bonded to the two iridium atoms. Isotropic thermal parameters were used for all other atoms. All hydrogen atoms were fixed at calculated positions by using a riding model in which the C-H vector is fixed at 0.96 Å and the isotropic thermal parameter for each hydrogen atom is given a value 20% greater than the carbon atom to which it is bonded. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[32] The final stages of refinement included an absorption correction.[33] The final R value of 0.050 was computed with a data to parameter ratio of 19.4. This yielded goodness-of-fit of 0.684 and a mean shift/esd of 0.015 for overall scale on the last cycle of refinement. A value of 3.0 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was located 0.78 Å from a chlorine atom in a disordered dichloromethane molecule. Due to the well-behaved thermal parameters of this molecule, no attempt was made to model the disorder. The weighting scheme used was $w = [\sigma^2(F_o)]^{-1}$. Corrections for anomalous dispersion were applied to all atoms.

$[Ir_2AuCl_4(CO)_2(\mu\text{-dpma})_2]Cl$ (5a). The positions of the two iridium atoms and the gold atom were generated from FMAP8. Other atoms positions were located from successive difference Fourier maps. Anisotropic thermal parameters were assigned to the elements iridium, gold, arsenic, phosphorus, and chloride while isotropic thermal parameters were used for the remaining atoms. The final stages of refinement included an absorption correction and the treatment of all hydrogen atoms as described for **4a**. The final R value of 0.067 was computed with a data to parameter ratio of 13.2. This yielded a goodness-of-fit of 1.287 and a mean shift/esd of 0.013 for overall scale on the last cycle of refinement. A value of 1.70 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was located 0.80 Å from Cl(5). The weighting scheme used was $w = [\sigma_2(F_o)]^{-1}$.

(32) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

(33) The method obtains an empirical absorption tensor form an expression relating F_o and F_c: Hope, H.; Moezzi, B. *Program XABS*; Department of Chemistry, University of California: Davis, CA.

Acknowledgment. We thank the National Science Foundation (Grant CHE8519557) for support, Bowdoin College for faculty study leave for J.K.N., Dow Corning Corp. for a fellowship for P.E.R., the Earl C. Anthony Fund for a fellowship to D.E.O., and Johnson Matthey Inc. for a loan of iridium.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for **4a** and **5b** (13 pages); listings of observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

Chemistry of Dibenzo[2.2]paracyclophane and Its Related Compounds. Evidence for the Existence of a Cyclophyne Intermediate[1]

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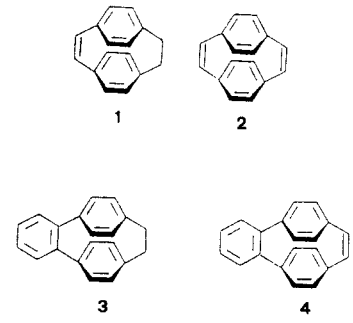
Contribution from the Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong. *Received May 29, 1987*

Abstract: The syntheses of dibenzo[2.2]paracyclophane (**5**), benzonaphtho[2.2]paracyclophane (**6**), benzofurano[*c*][2.2]-paracyclophane (**7**) and 1,2,3-selenadiazolobenzo[2.2]paracyclophane (**28**) are presented. The existence of the strained cyclophyne **10** as an intermediate was established by a trapping method. Benzofurano[*c*][2.2]paracyclophane (**7**) serves as a diene in the Diels-Alder reaction as illustrated by the preparation of the ester **34**. The preparation of a macroparacyclophane diacetylene **36** is described. The electronic spectra of some of the cyclophanes are discussed.

Cyclophanes belong to one of the remarkable compound classes that has attracted extensive studies.[3] In the domain of organic synthesis, preparation of the alkenes **1** and **2** (Chart I) pioneered the study of classically conjugated but orbitally unconjugated compounds.[4] The C-C double bonds in **1** and **2** are orthogonal to the central rings, because rotation of the benzene moiety is restricted by its large steric demand.

The introduction of aromatic rings orthogonal to the central benzenes in **1** and **2** has also attracted considerable attention. The rigid molecular frameworks of **3** and **4** provide fixed geometry for orthogonal benzenes.[5] We report here the synthesis of dibenzo[2.2]paracyclophane (**5**), benzonaphtho[2.2]paracyclophane (**6**), benzofuran[*c*][2.2]paracyclophane (**7**) as well as 1-methyldibenzo[2.2]paracyclophane (**8**) (Chart II). The *gem*-dibromide **9** will serve as the starting material. The detection of the existence of intermediate **10** in our synthesis is made possible by trapping

Chart I



(1) Arene Synthesis by Extrusion Reaction. 12. Part 11: Wong, H. N. C.; Man, Y.-M.; Mak, T. C. W. *Tetrahedron Lett.*, in press. Taken in part from: Chan, C. W. M. Phil. Thesis, The Chinese University of Hong Kong, 1987. A preliminary account of this work has appeared. See: Chan, C. W.; Wong, H. N. C. *J. Am. Chem. Soc.* **1985**, *107*, 4790-4791.

(2) Also known as Nai Zheng Huang.

