), ***transoid-anti*-10,20-dimethoxy-[2.2](1,3)naphthalenophane (17a)** (13 mg, 15%) [as a colorless solid: mp >300 °C; ^{1}H-NMR δ 2.67 (s, 6H), 2.75 (m, 2H), 2.82 (m, 2H), 2.97−3.00 (m, 2H), 3.56−3.60 (m, 2H), 7.38 (m, 2H), 7.45 (m, 2H), 7.69 (s, 2H), 7.81 (dd, J = 8.1; 1.2 Hz, 2H); 8.10 (dd, J = 8.1, 1.2 Hz, 2H); ^{13}C-NMR δ 26.87, 31.40, 57.42, 117.55, 119.61, 120.63, 121.57, 124.74, 125.31, 129.62, 130.65, 131.44, 154.06; MS m/z (%) 368 (59, M^+), 337 (23), 306 (100), 305 (20), 293 (3), 289 (4), 279 (4), 265 (4), 183 (13), 169 (7), 155 (12); HRMS M^+ 368.1703, calcd for $C_{26}H_{24}O_2$ 368.1776], ***transoid-anti*-11,21-dimethoxy-2-thia-[3.2](1,3)naphthalenophane (43)** (6 mg, 6%) [as a colorless solid: mp 188−190 °C; ^{1}H-NMR δ 2.64 (s, 3H), 2.94 (s, 3H), 3.05−2.83 (m, 3H), 3.60−3.48 (m, 2H), 3.63 (d, J = 13.2 Hz, 1H), 3.76 (d, J = 12.9 Hz, 1H), 4.22 (d, J = 13.2 Hz, 1H), 7.51−7.37 (m 4H), 7.72 (s, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.94 (s, 1H), 8.05 (d, J = 8.7 Hz, 1H), 8.17 (d, J = 8.7 Hz, 1H); MS m/z (%) 400 (94, M^+), 216 (13), 215 (89), 201 (7), 200 (6), 198 (7), 197 (8), 185 (100), 183 (24), 170 (14), 168 (57); HRMS M^+ 400.1493, calcd for $C_{26}H_{24}O_2S$, 400.1497], and ***transoid-syn*-10,20-dimethoxy-[2.2](1,3)naphthalenophane (17b)** (7 mg, 8%) [as a colorless solid: mp 195−197 °C; ^{1}H-NMR δ 2.74 (m, 2H), 3.46−3.36 (m, 4H), 3.65 (s, 6H), 3.94−3.84 (m, 2H), 5.91 (s, 2H), 6.88 (d, J = 8.1 Hz, 2H), 7.01- 6.97 (m, 2H), 7.27−7.22 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H); ^{13}C-NMR δ 23.89, 33.30, 62.16, 122.72, 123.07, 124.38, 124.83, 127.35, 127.43, 130.26, 131.75, 133.61, 158.48; MS m/z (%) 368 (40, M^+), 337 (22), 306 (100), 305 (18), 293 (4), 289 (4), 279 (4), 265 (4), 183 (14), 169 (8), 155 (11); HRMS M^+ 368.1735, calcd for $C_{26}H_{24}O_2$ 368.1776.

1,2,6,7-Tetrahydro-3,4:8,9-dibenzopyrene (7) from 3. Irradiation of **3** under identical conditions as were used with **5** afforded a product whose spectral and physical properties were identical with those of **7**.

X-ray Data for 1,2,6,7-tetrahydro-3,4:8,9-dibenzopyrene (7). Crystal data for **7**: $C_{24}H_{18}$, triclinic, space group $P2_1$ (#4), a = 11.229(5) Å, b = 15.31(1) Å, c = 14.338(4)Å, β = 105.08 (3)°, Z = 6, D_{calc} = 1.283 g/cm^3, crystal size = 0.400 × 0.400 × 0.100 mm. Intensity data were measured at 299 K on a Rigaku AFC6S diffractometer with Mo Kα (λ = 0.71069 Å) to $2\theta_{max}$ (deg) = 50.1°; 4394 unique reflections converged to a final R = 0.046, for 2123 reflections with $I > 2.00\sigma(I)$; R_w = 0.030, gof = 1.18. Atomic coordinates of the structure have been deposited with the Cambridge Crystallographic Data Centre. These coordinates are available, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EK, U.K.

