(d of ABq, 1 H, J = 14.4 Hz and J = 2.1 Hz, CH_2SO), 3.62 (d of ABq, 1 H, J = 14.4 Hz and J = 3.0 Hz, CH_2SO), 3.61–4.0 (m, OCH_2), 5.77 (unsymmetrical t, 1 H, J = 3.0 Hz and J = 2.1 Hz, CH), 7.3–7.9 (m, 4 H, aromatic). Anal. Calcd for $C_{12}H_{12}O_3S_2$: C, 53.71; H, 4.51. Found: C, 53.71, 53.77; H, 4.50, 4.48.

2,3-Dihydroindeno[1,2-*b*]-2-ethoxy-1,4-oxathiin 4,4-Dioxide (9). To a solution of **6a** (0.19 g, 0.76 mmol) in chloroform (10 mL) monoperphthalic acid (1.5 mmol) in chloroform (3 mL) was added. After stirring for 0.5 h at room temperature the reaction mixture was washed once with aqueous sodium carbonate, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with light petroleum–ethyl acetate (7:3) to give **9** (0.10 g, 50%) as colorless crystals: mp 127–129 °C (light petroleum–toluene); IR (KBr) 1615 (C=C), 1390 and 1295 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, 3 H, J = 7.2 Hz, CH_3), 3.47 (d, 2 H, J = 4.8 Hz, CH_2SO_2), 3.70 (s, 2 H, indene CH_2), 3.7–4.17 (m, 2 H, OCH_2), 5.73 (dd, 1 H, J = 6.0 Hz and J = 4.8 Hz), 7.3–8.5 (m, 4 H, aromatic). Anal. Calcd for $C_{13}H_{14}So_4S$: C, 58.63; H, 5.30. Found: C, 58.57, 58.60; H, 5.33, 5.30.

Registry No. **1a**, 105-53-3; **1c**, 16222-10-9; **1n**, 1127-35-1; **2a**, 17906-37-5; **2b**, 40195-27-5; **2d**, 96745-89-0; **2e**, 72223-17-7; **2f**, 13735-81-4; **2g**, 54731-27-0; **2h**, 55991-65-6; **2i**, 58518-76-6; **2j**, 52119-18-3; **2k**, 59790-53-3; **2l**, 10416-78-1; **2m**, 6651-36-1; **2o**, 56613-17-3; **3p**, 95683-64-0; **3q**, 96746-17-7; **4a**, 96745-90-3; **4b**, 96745-91-4; **4c**, 96745-92-5; **4d**, 96745-93-6; **4e**, 96745-94-7; *cis*-**4f**, 96745-95-8; *trans*-**4f**, 96745-96-9; *cis*-**4g**, 96745-97-0; *trans*-**4g**, 96745-98-1; *cis*-**4h**, 96745-99-2; *trans*-**4h**, 96746-00-8; *cis*-**4i**, 96746-01-9; *trans*-**4i**, 96746-02-0; *cis*-**4j**, 96746-03-1; *trans*-**4j**, 96746-04-2; *cis*-**4k**, 96746-05-3; *trans*-**4k**, 96746-06-4; **4l**, 96746-07-5; **4m**, 96746-08-6; **4n**, 96746-09-7; **4o**, 96746-10-0; **5**, 96746-11-1; *cis*-**6**, 96746-12-2; *trans*-**6**, 96746-13-3; *cis*-**7**, 96746-14-4; *trans*-**7**, 96746-15-5; **9**, 96746-16-6; α-(phenylsulfonyl)acetophenone, 3406-03-9; 2,3-dimethyl-1,3-butadiene, 513-81-5; thionyl chloride, 7719-09-7; ethyl vinyl ether, 109-92-2; 2,6-lutidine, 108-48-5.

Twin Benzoannulation of Naphthalene via 1,3-, 1,6-, and 2,6-Naphthodiyne Synthetic Equivalents. New Syntheses of Triphenylene, Benz[*a*]anthracene, and Naphthacene

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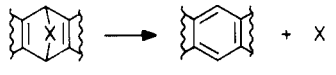
Received February 4, 1985

New syntheses of triphenylene (**4**), benz[*a*]anthracene (**5**), naphthacene (**6**), and the tetramethylated derivatives **17** and **25** are described that feature, as the key step, the formal Diels–Alder cycloaddition between a naphthodiyne synthon (**1**, **2**, or **3**) and a furan (**10** or **14**). Subsequent deoxygenation affords the arene in 16–28% overall yield from dibromo ditosylate **7**, **8**, or **9**. The latter are prepared in two steps from commercially available 2,3- or 2,7-dihydroxynaphthalene, and, with phenyllithium, serve as synthetic equivalents of **1**, **2**, and **3**. The X-ray structure of the anti isomer of **23** is discussed in some detail.

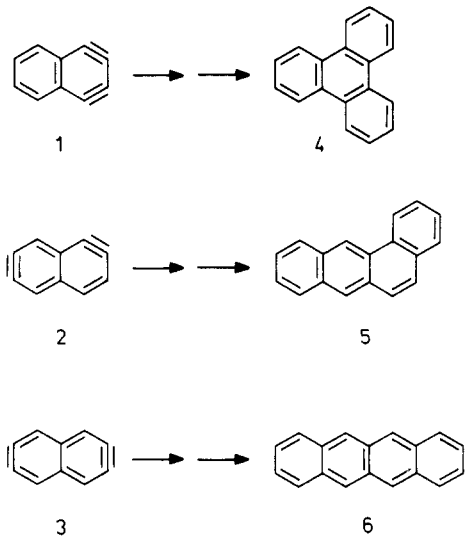
The extrusion of a bridging atom or atoms from suitable Diels–Alder adducts has been widely used to synthesize arenes, i.e., **A** → **B**.[1] In particular, the use of benzynes and other arynes in this methodology has proven to be a powerful tool for the synthesis of polycyclic aromatic hydrocarbons (PAH).[2]



A B

The pioneering work of Hart[3] and our own recent study[4] have illustrated the utility of bis(aryne) synthetic equivalents in the synthesis of PAH and related molecules. For example, in our previous paper we reported[4] a new chrysene synthesis using a synthetic equivalent of 1,5-naphthodiyne.

We now describe synthetic equivalencies of 1,3-naphthodiyne (**1**), 1,6-naphthodiyne (**2**), and 2,6-naphthodiyne (**3**), and illustrate their utility in new syntheses of triphenylene (**4**), benz[*a*]anthracene (**5**), and naphthacene (**6**), respectively.