(3) For reviews, see: Vögtle, F.; Neumann, P. *Top. Curr. Chem.* **1971**, *48*, 67-129. Vögtle, F.; Hohner, G. *Top. Curr. Chem.* **1978**, *74*, 1-29. Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 87-143. Vögtle, F.; Rossa, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 515-529. Kleinschroth, J.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 469-480. Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes*; Academic: New York, 1983; Vols. I, II.

(4) Dewhirst, K. C.; Cram, D. J. *J. Am. Chem. Soc.* **1958**, *80*, 3115-3125; *J. Am. Chem. Soc.* **1959**, *81*, 5963-5971.

(5) Jacobson, N.; Boekelheide, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 46-47.

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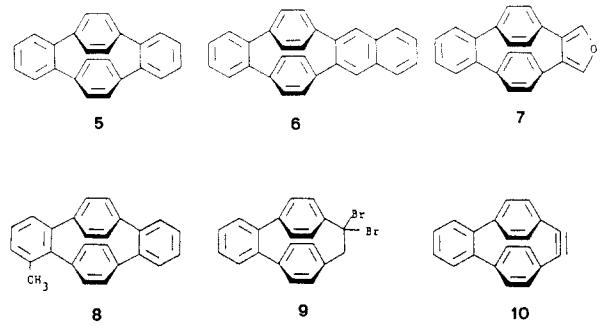
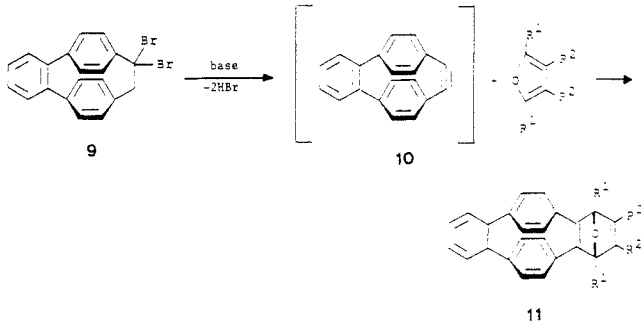
Chart II



Scheme I



of **10** with tetraphenylcyclopentadienone (tetracyclone).

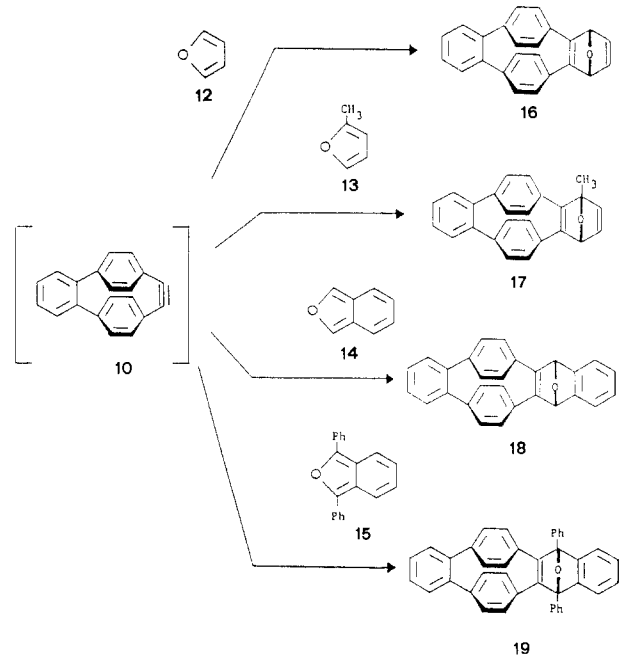
Results and Discussion

Syntheses of Dibenzo[2.2]paracyclophane (5), Benzonaphtho-[2.2]paracyclophane (6), and 1-Methyldibenzo[2.2]paracyclophane (8). It is well-known that the reactivity of strained cycloalkynes is extremely high so that they can take part in cycloaddition reactions.[6] Hence, we expected that the strained cyclophyne **10** might react with furans to furnish the desired endoxides **11**[7] (Scheme I). It appears that the desired precursor of **10** should be the *gem*-dibromide **9**, which was prepared from **3**.[5] Cyclophane **3**, in turn, was prepared from *o*-terphenyl through a number of steps.[8,9]

The functionalization of paracyclophanes on its carbon bridges has been explored by Cram and his co-workers.[4,10] Similar treatment of **3**[5] with an excess of *N*-bromosuccinimide (NBS) in refluxing carbon tetrachloride led to **9** in 29% yield after column chromatography; mp 222–223 °C. It has been pointed out[4] that, in the process of radical-mediated benzylic bromination, much more compression strain was relieved when the benzylic radical was generated by abstracting hydrogen from the carbon bearing the halogen atom than from the carbon not bearing halogen. Thus, the radical-mediated bromination of **3** gave predominantly *gem*-dibromide **9**.