3,4:8,9-Dibenzopyrene (9) from 7. A solution of **7** (20 mg, 0.065 mmol) and DDQ (41 mg, 0.163 mmol) in 8 mL of benzene was refluxed for 4 h. The solution was cooled to room temperature and then filtered through a short Florisil column and eluted with benzene. Evaporation of the solvent afforded **9** (12 mg, 61%) which was crystallized from benzene to give pale orange crystals, mp 310−312 °C (308 °C).[9]

1,2,6,7-Tetrahydro-3,4:9,10-dibenzopyrene (8) from 4. A solution of **4** (84 mg, 0.194 mmol) in 6 mL of trimethyl phosphite was irradiated for 24 h at 254 nm as described for **5**. After removal of the trimethyl phosphite by vacuum distillation, the crude product was dried under vacuum and then chromatographed by PLC using CH_2Cl_2:hexane (20:80) to give **8** as a pale yellow solid (18 mg, 30%): mp 175−177 °C; ^{1}H-NMR δ 3.10 (s, 4H), 3.4 (s, 4H), 7.50−741 (m, 4H), 7.59 (s, 2H), 7.80−7.74 (m, 2H), 8.13 and 8.01 (dd, 2H); ^{13}C-NMR δ 23.27, 29.90, 121.67, 122.86, 123.56, 124.36, 125.32, 125.48, 125.82, 126.52, 127.91, 127.99, 129.26, 130.53, 131.03, 133.15, 134.69; MS m/z (%) 306 (100, M^+), 305 (37), 304 (18), 304 (18), 303 (20), 302 (24), 290 (11), 289 (15), 153 (25), 150 (24), 145 (23), 138 (15); HRMS M^+ 306.1411, calcd for $C_{24}H_{18}$ 306.1409.

3,4:9,10-Dibenzopyrene (10) from 8. A solution of **8** (22 mg, 0.072 mmol) and DDQ (41 mg, 0.163 mmol) in 8 mL of benzene was refluxed for 4 h. The solution was cooled to room temperature, filtered through a short Florisil column, and eluted with benzene. Evaporation of the solvent afforded **10**, 17 mg (85%) of which was crystallized from benzene to give yellow leafy crystals, mp 281−282 °C (280 °C).[9]

2,6-Bis(bromomethyl)-4-*tert*-butylanisole (20). To a solution of 4.95 g (0.033 mol) of *p*-*tert*-butylanisole and 3.96 g (0.132 mol) of paraformaldehyde in 25 mL of acetic acid was added 25 mL of a solution of 15% hydrogen bromide in acetic acid dropwise over 10 min, at room temperature under N_2. The reaction temperature was raised to 90−95 °C and after 2 days, the reaction mixture was cooled to room temperature and then diluted with 50 mL of $CHCl_3$. The solution was washed several times with water and then with saturated aqueous $NaHCO_3$. The organic layer was separated and dried over anhydrous $MgSO_4$ and filtered and the solvent evaporated. The oily product was purified by column chromatography on SiO_2 using $CHCl_3$:petroleum ether (20:80) to give 4.66 g (40%) of a colorless solid: mp 95−96 °C; ^{1}H-NMR δ 1.31 (s, 9H), 4.01 (s, 3H), 4.56 (s, 4H) and 7.36 (s, 2H); ^{13}C-NMR δ 28.13, 31.25, 34.43, 62.11, 129.28, 131.0, 147.89, 154.27; MS m/z (%) 348 (9, M^+), 350 (18), 337 (6), 335 (12), 333 (6), 272 (14), 271 (100), 269 (99), 241 (16).

2,6-Bis(bromomethyl)anisole (21). To a solution of 1.17 g (8.57 mmol) of 2,6-dimethylanisole in refluxing CCl_4 (100 mL) under N_2, was added 3.66 g of *N*-bromosuccinimide (20.6 mmol) and 0.275 g of benzoyl peroxide[15] in portions, over 1 h. The reaction mixture was refluxed with stirring for an ad-

(15) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543.

ditional 24 h. The solution was cooled to room temperature and filtered. The filtrate was washed with aqueous saturated $NaHSO_3$. After drying and filtering, the solvent was evaporated on a rotary evaporator and the residue was chromatographed on SiO_2 using $CHCl_3$:petroleum ether (20:80) to give **21** as a colorless solid (0.98 g, 40%): mp 83−85 °C (lit.[16] mp 75 °C); ^{1}H-NMR δ 4.05 (s, 3H), 4.57 (s, 4H), 7.12 (q, 1H), and 7.38 (d, 2H); ^{13}C-NMR δ 27.50, 62.25, 125.07, 131.94, 132.24 and 156.56; MS *m*/*e* (%) 294 (12, M_1^+), 292 (6, M_2^+), 215 (81, $M_1^+ - Br$), 213 (84, $M_2^+ - Br$), 185 (21) 183 (20), 119 (10), 106 (27), 105 (100), 104 (22), 103 (16), 79 (6), 77 (12), 65 (26), 63 (12), 51 (14), 39 (19).