1 4

2 5

3 6

Previous examples of these naphthodiyne synthons are the tetramethyl derivative of **3** [3a,b,d] and 1,4-dibromo-

† Author to whom inquiries regarding the X-ray crystallographic data should be directed.

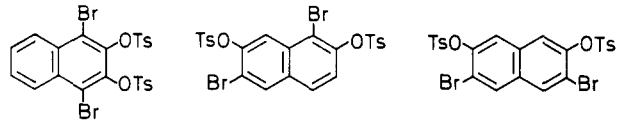
(1) For reviews, see: (a) Wong, H. N. C.; Ng, T.; Wong, T. *Heterocycles* **1983**, *20*, 1815. (b) Wong, H. N. C.; Ng, T.; Wong T.; Xing, Y. D. *Heterocycles* **1984**, *22*, 875.

0022-3263/85/1950-2934$01.50/0

naphthalene which has served as an equivalent of 1.[5]

Results and Discussion

Our previous success[4] with 2,6-dibromo-1,5-bis[(*p*-tolylsulfonyl)oxy]naphthalene led us to the preparation and study of 1,4-dibromo-2,3-bis[(*p*-tolylsulfonyl)oxy]-naphthalene (**7**), 1,6-dibromo-2,7-bis[(*p*-tolylsulfonyl)-oxy]naphthalene (**8**), and 3,6-dibromo-2,7-bis[(*p*-tolyl-sulfonyl)oxy]naphthalene (**9**) as synthetic equivalents of **1–3**, respectively.



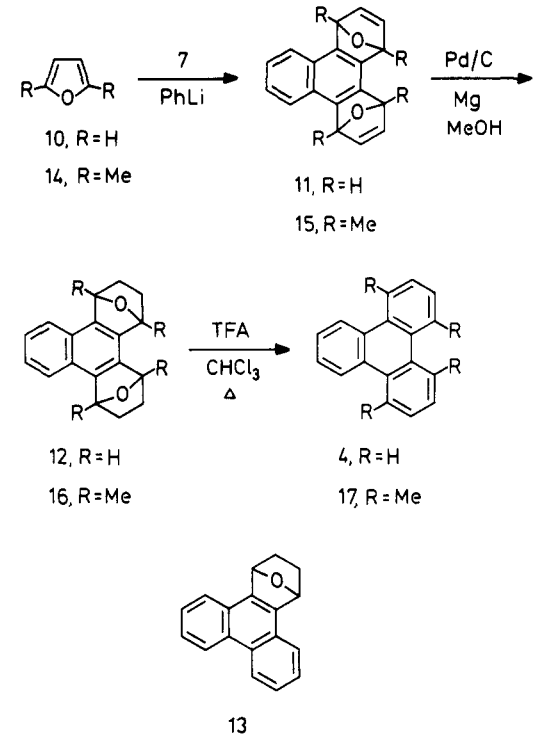
7 8 9

The syntheses of **7–9** were very straightforward since all three of the corresponding dibromodihydroxynaphthalenes are known compounds, being readily prepared by brominating the commercially available 2,3- or 2,7-dihydroxynaphthalene (Experimental Section). The tosylation procedure of Prajer-Janczewska and Postawka[6] (*p*-toluenesulfonyl chloride, acetone, aqueous NaOH, 0 °C) was used to convert the dibromodihydroxynaphthalenes to **7–9**, which were fully characterized by elemental and spectral analysis. In particular, the ^{13}C NMR spectra support the structural assignments, showing the expected 10, 18 (20 predicted), and 11 lines for **7**, **8**, and **9**, respectively.

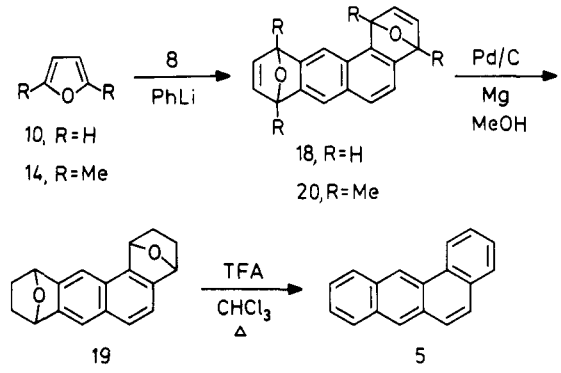
Triphenylenes. Our syntheses of triphenylene (**4**) and 1,4,5,8-tetramethyltriphenylene (**17**) are summarized in Scheme I. Treatment of a tetrahydrofuran (THF) solution of **7** and excess furan (**10**) with 2 equiv of phenyllithium at 0 °C gave the bis adduct **11** in 41% yield after flash chromatography (FC). It is presumed that this substance is a mixture of syn and anti isomers, as have been observed and isolated in equal amounts by Wege.[5] Since we were unable to separate these isomers by medium pressure liquid chromatography, the mixture was used as such in the ensuing reactions. Catalytic hydrogenation of **11** was conveniently performed by using Olah's procedure[7] (10% Pd/C, Mg, MeOH) to give **12** in 67% yield after FC. When **12** was treated with a minimal amount of trifluoroacetic acid (TFA) in refluxing $CHCl_3$ (48 h) there was isolated the monoepoxide **13** (30%)[5] and some of the desired triphenylene (**4**), as well as starting material (**12**). However, refluxing **12** with a solution of 15% TFA in $CHCl_3$ for 1.5 h gave **4** in 57% yield after column chromatography. These conditions also converted **13** into **4**. The overall yield of triphenylene (**4**) from **7** is 16%.

An attempt to deoxygenate **12** to **4** directly with $NaBH_4$/TFA[8] was unsuccessful.