Dehydrobromination of **9** with potassium *tert*-butoxide presumably produced the intermediate **10**, which was expected to be unstable. However, it could be trapped with dienes such as furan (**12**), 2-methylfuran (**13**), isobenzofuran (**14**),[11] and 2,5-diphenylisobenzofuran (**15**) (Scheme II). Use of an excess of these dienes should be helpful in improving the yields of the corresponding endoxides **16–19**. The yields of **16** and **17** are

Scheme II



Scheme III

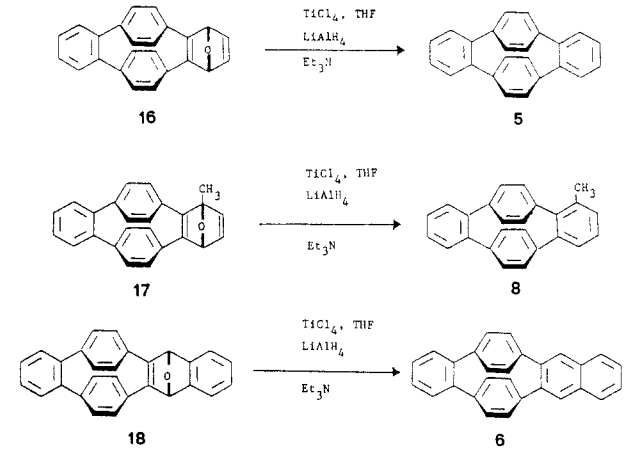
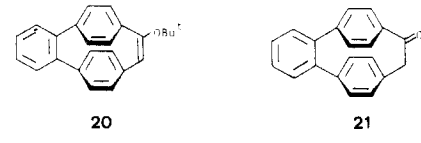


Chart III



generally low, being 11–47% and 11%, respectively. Since furan has an aromatic sextet, it is not as reactive as a normal diene. In comparison with furan (**12**), isobenzofuran (**14**) and its derivative **15** are much more reactive toward **10**, because aromaticity could be restored after the formation of endoxides **18** and **19**. Hence, the yields of **18** and **19** are higher, being 74% and 40%, respectively.

Apart from diene, another competing agent might also react with the unstable cyclophyne **10**; i.e., it has been reported[7] that *tert*-butoxide adds to strained cycloalkynes to form a *tert*-butyl enol ether. Thus, **10** might furnish *tert*-butyl enol ether **20** and subsequently hydrolyze in acidic medium to give the corresponding ketone **21** (Chart III). In practice, varying amounts of **21** were isolated from the preparation of **16–19**, thus providing partial evidence of the existence of **10**. Ketone **21** also served as a starting material in our latter reaction.

The proton NMR spectra of endoxides **16–19** have been recorded. The absorptions of the ortho aryl protons are found to be consistent with the parent compound **3**, except that the magnetic equivalency of the eight para aryl protons is destroyed by the

(6) For reviews, see: Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Verlag Chemie: Weinheim, 1967. Krebs, A. In *Chemistry of Acetylene*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; pp 987–1062. Nakagawa, M. In *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; pp 635–712. Meier, H. *Synthesis* **1972**, 235–253. Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189–233.

(7) For examples, see: Wong, H. N. C.; Sondheimer, F. *J. Org. Chem.* **1980**, *45*, 2438–2440; *Tetrahedron* **1981**, *37*(S1), 99–109.

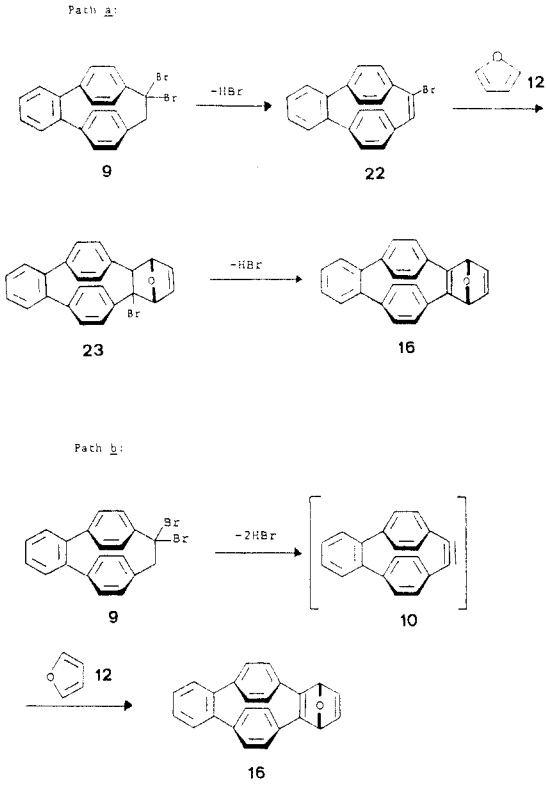
(8) Meyer, H.; Staab, H. A. *Justus Liebigs Ann. Chem.* **1969**, *724*, 30–33.

(9) Grütze, J.; Vögtle, F. *Chem. Ber.* **1977**, *110*, 1978–1993.

(10) Cram, D. J.; Helgeson, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 3516–3521.

(11) Naito, K.; Rickborn, B. *J. Org. Chem.* **1980**, *45*, 4061–4062.