1-Bromo-3,5-bis(bromomethyl)benzene (23). The procedure described above for **21** was employed to prepare **23** from 1-bromo-3,5-dimethylbenzene (2.58 g, 13.90 mmol). The crude product was chromatographed on SiO_2 using CH_2Cl_2:petroleum ether (10:90) and crystallized from hexane to give **23** (1.37 g, 29%); mp 97.5−99.0 °C (95−98 °C).[17]

1,3-Bis(mercaptomethyl)-2-methoxy-5-*tert*-butylbenzene (24). To a solution of **20** (1.25 g, 3.60 mmol) in 50 mL of DMSO was added thiourea (0.66 g, 8.64 mmol), with stirring under N_2. After 5 h at room temperature the reaction was quenched by pouring the mixture into a cold aqueous 10% solution of NaOH (50 mL). The mixture was stirred at room temperature for 2 h, after which it was cooled to 0 °C and neutralized by addition of aqueous 3 M HCl. The ensuing precipitate was filtered, washed with water, and air-dried. The colorless solid obtained was purified by flash chromatography on SiO_2 using $CHCl_3$:petroleum ether (70:30) to give **24** as a colorless solid (0.820 g, 89%): mp 80−81 °C (lit.[17] mp 81−82 °C); ^{1}H-NMR δ 1.31 (s, 9H), 1.90 (t, J = 7.5 Hz, 2H), 3.77 (d, J = 7.5 Hz, 4H), 3.88 (s, 3H) and 7.23 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ 23.51, 31.38, 34.45, 62.22, 126.20, 133.80, 147.62, 153.10; MS *m*/*e* (%) 258 (7), 257 (12), 256 (72, M^+), 243 (5), 242 (7), 241 (47), 223 (48), 178 (13), 177 (100), 165 (17), 161 (11).

2,6-Bis(mercaptomethyl)anisole (25). The procedure described above for **24** was employed to prepare **25** from **21**. Flash chromatography on SiO_2 using $CHCl_3$:petroleum ether (60:40) gave **25** as a colorless solid (0.24 g, 65%): mp 28−29 °C; ^{1}H-NMR δ 1.89 (t, J = 7.8 Hz, 2H), 3.78 (d, J = 7.8 Hz, 4H), 3.90 (s, 3H), 7.23−7.05 (m, 3H); ^{13}C-NMR δ 23.18, 62.32, 124.91, 129.22, 134.76, 155.36.

Preparation of dithia[3.3]metacyclophanes: 6,15-di-*tert*-butyl-9,18-dimethoxy-2,11-dithia[3.3]metacyclophane (26). Typical procedure. A solution of **24** (0.54 g, 2.11 mmol) and **20** (0.72 g, 2.1 mmol) in 55 mL of benzene was added dropwise over 10 h with stirring to a solution of 0.35 g of KOH in 250 mL of ethanol, under N_2. After the addition was complete the reaction was stirred for an additional 6 h. The mixture was then concentrated on a rotary evaporator and the residue dissolved in 50 mL of $CHCl_3$. The organic layer was washed with two 25-mL portions of aqueous 10% HCl, dried over $MgSO_4$ and filtered. The solvent was evaporated on a rotary evaporator and the residue was flash chromotographed on SiO_2 using $CHCl_3$:petroleum ether (80:20) to give **26** as a colorless solid (0.38 g, 38%): mp 253−255 °C (lit.[15] mp 257−258 °C); ^{1}H-NMR δ 1.36 (s, 18H), 3.21 (s, 6H), 3.39 (d, J = 13.5 Hz, 4H), 3.79 (d, J = 13.5 Hz, 4H), 7.29 (s, 4H); ^{13}C-NMR δ 26.96, 31.42, 34.31, 60.70, 127.59, 127.73, 145.85, 156.35; MS *m*/*e* (%) 444 (61, M^+), 4.29 (4), 387 (3), 267 (3), 253 (33), 223 (29), 222 (12), 221 (38), 220 (13), 192 (33), 191 (71), 189 (16), 177 (18), 176 (13), 175 (87), 165 (18).