Scheme I



Scheme II

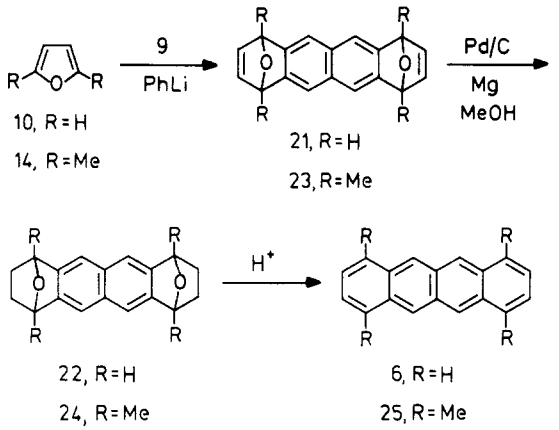


An identical sequence using 2,5-dimethylfuran (**14**) as the diene gave the previously unknown 1,4,5,8-tetramethyltriphenylene (**17**) in 22% overall yield from **7** (Scheme I). Not surprisingly, it was somewhat more difficult to dehydrate **16** to **17**. Presumably this is a consequence of the strain energy inherent in **17**—a 4,5-dimethylphenanthrene analogue.[9] We also observed that although **17** undergoes apparent protonation in neat TFA to give a deep purple colored solution, it does not tautomerize[3a,e] nor rearrange[10] since **17** was recovered upon neutralization and workup. The ultraviolet spectrum of **17** shows a single, broad featureless band at 266 nm, in contrast to the UV spectrum of **4** which exhibits main bands at 249 and 256 nm. This difference is similar to that observed in the UV spectra of 4,5-dimethylphenanthrene and phenanthrene.[11]

Attempts to trap the aryne derived from **7** with *N*-methylpyrrole and *N*-methylisoindole were largely un-

(2) Gribble, G. W.; LeHoullier, C. S.; Sibi, M. P.; Allen, R. W. *J. Org. Chem.* **1985**, *50*, 1611, and references cited therein.
(3) (a) Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7. (b) Hart, H.; Lai, C.-Y.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6649. (c) Hart, H.; Nwokogu, G. *J. Org. Chem.* **1981**, *46*, 1251. (d) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427. (e) Hart, H.; Shamouilian, S. *J. Org. Chem.* **1981**, *46*, 4874. (f) Hart, H.; Raju, N.; Meador M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357. (g) Hart, H.; Nwokogu, G. C. *Tetrahedron Lett.* **1983**, *24*, 5721. (h) Hart, H.; Ok, D. *Tetrahedron Lett.* **1984**, *25*, 2073.
(4) LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 1682.
(5) Stringer, M. B.; Wege, D. *Tetrahedron Lett.* **1980**, *21*, 3831.
(6) Prajer-Janczewska, L.; Postawka, A. *Rocz. Chem.* **1963**, *37*, 597; *Chem. Abstr.* **1963**, *59*, 9920e.
(7) Olah, G. A.; Prakash, S. G. K.; Arvanaghi, M.; Bruce, M. R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 91.
(8) Gribble, G. W.; Kelly, W. J.; Sibi, M. P. *Synthesis* **1982**, 143.
(9) Frisch, M. A.; Barker, C.; Margrave, J. L.; Newman, M. S. *J. Am. Chem. Soc.* **1963**, *85*, 2356.
(10) For example, 1,4,5,8-tetramethylnaphthalene rearranges to 1,4,5,7-tetramethylnaphthalene upon treatment with hot TFA (76% yield): Oku, A.; Yuzen, Y. *J. Org. Chem.* **1975**, *40*, 3850.
(11) Badger, G. M.; Campbell, J. E.; Cook, J. W.; Raphael, R. A.; Scott, A. I. *J. Chem. Soc.* **1950**, 2326.

Scheme III



successful, giving little or none of the desired Diels–Alder adducts.

Benz[*a*]anthracene. Our synthesis of benz[*a*]anthracene (**5**) is shown in Scheme II. Treatment of a THF solution of dibromo ditosylate **8** and excess furan (**10**) with phenyllithium (2 equiv, 0 °C) gave the expected adduct **18** (45%). The usual hydrogenation to **19** (68%) and acid treatment (91%) gave **5**, identical with a commercial sample of benz[*a*]anthracene. This represents a very simple synthesis of this ring system, examples of which are of importance to PAH cancer research.[12]

A similar sequence using 2,5-dimethylfuran (**14**) as the diene gave bis(epoxide) **20** in 45% yield following FC (Scheme II). This adduct was not carried on to the corresponding unknown tetramethylbenz[*a*]anthracene because of the extraordinary carcinogenicity of some methylated benz[*a*]anthracenes.[12]

Nevertheless, this approach to benz[*a*]anthracenes should be applicable to those derivatives having substituents in the two terminal rings.

Naphthacenes. Our syntheses of naphthacene (**6**) and 1,4,7,10-tetramethylnaphthacene (**25**) are illustrated in Scheme III. Treatment of dibromo ditosylate **9** and excess furan (**10**) with phenyllithium (2 equiv, 0 °C) gave the bis adduct **21** in 40% yield after FC. This substance behaved as a single compound and no attempt was made to separate the syn and anti isomers presumed to be present. Catalytic hydrogenation gave **22** (80% after FC) which was readily dehydrated to naphthacene (**6**) by acid treatment (78%) (TFA/$CHCl_3$ or HCl/MeOH). The bright orange solid so obtained was identical with a commercial sample of naphthacene.

The same sequence using 2,5-dimethylfuran (**14**) as the diene gave bis adduct **23** in 44% yield following FC (Scheme III). Recrystallization of this material from MeOH afforded the pure anti isomer, mp 204 °C, as shown by X-ray crystallographic analysis (vide infra).

The usual catalytic hydrogenation of **23** gave **24**, which, because of its extreme acid lability, was directly converted into 1,4,7,10-tetramethylnaphthacene (**25**) by treatment with aqueous HCl (56% yield after column chromatography).

We have been able to trap the aryne from dibromo ditosylate **9** with *N*-methylpyrrole and 2-methyl-4,5,6,7-tetrafluoroisoindole to give the Diels–Alder adducts **26** and **27**, respectively, albeit in low yields. Thus far, attempts to convert these compounds into **6** and octafluorohexacene by using known deamination methodologies[13] have not been successful.

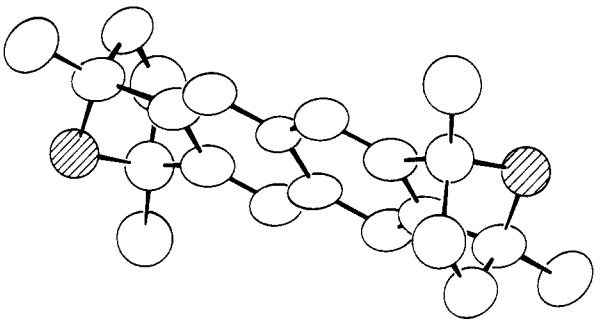


Figure 1. A perspective view of the anti isomer of 1,4,7,10-tetramethyl-1,4:7,10-diepoxy-1,4,7,10-tetrahydronaphthacene drawn with 50% thermal ellipsoids; oxygen atoms have been cross-hatched and hydrogen atoms have been omitted for clarity.