Scheme IV



introduction of the endoxide ring. Although the para aryl protons are separated into two sets of A_2X_2 systems, their chemical shifts do not exceed δ 7.0 because they are shielded by the opposite ring. The coupling constants of these A_2X_2 systems are approximately 8 Hz. The vinyl protons in **16** and **17** are abnormally deshielded (δ 7.0), similar to other paracyclophane alkenes **2** and **4**. The bridgehead protons in **16–18** experience the deshielding diamagnetic current exerted by the adjacent rings, and the signals appear at approximately δ 6.0. The low solubility of **19** in $CDCl_3$ prevented detailed analysis of its NMR spectrum.

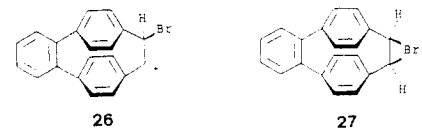
Deoxygenation[12] of endoxides **16–18** with low-valent titanium[13] gave the corresponding arenes **5**, **8**, and **6** respectively (Scheme III). The yields were 70–90%. However, treatment of **19** with either low-valent titanium or zinc–copper couple[14] did not give the desired product. Compounds **5** and **6** are highly symmetrical and rigid molecules. X-ray structural determination of **5** has confirmed its structure.[15] The molecule **5** was found to be of D_{2h} symmetry with only slight but perceptible deviations.[15]

The proton NMR data of **5** and **6** show no significant change in the chemical shifts and spin–spin coupling pattern, as compared with those of **3**. The presence of the ABC system in the ortho aryl protons of **8** complicates its analysis. The para aryl protons are found to be also shielded by the opposite ring.

Due to the high symmetry of the molecular structure, ESR spectroscopic studies of **5**[16] and work on PE spectroscopic studies of **5** have been carried out.[17]

Proof of the Existence of the Intermediacy of the Strained Cyclophyne 10. We are interested in the nature of the reactive species in the Diels–Alder cycloaddition reactions leading to the endoxides **16–19**. Two pathways can be formulated for the endoxide formation: (a) prior elimination of one HBr from **9** and cycloaddition of the resulting vinyl bromide **22** with furan produces **23**, which subsequently undergoes dehydrobromination to give endoxide **16**; (b) generation of the strained cyclophyne **10** by direct removal of two HBr from **9**, followed by cycloaddition with furan to give **16** (Scheme IV).

Chart IV



To decide between these hypotheses, two independent experiments have been carried out. The first experiment involves the preparation of the vinyl bromide **22** and the examination of its reactivity toward furan. The second experiment involves trapping of the transient intermediate **10** in the process of the cycloaddition reaction.

To accomplish the first goal, cyclophane **3** was converted to the bromide **24**,[5] which underwent dehydrobromination to afford the cyclophane **4**.[5] Addition of bromine to **4** followed by dehydrobromination then yielded the desired vinyl bromide **22**. In the process of bromination of **4**, two stereoisomers were isolated in 26% and 23% yields after column chromatography. They were assigned cis- and trans-vicinal dibromides **25** by proton NMR spectroscopy (Scheme V).

The cis isomer **25** has higher symmetry than the trans isomer **25**, therefore, the spin–spin coupling pattern for the para aryl protons should be simpler for the former. In addition, the R_f value of *cis*-**25** on TLC is smaller than that of *trans*-**25** because the cis configuration of the vicinal dibromide could result in higher polarity. Further confirmation of the stereochemistry of **25** was made through the examination of their relative chemical reactivities toward dehydrobromination with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in refluxing benzene.[7] Due to the fact that elimination of HBr should be trans and that the rigid molecular frameworks restrict C–C bond rotation, the cis isomer should react faster than the trans isomer. In fact, in order to complete the elimination of HBr, the *trans*-**25** required 63 h with a 20-fold excess of DBN, whereas the *cis*-**25** required only 24 h with only a 10-fold excess of DBN.

The fact that yields of *cis*-**25** and *trans*-**25** are nearly equal indicates the presence of the classic carbocationic intermediate **26** rather than the nonclassic bromonium ion intermediate **27** in the process of bromination.[18] The absence of **27** might be attributed to the strain of this intermediate (Chart IV).

Vinyl bromide **22** was prepared separately from *cis*- and *trans*-**25**, respectively, in 60–80% yield; mp 210–213 °C. There is no change in the NMR signals of the ortho aryl protons of **22** when compared with **3**, but the vinyl proton is further deshielded by the adjacent bromine atom to δ 7.55. The para aryl protons appear as a singlet at δ 6.69 and a multiplet at δ 6.62 (A_2X_2, J_{AX} = 8.5 Hz).

When a solution of the vinyl bromide **22** and furan (**12**) was stirred at room temperature for 24 h, no cycloaddition product **23** formed. Therefore, it is safe to propose that **10** might be an intermediate in the process of endoxide formation (viz., the endoxide formation follows path b).

In order to prove the existence of the strained cyclophyne **10**, it was desirable to generate the cyclophyne **10** directly. As pointed out earlier, cyclophyne **10** generated from dehydrobromination of **9** could suffer from the interference of *tert*-butoxide, therefore it was desirable to generate **10** through other conditions. The 1,2,3-selenadiazole compound **28** appeared to be a suitable candidate, because it can be prepared conveniently from ketone **21**.[10] It is of interest to note that the first evidence for the existence

(12) Xing, Y. D.; Huang, N. Z. *J. Org. Chem.* **1982**, *47*, 140–142. For a review, see: Wong, H. N. C.; Ng, T.-K.; Wong, T.-Y. *Heterocycles* **1983**, *20*, 1815–1840. Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817–826.