Compounds **27**−**29** were obtained in the same manner as described above.

***anti*- and *syn*-6-*tert*-Butyl-9,18-dimethoxy-2,11-dithia[3.3]metacyclophane (27a and 27b).** A solution of **21** (0.69g) and **24** (0.60 g) in 50 mL of benzene was added to ethanolic KOH (0.32 g in 250 mL) over 16 h. Chromatographic separation on SiO_2 using $CHCl_3$:petroleum ether (70:30) gave two compounds in order of increasing polarity: **27a** and **27b**.

***anti*-6-*tert*-Butyl-9,18-dimethoxy-2,11-dithia[3.3]metacyclophane (27a)** was a colorless solid (0.075 g): mp 163−165 °C; ^{1}H-NMR δ 1.37 (s, 9H), 3.20 (s, 3H), 3.27 (s, 3H), 3.39 (d, J = 13.5 Hz, 2H), 3.42 (d, J = 13.5 Hz, 2H), 3.77 (d, J = 13.5 Hz, 2H), 3.80 (d, J = 13.5 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.5 Hz, 2H), 7.30 (s, 2H); ^{13}C-NMR δ 26.34, 27.53, 29.66, 31.42, 34.27, 60.94, 123.72, 127.33, 127.87, 129.03, 130.45, 145.94, 156.6, 158.42; MS *m*/*e* (%) 388 (59, M^+), 373 (4), 331 (3), 253 (13), 223 (13), 221 (25), 220 (11), 207 (13), 192 (13), 191 (43), 175 (74); HRMS M^+ 388.1520, calcd for $C_{22}H_{28}S_2O_2$ 388.1529.

***syn*-6-*tert*-Butyl-9,18-dimethoxy-2,11-dithia[3.3]metacyclophane (27b)** was a colorless glassy oil which solidified after refrigeration to give a colorless solid (0.35 g): mp 107−108 °C; ^{1}H-NMR δ 1.19 (s, 9H), 3.35 (d, J = 14.7 Hz, 2H), 3.51 (s, 3H), 3.52 (s, 3H), 4.41 (d, J = 14.7 Hz, 2H), 6.64 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 7.5 Hz, 2H), 6.97 (s, 2H); ^{13}C-NMR δ 14.2, 30.11, 30.46, 31.23, 34.15, 62.19, 124.45, 126.45, 129.18, 129.50, 130.70, 145.56, 154.95, 156.97; MS *m*/*e* (%) 388 (79, M^+), 373 (5), 331 (4), 253 (16), 223 (17), 221 (29), 220 (16), 207 (15), 197 (13), 192 (19), 191(60), 177 (13), 176(13), 175 (83); HRMS M^+ 388.1515, calcd for $C_{22}H_{28}S_2O_2$ 388.1529.

***anti*- and *syn*-9,18-Dimethoxy-2,11-dithia[3.3]metacyclophane (28a and 28b).** A solution of **21** (0.33 g) and **25** (0.23 g) in 60 mL of benzene was added to ethanolic KOH (0.73 g in 150 mL) over 8 h and the reaction was left stirring overnight. PLC separation using $CHCl_3$ gave two compounds in order of increasing polarity: **28a** and **28b**.

***anti*-9,18-Dimethoxy-2,11-dithia[3.3]metacyclophane (28a)** was a colorless solid (36 mg, 10%): mp 248−25 °C; ^{1}H-NMR δ 3.26 (s, 6H), 3.43 (d, J = 13.5 Hz, 4H), 3.80 (d, J = 13.5 Hz, 4H), 7.04 (t, J = 7.5 Hz, 2H), 7.30 (d,J = 7.5 Hz, 4H); ^{13}C-NMR δ 26.93, 61.18, 123.82, 128.83, 130.69 and 158.67; MS *m*/*e* (%) 332 (43, M^+), 197 (19), 167 (16), 165 (25), 151 (15), 136 (12), 135 (40), 134 (27), 121 (29), 119 (27) 105 (44); HRMS M^+ 332.0903, calcd for $C_{18}H_{20}S_2O_2$ 332.0905.