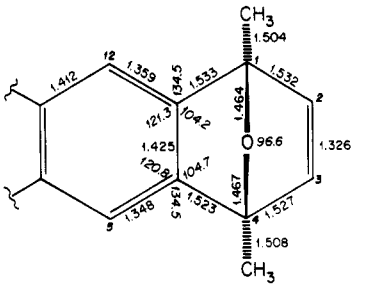
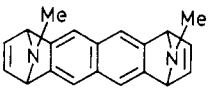


Figure 2. Selected bond lengths and angles; estimated standard deviations in distances ca. +0.004 Å and in angles ca. +0.2°.

Table I. Fractional Atomic Coordinates (×10⁴) for Non-Hydrogen Atoms (Estimated Standard Deviations are in Parentheses)

atom	*x/a*	*y/b*	*z/c*
O (1)	7129 (2)	5323 (3)	8603 (2)
C (1)	6148 (3)	6881 (4)	8337 (2)
C (2)	5950 (4)	7083 (4)	7180 (2)
C (3)	7368 (4)	6435 (4)	7128 (2)
C (4)	8490 (3)	5833 (4)	8239 (2)
C (4a)	9101 (3)	7404 (4)	8905 (2)
C (5)	10646 (3)	8144 (4)	9393 (2)
C (11a)	9227 (3)	10352 (4)	10021 (2)
C (12)	7634 (3)	9532 (4)	9510 (2)
C (12a)	7579 (3)	8103 (4)	8963 (2)
C (13)	4553 (3)	6812 (5)	8587 (3)
C (14)	9778 (4)	4456 (4)	8369 (2)



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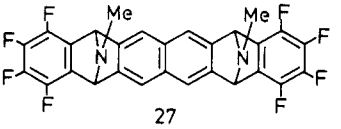


27

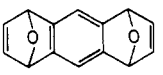
X-ray Structure. Molecules of the anti isomer of **23** (Figure 1) lie on crystallographic centers of symmetry. Figure 2 shows selected bond lengths and angles in the unique portion of the molecule. Table I contains atomic

(12) (a) "Polycyclic Hydrocarbons and Cancer;" Gelboin, H. V., Ts'O, P. O. P., Eds.; Academic Press: New York, 1978; Vol. 1–3. (b) Dipple, A. *ACS Monogr.* **1976**, No. 173, 245–314.

(13) (a) Gribble, G. W.; Allen, R. W.; Anderson, P. S.; Christy, M. E.; Colton, C. D. *Tetrahedron Lett.* **1976**, 3673. (b) Gribble, G. W.; Allen, R. W.; LeHoullier, C. S.; Eaton, J. T.; Easton, N. R., Jr.; Slayton, R. I.; Sibi, M. P. *J. Org. Chem.* **1981**, *46*, 1025.

positional parameters for the non-hydrogen atoms.

The bond lengths are generally similar to those in 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene, **28**,[3f] however, there are several differences worthy of note. The C(2)–C(3) bond length in *anti*-**23** is 1.326 (4) Å, similar to the predicted 1.33 Å.[14] This observed value lies between that observed in **28**, 1.301 (6) Å, and those in 1,4-dihydro-1,4-epoxynaphthalene, **29**,[15] 1.39 (1) and 1.40 (1) Å.[16] The C–O bond lengths in *anti*-**23** (mean 1.466 Å) are longer than those in **28** (mean 1.447 Å) but similar to those in **29** and in a 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene derivative.[17] Consonant with the fact that the central two rings in *anti*-**23** form a naphthalene unit and the central ring in **28** is benzenoid, is the significantly longer C(4a)–C(12a) bond length in *anti*-**23** (1.425 (3) vs. 1.388 (4) Å).



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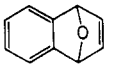

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The oxa bridge in *anti*-**23** is tilted slightly away from the C(2)–C(3) double bond. The dihedral angles between the C(1)–O(1)–C(4) plane and the C(1), C(2), C(3), C(4) and C(4), C(4a), C(12a), C(1) planes are 126.4 and 122.4°, respectively. These values are in close agreement with the calculated geometry for 2,3-dimethylidene-7-oxabicyclo-[2.2.1]hept-5-ene[18] (analogous angles, 126.0 and 123.6°).

Summary. In summary, we have demonstrated that the bis(aryne)/Diels–Alder annulation methodology can be used to synthesize the tetracyclic arenes triphenylene, benz[*a*]anthracene, and naphthacene in five steps from commercially available dihydroxynaphthalenes and furan. Noteworthy is our use of dibromo ditosylate **9** for the unsubstituted 2,6-naphthodiyne synthon (**3**). This avoids having to employ 2,3,6,7-tetrahalonaphthalenes which are difficult to synthesize[19] and are structural and possibly toxic analogues[20] of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).

Experimental Section

General techniques and the instruments used in this research have been described.[4] In addition, flash chromatography (FC)[21] employed silica gel (230–400 mesh) and medium pressure liquid chromatography used a system similar to that described by Meyers.[22]

The phrase "usual workup" refers to washing the organic extract with H_2O and then brine, drying over Na_2SO_4, and concentrating in vacuo on a rotary evaporator.

All reactions were run under N_2.

1,4-Dibromo-2,3-bis[(*p*-tolylsulfonyl)oxy]naphthalene (7). To a magnetically stirred solution of 1,4-dibromo-2,3-dihydroxynaphthalene (6.00 g, 0.0189 mmol) (prepared in 82% yield from 2,3-dihydroxynaphthalene (Aldrich) according to the procedure of Zincke[23]) and *p*-toluenesulfonyl chloride (7.20 g, 0.0378 mol) in acetone (100 mL) at 0 °C was added dropwise over 30 min 10% aqueous NaOH (100 mL). The resulting yellow suspension was diluted with H_2O (50 mL) and stirred for 15 min. The solid was collected by filtration, washed with H_2O, and dried (0.1 torr) to afford 7.33 g (62%) of crude **7**. Recrystallization from aqueous acetone gave 4.87 g (41%) of **7** as a yellow powder. Chromatography of the mother liquor over silica gel (CH_2Cl_2) afforded an additional 9% of **7**. Two additional crystallizations from aqueous acetone gave the analytical sample: mp 185–186 °C; ^1H NMR ($CDCl_3$) δ 2.45 (s, 6 H), 7.1–8.4 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 119.0, 128.2, 128.8, 129.0, 129.6, 131.0, 133.3, 139.8, 145.7; IR (KBr) 1600 (m), 1364 (s), 1204 (s), 1180 (s), 922 (s), 715 (s) cm^{-1}; mass spectrum, *m/e* 628, 626 (M^+), 624, 260, 235, 219, 209, 207, 181, 179, 155 (100%), 139, 91.