(13) Wong, H. N. C.; Xing, Y. D.; Zhou, Y. F.; Gong, Q. Q.; Zhang, C. *Synthesis* **1984**, *787*–790.

(14) Xing, Y. D.; Gong, Q. Q.; Huang, N. Z. *Acta Chim. Sin.* **1983**, *41*, 934–937.

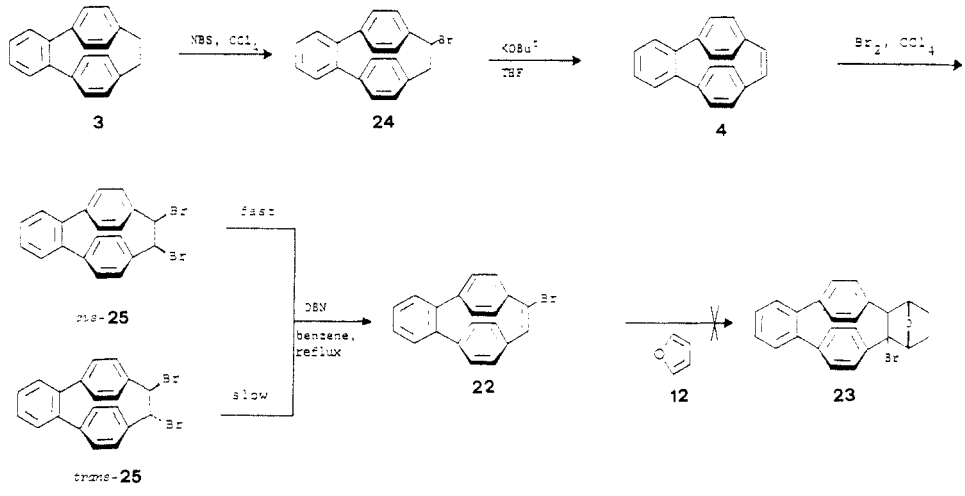
(15) Wong, H. N. C.; Chan, C. W.; Mak, T. C. W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 703–705.

(16) Gerson, F.; Martin, W. B., Jr.; Wong, H. N. C.; Chan, C. W. *Helv. Chim. Acta* **1987**, *70*, 79–90.

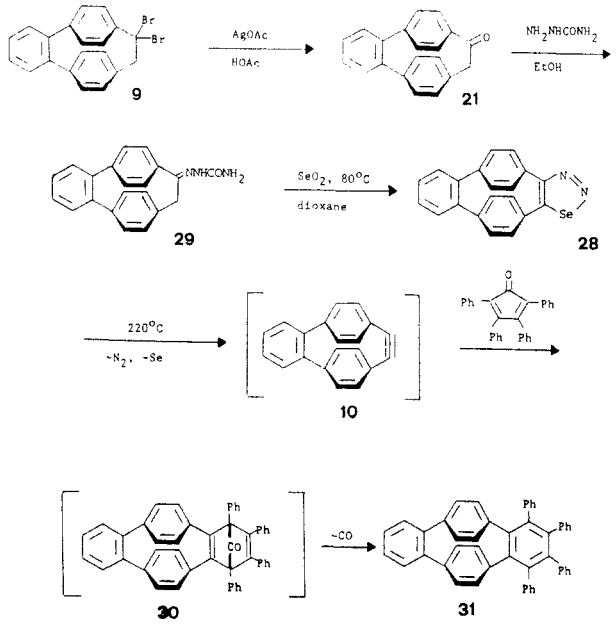
(17) Yang, Z.-Z.; Kovač, B.; Heilbronner, E.; Lecoultre, J.; Chan, C. W.; Wong, H. N. C.; Hopf, H.; Vögtle, F. *Helv. Chim. Acta* **1987**, *70*, 299–307.

(18) For a review of the stereochemistry of electrophilic additions to double and triple bonds, see: Fahey, R. C. *Top. Stereochem.* **1968**, *3*, 237–342.

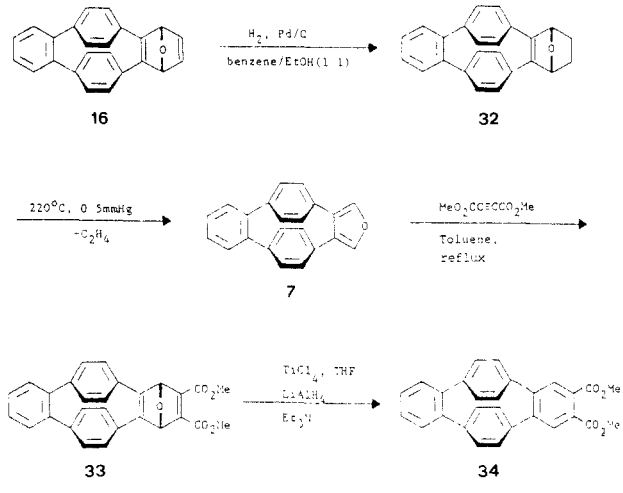
Scheme V



Scheme VI



Scheme VII



of a cyclophyne intermediate was provided by Hopf.[19]