***syn*-9,18-Dimethoxy-2,11-dithia[3.3]metacyclophane (28b)** was a colorless solid (136 mg, 36%): mp 220−223 °C; ^{1}H-NMR δ 3.37 (d, J = 14.7 Hz, 4H), 3.52 (s, 6H), 4.42 (d, J = 14.7 Hz, 4H), 6.64 (t, J = 7.8 Hz, 2H), 6.97 (d, J = 7.8 Hz, 4H); ^{13}C-NMR δ 30.16, 62.18, 124.23, 129.56, 130.55, 156.98; MS *m*/*e* (%), 332 (100, M^+), 298 (3), 198 (5), 197 (48), 167 (35), 166 (16), 165 (47), 164 (28), 151 (20), 136 (32), 135 (79), 134 (52), 133 (56), 121 (42), 119 (36); HRMS M^+ 332.0896, calcd for $C_{18}H_{20}S_2O_2$ 332.0905.

6-*tert*-Butyl-9-methoxy-2,11-dithia[3.3]metacyclophane (29). A solution of **22** (0.63 g, 2.47 mmol) and **24** (0.65 g, 2.47 mmol) in 50 mL of benzene was added to ethanolic KOH (300 mL) over 6 h. The reaction mixture was stirred for an additional 2 h before workup. The crude product was flash chromatographed on SiO_2 using $CHCl_3$:petroleum ether (80:20) to give **29** as a colorless solid (0.655 g), which could be crystallized from hexane:benzene (10:1) to give needles (0.45 g): mp 177−178 °C (lit.[18] mp 182.5−183 °C); ^{13}C-NMR δ 31.10, 31.31, 34.10, 37.88, 62.10, 126.39, 126.61, 128.55, 129.25, 130.10, 137.79, 146.39, 154.10.

15-Bromo-6-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metacyclophane (30). A solution of **23** (1.44 g, 4.26 mmol) and **24** (1.09 g, 4.26 mmol) in 230 mL of benzene was added dropwise to the ethanolic KOH solution (570 mL) over 16 h. The crude product was chromatographed on SiO_2 using $CHCl_3$: petroleum ether (80:20) to give **30** as a colorless solid (0.61 g, 58%) which was crystallized from hexane/benzene (1:1): mp 212−214 °C (lit.[18] mp 218−219 °C).

2,7-Di-*tert*-butyl-4,5,9,10-tetrahydropyrene (33). Typical Procedure. A solution of **26** (97 mg, 0.22 mmol) in 4.5 mL of triethyl phosphite in a quartz tube was irradiated at 254 nm with stirring and under Ar for 18 h. The triethyl phosphite was removed by vacuum distillation, and the crude product was dried under vacuum and then chromatographed by PLC using $CHCl_3$:petroleum ether (1:9) to give **33** as a colorless solid (39 mg, 56%): mp 232−233 °C (lit.[19] mp 234−235 °C); ^{1}H-NMR δ 1.34 (s, 18H), 2.87 (s, 8H), 7.07 (s, 4H);

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^{13}C-NMR δ 28.73, 31.46, 34.54, 122.78, 128.12, 134.55, 149.60; MS *m/e* (%) 318 (79, M^+), 304 (26), 303 (100), 273 (8), 205 (8), 203 (8), 202 (7), 144 (28).

2-*tert*-Butyl-4,5,9,10-tetrahydropyrene (34). A solution of **27** (0.16 g, 0.44 mmol) in 4.5 mL of triethyl phosphite was photolyzed as above for 18 h. After workup, the crude product was chromatographed by PLC using $CHCl_3$:petroleum ether (20:80) to give **34** as a colorless solid (26 mg, 22%): mp 94−95 °C (lit.[19] mp 108−109.5 °C); ^{13}C-NMR ($CDCl_3$) δ 28.43, 28.61, 31.43, 34.58, 122.91, 122.75, 125.77, 126.62, 128.1, 130.62, 134.90, 135.05, 150.11.

Alternatively, **34** (25 mg, 34%) was also obtained from the photolysis of **29** (110 mg, 0.284 mmol) in 4.0 mL of triethyl phosphite.

4,5,9,10-Tetrahydropyrene (35). A solution of **28** (0.15 g, 0.35 mmol) in 4.5 mL of triethyl phosphite was photolyzed as above for 18 h. After workup, the crude product was purified by PLC using $CHCl_3$:petroleum ether (20:80) to give **35** as a colorless solid (15 mg, 33%): mp 132−134 °C (lit.[19] mp 136−138 °C); ^{1}H-NMR δ 2.88 (s, 8H) and 7.51−7.05 (m, 6H); ^{13}C-NMR δ 28.33, 125.90, 127.02, 130.59 and 135.38; MS *m/e* (%) 206 (100, M^+).