Anal. Calcd for $C_{24}H_{18}Br_2S_2O_6$: C, 46.02; H, 2.90; Br, 25.52; S, 10.24. Found: C, 45.95; H, 2.91; Br, 25.60; S, 10.24.

1,6-Dibromo-2,7-bis[(*p*-tolylsulfonyl)oxy]naphthalene (8). The same procedure as described above for the preparation of **7** was used to convert 1,6-dibromo-2,7-dihydroxynaphthalene (prepared from 2,7-dihydroxynaphthalene (Aldrich) according to the procedure of Cooke[24]) to **8**. The reaction mixture was diluted with H_2O and extracted with CH_2Cl_2. The usual workup gave **8** as a brown oil. Column chromatography over silica gel (Et_2O/hexane) gave **8** (90%), which slowly crystallized on standing. The analytical sample was prepared by recrystallization from acetone: mp 130–132 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 6 H), 7.2–8.0 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 21.77, 21.80, 115.6, 116.7, 121.5, 123.2, 127.7, 128.6, 128.7, 128.8, 129.9, 131.4, 132.2, 132.3, 132.5, 133.1, 145.9, 146.0; IR (KBr) 1600 (m), 1485 (m), 1375 (s), 1195 (s), 1180 (s), 815 (s) cm^{-1}; mass spectrum, *m/e* 626 (M^+), 471, 155 (100%), 139, 91, 77.

Anal. Calcd for $C_{24}H_{18}Br_2S_2O_6$: C, 46.02; H, 2.90; Br, 25.52; S, 10.24. Found: C, 46.12; H, 2.94; Br, 25.45; S, 10.21.

3,6-Dibromo-2,7-bis[(*p*-tolylsulfonyl)oxy]naphthalene (9). The same procedure as described above for the preparation of **7** was used to convert 3,6-dibromo-2,7-dihydroxynaphthalene (prepared in 73% yield from 2,7-dihydroxynaphthalene (Aldrich) according to the procedure of Cooke[24]) to **9**. The reaction mixture was diluted with H_2O and the solid was collected to give crude **9** (91%). Recrystallization from benzene/hexane gave pure **9** (77%): mp 164–165 °C; ^1H NMR ($CDCl_3$) δ 2.45 (s, 6 H), 7.55 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 116.5, 121.1, 128.5, 129.8, 131.2, 131.4, 131.5, 132.3, 144.9, 145.9; IR (KBr) 1595 (m), 1476 (m), 1380 (s), 1350 (s), 1192 (s), 1175 (s), 1157 (s), 1000 (m) cm^{-1}; mass spectrum, *m/e* 628, 626 (M^+), 624, 471, 219, 155, 139, 91 (100%).

Anal. Calcd for $C_{24}H_{18}Br_2S_2O_6$: C, 46.02; H, 2.90; Br, 25.52; S, 10.24. Found: C, 46.07; H, 2.93; Br, 25.42; S, 10.15.

1,4:5,8-Diepoxy-1,4,5,8-tetrahydrotriphenylene (11). To a magnetically stirred solution of **7** (2.00 g, 0.0032 mol) and furan (**10**) (5 mL) in THF (15 mL) at 0 °C was added dropwise over 10 min phenyllithium (2.30 M in 70:30 cyclohexane/Et_2O, 2.80 mL, 0.0064 mol). The solution was stirred at room temperature overnight and then evaporated in vacuo. The residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL), and the aqueous layer was further extracted with CH_2Cl_2 (25 mL). The usual workup of the organic extract followed by flash chromatography (1:1 Et_2O/hexane) of the residue gave 0.34 g (41%) of **11** as an off-white powder, mp 139–143 °C. The analytical sample was prepared by medium pressure liquid chromatography followed by crystallization from Et_2O/hexane: mp 155 °C dec (ill-defined); ^1H NMR ($CDCl_3$) δ 6.0 (m, 2 H), 6.25 (m, 2 H), 7.0–7.5 (m, 6 H), 7.8 (m, 2 H); IR (KBr) 3000 (w), 1273 (m), 1018 (m), 857 (s), 822 (s), 710 (m), 695 (m), 628 (m) cm^{-1}; mass spectrum, *m/e* 260 (M^+), 234, 208, 206, 203, 202, 178, 176, 152, 100 (100%).

(14) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960.
(15) Raston, C. L.; Wege, D.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 2153.
(16) There are two independent molecules in the asymmetric unit.
(17) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H. A.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095.
(18) Pinkerton, A. A.; Schwarzenbach, D.; Birbaum, J.-L.; Carrupt, P.-A.; Schwager, L.; Vogel, P. *Helv. Chim. Acta* **1984**, *67*, 1136.
(19) (a) McKinney, J.; Singh, P.; Levy, L.; Walker, M.; Cox, R.; Bobenrieth, M.; Bordner, J. *J. Agric. Food Chem.* **1981**, *29*, 180. (b) Levy, L. A. *Syn. Comm.* **1983**, *13*, 639.
(20) Goldstein, J. A.; Linko, P. C.; Levy, L. A.; McKinney, J. D.; Gupta, B. N.; Moore, J. A. *Biochem. Pharmacol.* **1979**, *28*, 2947.
(21) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(22) Meyers, A. I.; Slade, J.; Smith, R. K.; Mihelich, E. D.; Hershenson, F. M.; Liang, C. D. *J. Org. Chem.* **1979**, *44*, 2247.
(23) Zincke, T.; Fries, K. *Liebigs Ann. Chem.* **1904**, *334*, 342.
(24) (a) Cooke, R. G.; Johnson, B. L.; Owen, W. R. *Aust. J. Chem.* **1960**, *13*, 256. (b) Cooke, R. G.; Johnson, B. L.; Owen, W. R. *Chem. Ind.* (London) **1957**, 1623.

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.78; H, 4.81.