Acetolysis of the *gem*-dibromide **9** aided by silver acetate produced the ketone **21** in 40% yield; mp 217–219 °C (Scheme VI). Condensation of **21** with semicarbazide[20] afforded the corresponding semicarbazone **29** in 57% yield; mp 263–264 °C. Compound **29** is insoluble in most organic solvents. Without purification, **29** was oxidized by selenium dioxide[20] in dioxane to give **28** in 50% yield, mp 194 °C dec. The low solubility of **28** in dimethyl sulfoxide permits the recording of its proton NMR spectrum. A multiplet of eight para aryl protons appears at δ 6.71, and a A_2B_2 multiplet of four ortho aryl protons appears at δ 7.54. The mass spectrum of **28** reveals only the fragment after elimination of nitrogen, indicating that **28** was thermally labile. Generation of **10** was thus carried out at high temperatures.

Pyrolysis of **28** at 220 °C in a solution of tetraphenylcyclopentadienone (tetracyclone) in DMSO generated **10**, which underwent cycloaddition with tetracyclone to give **30** as a reactive intermediate. Extrusion of carbon monoxide from **30** at high temperature then furnished **31** in 8% yield after thick-layer chromatography on silica gel (benzene). Compound **31** is characterized by high-resolution mass spectrometry and proton NMR spectrometry. In its NMR spectrum, the ortho and para aryl protons appear at δ 7.49 (A_2B_2, J = 5.5 Hz, J' = 3.4 Hz) and at δ 6.68 (A_2X_2, J_{AX} = 8.1 Hz), which is not much different from other related compounds. The protons on phenyl groups are recognized at δ 7.01 as a broad multiplet.

Even though **31** was isolated in low yield, the existence of **10** as a reactive dienophile seems evident.

Synthesis of Benzofurano[c][2.2]paracyclophane (7) and Its Diels–Alder Reaction with Dimethyl Acetylenedicarboxylate. During the course of the synthesis of dibenzo[2.2]paracyclophane (**5**), alternative routes have been explored in order to obtain derivatives of **5** that bear substituents at carbons 2 and 3. Direct electrophilic aromatic substitution reaction of **5** might produce a mixture of products, because the two types of benzene nuclei in **5** have different reactivities.

A search of the literature reveals that [2.2](2,5)furanophane reacts with dimethyl acetylenedicarboxylate (DMAD) to give an endoxide intermediate.[21]

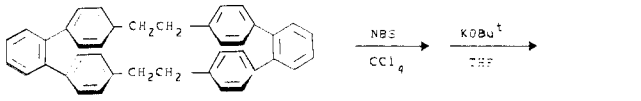
With this idea in mind, we therefore designed a furan-fused benzo[2.2]paracyclophane **7**, so that endoxides **11** (R^1 = H, R^2 = electron-withdrawing group) could be prepared by facile cycloaddition of **7** with dienophiles containing electron-withdrawing groups, such as dimethyl acetylenedicarboxylate (DMAD). Deoxygenation of this Diels–Alder adduct therefore yields the desired cyclophane containing electron-withdrawing groups at carbons 2 and 3.

(19) Psiorz, M.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 623–624. Hopf, H.; Psiorz, M. *Chem. Ber.* **1986**, *119*, 1836–1844. See also: Stöbbe, M.; Reiser, O.; Näder, R.; de Meijere, A. *Chem. Ber.* **1987**, *120*, 1667–1674.

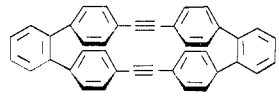
(20) Meier, H.; Voigt, E. *Tetrahedron* **1972**, *28*, 187–198. Gugel, H.; Meier, H. *Chem. Ber.* **1980**, *113*, 1432–1443. Lorch, M.; Meier, H. *Chem. Ber.* **1981**, *114*, 2382–2391. Echter, T.; Meier, H. *Chem. Ber.* **1985**, *118*, 182–197. Hanold, N.; Meier, H. *Chem. Ber.* **1985**, *118*, 198–209.

(21) Cram, D. J.; Knox, G. R. *J. Am. Chem. Soc.* **1961**, *83*, 2204–2205. Cram, D. J.; Montgomery, C. S.; Knox, G. R. *J. Am Chem. Soc.* **1966**, *88*, 515–525.

Scheme VIII



35



36

The synthesis of **7** was realized by starting from the endoxide **16**. Thus, regioselective hydrogenation of the less substituted double bond of **16** afforded **32** in 97% yield (Scheme VII). No melting point could be recorded for compound **32**, because ethylene was extruded from its endoxide ring when **32** was heated to 213 °C, leaving the furano compound **7** as the retro-Diels–Alder product.[13] The yield of **7** was generally high when extrusion of ethylene from **32** was carried out with a small quantity in the solid state under vacuum (0.5 mmHg).