Photolysis of 30. A solution of **30** (0.150 g, 0.35 mmol) in 5.0 mL of triethyl phosphite was photolyzed as above for 6 h. After workup, the crude product was chromatographed by PLC using $CHCl_3$:petroleum ether (20:80) to give three fractions in increasing order of polarity which consisted of 2, 6, and 20 mg. None of the spectral characteristics of these products were consistent with those anticipated for 2-bromo-7-*tert*-butyl-4,5,9,10-tetrahydropyrene. These products could not be further characterized.

Oxidation of 33 with DDQ. Typical Procedure. A solution of **33** (65 mg, 0.204 mmol) and 116 mg of DDQ in 25 mL of benzene was refluxed for 8 h. After cooling, the reaction mixture was filtered through a short column of Florisil and washed with benzene. The solvent was evaporated to dryness on a rotary evaporator to give 62 mg (97%) of 2,7-di-*tert*-butylpyrene, which after crystallization from hexane afforded pale yellow crystals: mp 204−206 °C (lit.[19] mp 210−212 °C). In a similar manner, 2-*tert*-butylpyrene[19] and pyrene were obtained from **34** and **35**, respectively.

2,4-Bis(mercaptomethyl)-1-methoxynaphthalene (40). To a solution of 0.85 g (2.5 mmol) of 2,4-bis(bromomethyl)-1-methoxynaphthalene (**39**)[2] in 50 mL of DMSO was added 0.473 g (0.21 mmol) of thiourea, with stirring, under N_2. After 6 h at room temperature the reaction was quenched by pouring the mixture into a cold aqueous 10% solution of NaOH (50 mL). The mixture was stirred at room temperature for 2 h, after which it was cooled to 0 °C and acidified by addition of aqueous 4 M HCl. The reaction mixture was extracted twice with 30-mL portions of CH_2Cl_2. The organic layers were combined and washed with two 20-mL portions of water. The organic layers were combined and dried over anhydrous $MgSO_4$ and filtered, and the solvent was evaporated on a rotary evaporator. The crude product was flash chromatographed on SiO_2 using CH_2Cl_2:petroleum ether (40:60) to give 0.45 g (1.8 mmol, 73%) of **40** as an oil: ^{1}H-NMR δ 1.89 (t, J = 6.9 Hz, 1H), 1.92 (t, J = 7.5 Hz, 1H), 3.92 (d, J = 7.5 Hz, 2H), 3.99 (s, 3H), 4.15 (d, J = 6.9 Hz, 2H), 7.42 (s, 1H), 7.52−7.58 (m, 2H), 8.02−8.05 (m, 1H), 8.11−8.14 (m, 1H); ^{13}C-NMR δ 23.00, 26.35, 62.70, 123.08, 124.09, 126.20, 126.44, 127.67, 128.55, 128.98, 131.36, 133.48, 152.77; MS *m/e* (%) 251 (5, $M^+ + 1$), 250 (35, M^+), 218 (15), 217 (100), 184 (10), 183 (32), 171 (10), 154 (10), 141 (18), 115 (15), 28 (33); HRMS M^+ 250.0486, calcd for $C_{13}H_{14}S_2O$ 250.0485.