Wege[5] has reported mp 195–215 °C (dec) and 148–157 °C (dec) for the two separate isomers, which have nearly identical ^1H NMR spectra. Our ^1H NMR data for **11** (vide supra) agree with those reported.[5]

1,4:5,8-Diepoxy-1,2,3,4,5,6,7,8-octahydrotriphenylene (12). To a magnetically stirred suspension of **11** (0.262 g, 0.00101 mol) and 10% Pd/C (0.01 g) in MeOH (25 mL) at room temperature was added oven-dried Mg turnings (0.21 g, 0.0086 mol). The reaction mixture was stirred overnight and then poured into ice-cold 3 N HCl (20 mL) and extracted with CH_2Cl_2 (4 × 20 mL). The usual workup gave 0.257 g (96%) of **12** as a yellow solid. Flash chromatography (2:1 hexane/Et_2O) afforded 0.178 g (67%) of **12** as a pale yellow solid. The analytical sample was prepared by crystallization from Et_2O: mp 165–167 °C; ^1H NMR ($CDCl_3$) δ 1.1–1.5 (m, 4 H), 1.9–2.5 (m, 4 H), 5.6 (m, 2 H), 5.9 (m, 2 H), 7.3–7.6 (m, 2 H), 7.7–8.0 (m, 2 H); IR (KBr) 2940 (m), 1300 (m), 1166 (m), 988 (s), 908 (s), 864 (s), 806 (s), 743 (s) cm^{-1}; mass spectrum, m/e 264 (M^+), 236, 209, 208 (100%), 178, 165, 149, 100.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.64; H, 6.43.

Wege[5] has reported mp 185–186 °C and 253–254 °C for the two separate isomers, which have nearly identical ^1H NMR spectra. Our ^1H NMR data for **12** (vide supra) agree with those reported.[5]

1,4-Epoxy-1,2,3,4-tetrahydrotriphenylene (13). A magnetically stirred solution of **12** (0.177 g, 0.00067 mol) in $CHCl_3$ (25 mL) was treated with trifluoroacetic acid (TFA) (ca. 1 mL) and refluxed for 48 h. TLC indicated that the reaction mixture contained **12**, triphenylene (**4**), and another product (**13**). The mixture was evaporated in vacuo and the residue subjected to flash chromatography (5:2 hexane/Et_2O) to give 0.050 g (30%) of **13** as a pale orange solid. The analytical sample was prepared by crystallization from hexane to afford colorless prisms: mp 161–162 °C (lit.[5] mp 164 °C); ^1H NMR ($CDCl_3$) δ 1.1–1.5 (m, 2 H), 1.95–2.3 (m, 2 H), 6.0 (m, 2 H), 7.3–8.0 (m, 6 H), 8.6 (m, 2 H); IR (KBr) 2940 (w), 1001 (m), 927 (s), 870 (m), 835 (s), 757 (s), 721 (s) cm^{-1}; mass spectrum, m/e 246 (M^+), 228, 218 (100%), 189, 109, 95.

Anal. Calcd for $C_{18}H_{14}O_2$: C, 87.77; H, 5.73. Found: C, 87.67; H, 5.76.

Triphenylene (4). A solution of **12** (63 mg, 0.24 mmol) in 15% TFA–$CHCl_3$ (10 mL) was refluxed for 90 min (reaction monitored by UV spectroscopy). The reaction mixture was allowed to cool and then neutralized with saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the usual workup gave 52 mg of crude **4** as a tan powder. Column chromatography (silica gel, hexane) afforded 31 mg (57%) of **4** as colorless needles, mp 190–193 °C. Crystallization from Et_2O gave long colorless needles, mp 193–195 °C, which were identical with a commerical sample of triphenylene (TLC, IR, UV, ^1H NMR).

1,4,5,8-Tetramethyl-1,4:5,8-diepoxy-1,4,5,8-tetrahydrotriphenylene (15). The same procedure as for the preparation of **11** was used, except that 2,5-dimethylfuran (**14**) was employed to afford **15** (47%) as a viscous orange oil following flash chromatography (1:1 Et_2O/hexane): ^1H NMR ($CDCl_3$) δ 2.05 (s, 3 H), 2.1 (s, 3 H), 2.2 (s, 6 H), 6.8–7.4 (m, 6 H), 7.8–8.1 (m, 2 H); IR (neat) 2990 (m), 1387 (s), 1306 (s), 1160 (s), 1130 (s), 870 (s) cm^{-1}; mass spectrum, m/e 316 (M^+), 301, 290, 275, 274, 273, 264, 247, 231, 230, 121, 91 (100%); high resolution mass spectrum m/e 316.1462, calcd for $C_{22}H_{20}O_2$ 316.1462.

1,4,5,8-Tetramethyl-1,4:5,8-diepoxy-1,2,3,4,5,6,7,8-octahydrotriphenylene (16). The usual Olah hydrogenation procedure on **15** gave **16** (46%) as a colorless glass after flash chromatography (1:1 Et_2O/hexane): ^1H NMR ($CDCl_3$) δ 1.1–2.4 (m, 8 H), 2.0 (s, 3 H), 2.1 (s, 3 H), 2.2 (s, 6 H), 7.2–7.6 (m, 2 H), 8.0–8.4 (m, 2 H); IR (KBr) 2960 (m), 1258 (s), 1065 (s), 1015 (s), 795 (s) cm^{-1}; mass spectrum, m/e 320 (M^+), 292, 264 (100%), 249, 211, 132; high resolution mass spectrum m/e 320.1776, calcd for $C_{22}H_{24}O_2$ 320.1775.

1,4,5,8-Tetramethyltriphenylene (17). A solution of **16** (52 mg, 0.16 mmol) in 15% TFA–$CHCl_3$ (12 mL) was refluxed for 2.5 h (monitored by UV). The purple solution was allowed to cool to room temperature and enough saturated aqueous $NaHCO_3$ was added to neutralize the TFA. The organic layer was separated and the usual workup gave, after column chromatography (silica gel, hexane), 27 mg (59%) of **17** as a colorless oil which crystallized from EtOH, mp 105–106 °C. The analytical sample was prepared by recrystallization from aqueous EtOH: mp 106–107 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 6 H), 2.9 (s, 6 H), 7.0–7.6 (m, 6 H), 8.1–8.5 (m, 2 H); IR (KBr) 2950 (m), 1445 (s), 1428 (s), 804 (s), 768 (s) cm^{-1}; mass spectrum, m/e 284 (M^+, 100%), 269, 254, 253, 252, 239, 149, 132, 126.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.87; H, 7.13.