The desired endoxide **33** was then prepared by refluxing **7** with excess DMAD in toluene.[22] The yield was 83%. Subsequent deoxygenation of **33** with the aforementioned low-valent titanium[12,13] then furnished the substitution product **34** in 70% yield; mp 273 °C dec.

The spin–spin coupling pattern of the para aryl protons in **32** is much simpler than that in **16**. However, the corresponding patterns for the two endoxides **16** and **33** are very similar, and the chemical shifts are nearly the same. After all, the basic features of these NMR data are consistent with those of the other paracyclophanes mentioned earlier.

Synthesis of 9,10,23,24-Tetradehydro-5,8:11,14:19,22:25,28-tetraethenodibenzocyclotetracosene (36), the Macroparacyclophane Diacetylene. It is known that preparation of paracyclophanes by a coupling reaction under high dilution would inevitably produce considerable amounts of oligomers and polymers.[23] In our preparation of benzo[2.2]paracyclophane (**3**) (vide ante), a dimer **35** could be isolated in 7% yield after column chromatography; mp 245–246 °C.

A ball-and-stick model of **35** reflects the molecular flexibility of the macrocycle, i.e., the ethane bridges could freely rotate with respect to each other with the para fused benzenes remaining static. Therefore, the proton NMR signal of these benzylic protons appears as a singlet, because the environment of these protons is averaged by this dynamic process.

It was interesting to investigate whether or not reduction of the degree of flexibility of **35** might influence the transannular effect in such a macroparacyclophane. Triple bonds were chosen and introduced to reduce the degree of freedom in **35**. Upon successive bromination with NBS and dehydrobromination with potassium *tert*-butoxide, **35** was converted to the desired diacetylene **36** in 12% overall yield after chromatography. The unusually high melting point (>300 °C) fits the highly symmetrical skeleton of the diacetylene **36** with the para benzene nuclei aligned by the appended triple bonds (Scheme VIII).

Comparison of the NMR data of ortho aryl protons in **35** and **36** with those of smaller ring size paracyclophanes (**3**, etc.) shows that there is a slight but perceptible upfield shift in the macro ring compounds. Presumably, enlargement of the paracyclophane ring in **35** and **36** might lead to a larger cavity enclosed by the para aryl rings and, hence, might shorten the distance between the ortho aryl protons and the shielding region of the para aryl rings. The downfield shift of the para aryl protons in **35** and **36** suggests less shielding from the opposite ring and hence an increase in interring distances, in agreement with the above argument. The larger downfield shift of the para aryl protons in **36** might also be attributed to the adjacent triple bond.

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Table I. UV Absorptions of **3–5**, **5** + TCNE, **6**, **7**, and **36**

	λ_{max} nm (log ϵ)		
compd	I	II	III
3	220 (4.7)	270 (3.2)	311 (2.1)
4	217 (4.8)	260 (3.9)	339 (2.9)
5	222 (4.7)	266 (3.6)	295 (2.4)
6	229 (4.5)	267 (3.7)	307 (2.7)
7	219 (4.6)	267 (3.3)	
36	291 (3.7)	296 (3.7)	305 (3.6)
5 + TCNE	402 (4.4)	420 (4.4)	474 (3.6)

Brief Discussion of the Ultraviolet Spectroscopic Study on Dibenzo[2.2]paracyclophane (5) and Related Compounds. The UV spectra of **3–5**, **5** + TCNE, **6**, **7**, and **36** were recorded, and part of the data are tabulated in Table I: column I indicates the relative constant degree of π–π transannular interaction in the series of benzo annulated [2.2]paracyclophanes; column II reflects the same amount of bending of para benzene nuclei; and column III shows that there is no conjugation between the ortho benzene and para benzene nuclei in the series of benzo-annulated [2.2]paracyclophanes. The UV spectrum of **36** shows absorptions in longer wavelength than the above paracyclophanes because of the highly conjugated para phenylacetylene system. The UV absorption of **5** in the presence of tetracyanoethylene (TCNE) shows charge-transfer bands in the 400–500 nm region with high intensity. This result indicates that the π-basicity of the para benzene nuclei was larger than that of the ortho benzene nuclei in the same molecule.[24]

Conclusion

The most important step in the synthesis of dibenzo[2.2]paracyclophane (**5**) is the trapping of the strained cyclophyne **10** with furan (**12**). However, the yield of the endoxide **16** was somewhat limited due to the side reaction between the cyclophyne **10** and *tert*-butoxide, which was used for the dehydrobromination of the dibromide **9**. Therefore, another synthetic route has been developed, in which the cyclophyne **10** was generated from the 1,2,3-selenadiazole compound **28** under neutral conditions and in the absence of a nucleophile such as *tert*-butoxide. Nevertheless, cyclophyne **10** generated by this thermal reaction could only be trapped by a high-boiling diene, i.e., tetraphenylcyclopentadienone (tetracyclone), and this reaction is hence not applicable to the preparation of the cyclophane **5**.