Base-Mediated Coupling of 39 with 40. To a solution of ethanolic KOH (398 mg in 250 mL 95% ethanol) was added a solution of **39** (610 mg, 1.78 mmol) and **40** (445 mg, 1.78 mmol) in 110 mL of benzene dropwise over 12 h under Ar at room temperature. The reaction was left stirring for an additional 24 h, after which the reaction solvent was evaporated on a rotary evaporator. The residue was dissolved in 50 mL of CH_2Cl_2 and the organic solution was washed with two 25-mL portions of aqueous 10% HCl. The organic layers were combined, dried over anhydrous $MgSO_4$, and filtered, and the solvent was evaporated on a rotary evaporator. The crude product was flash chromatographed on SiO_2 using CH_2Cl_2:petroleum ether (40:60) to give 0.711 g (1.65 mmol, 91%) of a mixture of isomers **37** and **38**. A small amount of 5,16-dimethoxy-2,13-dithia[3.3](1,3)naphthalenophane (**37**) was obtained in a pure enough state from repeated PLC separation using CH_2Cl_2:petroleum ether (40:60) to be characterized: mp 191−193 °C; ^{1}H-NMR δ 3.82 (s, 6H), 4.02 (s, 4H), 4.18 (s, 4H), 7.21 (s, 2H), 7.24−7.29 (m, 4H), 7.78−7.81 (m, 2H), 7.97−8.00 (m, 2H); ^{13}C-NMR δ 31.59, 35.92, 62.19, 122.14, 124.32, 124.46, 125.22, 125.42, 127.71, 130.98, 131.21, 152.75; MS *m/e* (%) 433 (16, $M^+ + 1$), 432 (48, M^+), 247 (11), 216 (11), 215 (35), 201 (10), 186 (17), 185 (100), 183 (14), 172 (7), 171 (23), 170 (25), 154 (11), 153 (13), 141 (25), 139 (11), 129 (11), 128 (11).

The mixture consisting of **37** and **38** could not be further separated using either flash chromatography or PLC and was used as a mixture directly in the subsequent photolytic step.

***transoid-anti*-4,14-Dimethoxy[2.2](1,3)naphthalenophane (41) and *cisoid-anti*-4,18-Dimethoxy[2.2](1,3)naphthalenophane (42).** A solution of the mixture of **37** and **38** (150 mg, 0.35 mmol), obtained as described above, in 3.5 mL of trimethyl phosphite in a quartz tube was irradiated at 254 nm with stirring and under Ar for 24 h. The trimethyl phosphite was removed by vacuum distillation and the yellow residue was dried under vacuum and then chromatographed by PLC with CH_2Cl_2:hexane (45:55) to give two fractions, in order of increasing polarity: **41** and **42**.

***transoid-anti*-4,14-Dimethoxy[2.2]-(1,3)naphthalenophane (41)** was obtained as a colorless solid (21 mg, 15%): mp 230−233 °C; ^{1}H-NMR δ 2.00 (m, 2H), 2.24 (m, 2H), 3.72 (m, 2H), 3.95 (m, 2H), 4.10 (s, 6H), 4.51 (s, 2H), 7.52−7.55 (m, 4H), 8.13−8.16 (m, 4H), 8.21−8.24 (m, 2H); ^{13}C-NMR δ 33.14, 35.23, 62.99, 122.98, 123.65, 125.22, 125.35, 128.67, 129.45, 131.87, 136.26, 152.49; MS *m/e* (%) 369 (21, $M^+ + 1$), 368 (53, M^+), 367 (26), 354 (16), 353 (12), 352 (55), 339 (16), 336 (28), 335 (18), 321 (12), 307 (7), 184 (20), 183 (100), 169 (17), 155 (28), 141 (58), 115 (57), 28 (37); HRMS M^+ 368.1777, calcd for $C_{26}H_{24}O_2$ 368.1775.

***cisoid-anti*-4,18-Dimethoxy[2.2](1,3)naphthalenophane (42)** was obtained as a colorless solid which was further purified by PLC using ethyl acetate: petroleum ether (1:9) to give 28 mg (22%) of **42**: mp 189−191 °C; ^{1}H-NMR δ 2.01 (d, J = 10 Hz, 2H), 2.16 (d, J = 9 Hz, 2H), 3.72 (d, J = 9 Hz, 2H), 3.97 (d, J = 10 Hz, 2H), 4.08 (s, 6H), 4.45 (s, 2H), 7.52−7.55 (m, 4H), 8.16−8.23 (m, 2H); ^{13}C-NMR δ 33.64, 34.66, 62.98, 122.99, 123.53, 125.29, 125.39, 127.39, 128.72, 130.68, 132.04, 136.16, 152.25 MS *m/e* (%) 368 (86, M^+), 353 (56), 340 (17), 339 (17), 338 (24), 337 (17), 337 (63), 322 (8), 321 (9), 306 (12), 184 (44), 183 (99), 169 (26), 155 (22), 154 (52), 153 (34), 152 (34), 144 (10), 141 (62); HRMS M^+ 368.1765, calcd for $C_{26}H_{24}O_2$ 368.1775.

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Supporting Information Available: High-resolution ^{1}H, ^{13}C NMR spectra and mass spectra of all the new compounds reported in this paper (61 pages). This material is contained in libraries on microfiche, immediately follows the article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for the ordering information.

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