1,4:8,11-Diepoxy-1,4,8,11-tetrahydrobenz[*a*]anthracene (18). The same procedure as described for the preparation of **11**, but with bromo tosylate **8**, gave **18** (45%) as a viscous yellow oil after flash chromatography (1:1 Et_2O/hexane). TLC (Et_2O) showed two overlapping spots: ^1H NMR ($CDCl_3$) δ 5.7–5.8 (m, 3 H), 6.2 (m, 1 H), 6.9–7.5 (m, 8 H); mass spectrum, m/e 260 (M^+), 234, 203, 176, 163, 152, 121. This material was used directly in the next reaction.

1,4:8,11-Diepoxy-1,2,3,4,8,9,10,11-octahydrobenz[*a*]anthracene (19). Olah hydrogenation of crude **18** gave **19** (68%) as a greenish oil; ^1H NMR ($CDCl_3$) δ 1.1–1.6 (m, 4 H), 2.1 (m, 4 H), 5.6 (m, 3 H), 5.95 (m, 1 H), 7.2–7.8 (m, 4 H); mass spectrum, m/e 264 (M^+), 236, 208 (100%), 178, 165, 152, 135, 121, 104. This material was used directly in the next reaction.

Benz[*a*]anthracene (5). The crude **19** from the previous reaction was dehydrated with TFA/$CHCl_3$ under the usual conditions to give **5** (91%) after column chromatography (silica gel, benzene). A second, flash chromatography (hexane) gave **5** as colorless flakes, mp 153–154 °C, identical with a commercial sample of benz[*a*]anthracene (TLC, UV).

1,4,8,11-Tetramethyl-1,4:8,11-diepoxy-1,4,8,11-tetrahydrobenz[*a*]anthracene (20). The same procedure as described for the preparation of **11**, but with bromo tosylate **8** and a solution of 2,5-dimethylfuran (**14**) in THF, gave **20** (45%) as a yellow gum after flash chromatography (3:2 hexane/Et_2O): ^1H NMR ($CDCl_3$) δ 1.95 (broad s, 9 H), 2.2 (s, 3 H), 6.7–8.0 (m, 8 H); mass spectrum, m/e 316 (M^+), 290, 273, 247, 232, 207, 154, 139, 121 (100%); high resolution mass spectrum m/e 316.1462, calcd for $C_{22}H_{20}O_2$ 316.1462.

1,4:7,10-Diepoxy-1,4,7,10-tetrahydronaphthacene (21). The same procedure as described for the preparation of **11**, but with bromo tosylate **9**, gave **21** (40%) as a yellow solid after flash chromatography (2:1 Et_2O/hexane then Et_2O). Recrystallization from CH_2Cl_2/Et_2O gave **21** as a colorless powder: mp >300 °C dec; ^1H NMR ($CDCl_3$) δ 5.8 (s, 4 H), 6.95 (s, 4 H), 7.5 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 81.8, 119.0, 129.9, 141.8, 145.0; IR (KBr) 2960 (m), 1640 (m), 1280 (s), 983 (s), 838 (s) cm^{-1}; mass spectrum, m/e 260 (M^+), 231, 203, 181, 176, 149; high resolution mass spectrum m/e 260.0828, calcd for $C_{18}H_{12}O_2$ 260.0837.

1,4:7,10-Diepoxy-1,2,3,4,7,8,9,10-octahydronaphthacene (22). Olah hydrogenation of **21** gave **22** (80%) as a light yellow powder after flash chromatography (1:1 Et_2O/hexane): mp 220–225 °C dec to naphthacene; ^1H NMR ($CDCl_3$) δ 1.2–1.65 (m, 4 H), 1.9–2.35 (m, 4 H), 5.5 (broad s, 4 H), 7.6 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 27.4, 78.7, 117.1, 131.9, 143.7; IR (KBr) 2940 (s), 1291 (s), 970 (s), 856 (s), 812 (s), 597 (s) cm^{-1}; mass spectrum, m/e 264 (M^+), 236 (100%), 228, 218, 208, 189, 184, 178, 165, 152, 104; high resolution mass spectrum m/e 264.1176, calcd for $C_{18}H_{16}O_2$ 264.1150.

Naphthacene (6). A solution of **22** (32 mg, 0.12 mmol) in 15% TFA–$CHCl_3$ (5 mL) was refluxed for 1 h, during which time a bright orange finely divided solid formed. The mixture was cooled to 0 °C and the solid collected by filtration and dried (0.2 torr, 20 °C) to give 22 mg (78%) of **6** as a bright orange powder. This could be sublimed (153 °C, 0.025 torr) or crystallized from xylene to give pure naphthacene (**6**), mp 341 °C, identical with a commerical sample (TLC, IR, UV, m mp 341 °C).

1,4,7,10-Tetramethyl-1,4:7,10-diepoxy-1,4,7,10-tetrahydronaphthacene (23). The same procedure as described for the preparation of **11**, but with bromo tosylate **9** and a solution of 2,5-dimethylfuran (**14**) in THF (1:2), gave **23** (44%) after flash chromatography (1:1 Et_2O/hexane). Recrystallization from MeOH afforded **23** as colorless prisms: mp 204 °C dec (used for the X-ray analysis); ^1H NMR ($CDCl_3$) δ 1.9 (s, 12 H), 6.7 (s, 4 H), 7.4 (s, 4 H); IR (KBr) 2960 (m), 1377 (s), 1306 (s), 1152 (s), 1131 (s), 851 (s) cm^{-1}; mass spectrum, m/e 316 (M^+), 290, 281, 273, 259, 247 (100%), 230, 215, 139; high resolution mass spectrum m/e

316.1462, calcd for $C_{22}H_{20}O_2$ 316.1462.

1,4,7,10-Tetramethylnaphthacene (25). To a magnetically stirred solution of **23** (90 mg, 0.28 mmol) in CH_2Cl_2/MeOH (1:10, 11 mL) was added 10% Pd/C (20 mg) and oven-dried Mg turnings (100 mg, 4.1 mmol). The mixture was stirred at room temperature overnight to complete the formation of **24**. The mixture was poured into ice-cold 3 N HCl (20 mL), resulting in the immediate formation of an orange solid. The mixture was extracted with CH_2Cl_2 and the usual workup followed by column chromatography (silica gel, hexane) gave 45 mg (56%) of **25** as an orange powder: mp 269–273 °C; ^1H NMR ($CDCl_3$) δ 2.8 (s, 12 H), 7.05 (s, 4 H), 8.65 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.8, 123.4, 124.8, 131.4, 132.2; IR (KBr) 1622 (w), 885 (s), 813 (m) cm^{-1}; mass spectrum, *m/e* 284 (100%), 269, 253, 239, 142, 135, 127.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.54; H, 7.30.

13,14-Dimethyl-1,4,7,10-tetrahydronaphthacene-1,4:7,10-diimine (26). The same procedure as described for the preparation of **11**, but with bromo tosylate **9** and a solution of freshly distilled *N*-methylpyrrole in THF (1:2), gave **26** (26%) as a bright yellow powder after column chromatography (activity III basic Al_2O_3, 95:5 EtOAc/Et_3N): mp >160 °C dec; ^1H NMR ($CDCl_3$) δ 2.2 (broad s, 6 H), 4.5 (broad s, 4 H), 6.8 (broad s, 4 H), 7.5 (s, 4 H); IR (KBr) 2950 (m), 1309 (m), 1270 (m), 928 (m), 798 (s), 705 (m) cm^{-1}; mass spectrum, *m/e* 286 (M^+), 271, 257, 244, 215, 202, 143, 84 (100%).

17,18-Dimethyl-1,2,3,4,9,10,11,12-octafluoro-5,8,13,16-tetrahydrohexacene-5,16:8,13-diimine (27). The same procedure as described for the preparation of **11**, but with bromo tosylate **9** and a solution of *N*-methyl-4,5,6,7-tetrafluoroisoindole (5 mmol) in THF (25 mL), gave **27** (16%) as a brown solid after flash chromatography (95:5 EtOAc/Et_3N), mp 155–165 °C; ^1H NMR ($CDCl_3$) δ 2.3 (s, 6 H), 5.4 (broad s, 4 H), 7.7 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 36.2, 69.5, 121.0, 128.2, 128.4, 130.1, 131.0, 142.8; IR (KBr) 1495 (s), 1481 (s), 1261 (m), 1045 (m), 740 (m) cm^{-1}; high resolution mass spectrum *m/e* 530.1009 (M^+, 100%), calcd for $C_{28}H_{14}F_8N_2$ 530.1029, 515, 501, 486, 472, 459.

Crystallographic Data and X-ray Structure Analysis of the Anti Isomer of 23. Crystal data: $C_{22}H_{20}O_2$, M_r = 316.4, monoclinic, a = 8.393 (2) Å, b = 8.019 (2) Å, c = 13.656 (2) Å, β = 112.45 (1)°, U = 849.4 (3) Å^3, D_c = 1.237 g cm^{-3}, Z = 2, Cu Kα radiation (λ = 1.5418 Å), μ = 6.2 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$.

Data were collected ($4° < 2\theta < 130°$) with a variable speed, $\theta/2\theta$ scanning technique on a Syntex $P2_1$ diffractometer. Of the 1344 unique reflections collected, the 1023 with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure was solved by using the MULTAN80 suite of programs[25] and refined with full-matrix least-squares iterations (anisotropic C, O; isotropic H).[26] The final R was 0.056.

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Registry No. **1**, 96965-60-5; **2**, 96998-98-0; **3**, 96965-61-6; **4**, 217-59-4; **5**, 56-55-3; **6**, 92-24-0; **7**, 96965-62-7; **8**, 96965-63-8; **9**, 96965-64-9; **10**, 110-00-9; **11**, 97058-39-4; **12**, 97058-40-7; **13**, 77037-26-4; **14**, 625-86-5; **15**, 96965-65-0; **16**, 96965-66-1; **17**, 96965-67-2; **18**, 96965-68-3; **19**, 96965-69-4; **20**, 96965-70-7; **21**, 96965-71-8; **22**, 96965-72-9; *anti*-**23**, 96965-73-0; **24**, 96965-74-1; **25**, 96965-75-2; **26**, 96965-76-3; **27**, 96965-77-4; 1,4-dibromo-2,3-dihydroxynaphthalene, 52864-96-7; 1,6-dibromo-2,7-dihydroxynaphthalene, 96965-78-5; 3,6-dibromo-2,7-dihydroxynaphthalene, 96965-79-6; *N*-methyl-4,5,6,7-tetrafluoroisoindole, 38053-09-7; *N*-methylpyrrole, 96-54-8.

Supplementary Material Available: Tables II–IV listing thermal parameters for non-hydrogen atoms, hydrogen atom parameters, bond lengths, valency angles, and torsion angles, all with estimated standard deviations (4 pages). Ordering information is given on any current masthead page.

(25) Main, P.; Fiske, S. J.; Hall, S. E.; Lessinger, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 80, Universities of York, England, and Louvain, Belgium, 1980.

(26) All calculations were carried out on a VAX 11/780 computer. The least-squares refinement program was based on FMLS (Ganzel, P. L.; Sparks, R. A.; Trueblood, K. N.), UCLA, and modified by McPhail, A. T., Duke University. Figure 1 was drawn with ORTEP, crystallographic illustration programs, Johnson, C. K., Oak Ridge, ORNL-3794.

Metacyclophanes and Related Compounds. 14. Preparation of 8,16-Difluoro[2.2]metacyclophane[1]

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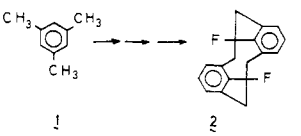
Although preparation of 8,16-difluoro-, 8,16-dichloro-, and 8,16-dibromo[2.2]metacyclophanes was attempted, only 8,16-difluoro[2.2]metacyclophane was obtained from fluorobenzene in seven steps by using a *tert*-butyl group as a positional protective function.

Although some [2.2]metacyclophanes ([2.2]MCP) having functional groups such as alkyl,[2-5] halomethyl,[5] alkoxy,[6] hydroxy,[7] and formyl[8] at their 8,16-positions have been prepared, there are few reports concerning the preparation

Scheme I



1 2

(1) Part 13: Tashiro, M.; Yamato, T. *Org. Prep. Proced. Int.*, in press.
(2) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695.
(3) Boekelheide, V.; Miyasaka, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 1709.
(4) Boekelheide, V.; Hylton, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 3696.
(5) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543.
(6) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 4556.

0022-3263/85/1950-2939$01.50/0