It is envisaged that the two sets of benzene nuclei of dibenzo[2.2]paracyclophane (**5**) should have different reactivities. In order to prove this assumption, it would be of interest to prepare the tricarbonylchromium complex of dibenzo[2.2]paracyclophane and to examine its reactivity toward various electrophiles[25] and nucleophiles.[26]

Experimental Section

Solvents used were purified by standard procedures. All evaporation of organic solvents was carried out by a rotary evaporator in conjunction with a water aspirator.

Proton NMR spectra were recorded on a Bruker Cryospec WM 250 (250-MHz) spectrometer or a JEOL PMX 60 SI (60-MHz) spectrometer. Deuteriated chloroform was used as solvent unless stated otherwise, and the chemical shift (δ) was measured with tetramethylsilane (TMS) serving as an internal standard. Mass spectra were recorded on a VG Micromass 7070F spectrometer. UV spectra were recorded on a 323 Hitachi recording spectrophotometer in ethanol. Elemental analyses were carried out by Drs. C. H. L. Kennard and G. Smith at Queensland Institute of Technology, Queensland, Australia.

Merck silica gel (60 F_{254}) precoated on aluminum sheets was used for TLC studies, and Merck silica gel (70–230 mesh) was used for column

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chromatography. R_f values of all compounds on TLC were used for reference only. Melting points were measured on a hot-stage microscope and were uncorrected.

4,4″-Dibromo-*o*-terphenyl.[8] Iron powder (ca. 0.1 g, activated in an oven) was mixed with *o*-terphenyl (2.0 g, 8.7 mmol) in chloroform (8 mL). A chloroform solution (3 mL) of bromine (0.94 mL, 18.5 mmol) was added to the above mixture over 1.2 min. The resulting mixture was stirred for 1.2 h and was monitored by TLC (silica gel, hexanes, R_f 0.55). Chloroform (25 mL) was added, and the mixture was washed with 15% potassium hydroxide solution (100 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated. The white solid obtained was recrystallized twice from glacial acetic acid and once from petroleum ether (90–100 °C) to yield crystalline product 4,4″-dibromo-*o*-terphenyl: 1.32 g (39%); mp 164 °C (lit.[8] mp 170 °C); $C_{18}H_{12}Br_2$; MS, *m/e* 388 (M^+); ^1H NMR (60 MHz) δ 7.0–7.1 (m, 4 H, o-Ar H), 7.3–7.5 (m, 8 H, p-Ar H).

4,4″-Bis(hydroxymethyl)-*o*-terphenyl.[9] 4,4″-Dibromo-*o*-terphenyl (2.8 g, 7.2 mmol) in anhydrous THF (40 mL) was added dropwise to a refluxing mixture of magnesium turnings (activated in an oven) (0.35 g, 14.4 mmol) in anhydrous THF (10 mL). The completeness of the formation of the Grignard reagent was monitored by TLC. Then formaldehyde gas [prepared by pyrolyzing paraformaldehyde (1.1 g, 36.7 mmol) at 200 °C] was passed into the aforementioned vigorously stirred Grignard reagent by nitrogen flow for 30 min. Water (3 mL) was then added to dilute the solution, followed by 1 M sulfuric acid (80 mL). The aqueous layer was extracted with chloroform (3 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate and evaporated. The desired product 4,4″-bis(hydroxymethyl)-*o*-terphenyl was separated (0.3 g, 14%) after column chromatography on silica gel (hexanes/ethyl acetate = 1/1, R_f 0.33): mp 117–120 °C (from acetone) (lit.[9] mp 119–120 °C); $C_{20}H_{18}O_2$; MS, *m/e* 290 (M^+); ^1H NMR (60 MHz) δ 1.9 (s, 2 H, OH), 4.6 (s, 4 H, CH_2), 7.2–7.4 (m, 8 H, p-Ar H), 7.5 (m, 4 H, o-Ar H).

4,4″-Bis(bromomethyl)-*o*-terphenyl.[9] Finely powdered 4,4″-bis(hydroxymethyl)-*o*-terphenyl (0.29 g, 1.02 mmol) was added to a vigorously stirred hydrobromic acid solution (48%, 2.4 mL) at 100 °C. After the mixture stood for about 5 min, a colorless emulsion formed that solidified upon cooling. The solid was dissolved in chloroform (10 mL) and neutralized with saturated sodium bicarbonate solution (10 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated. 4,4″-bis(bromomethy)-*o*-terphenyl was obtained (0.29 g, 68%) after recrystallization from acetone: mp 113–115 °C (from acetone) (lit.[9] mp 115–117 °C); $C_{20}H_{16}Br_2$; MS, *m/e* 414 (M^+); ^1H NMR (60 MHz) δ 4.3 (s, 4 H, CH_2Br), 7.1–7.3 (A_2X_2, 8 H, p-Ar H, J_{AX} = 8.0 Hz), 7.4 (s, 4 H, o-Ar H).

Benzo[2.2]paracyclophane (3).[5] Phenyllithium was prepared by adding bromobenzene (1.44 g, 9.2 mmol) in anhydrous ether (14 mL) dropwise to a stirred suspension of finely divided lithium (0.13 g, 18.4 mmol) in anhydrous ether (14 mL).[27] 4,4″-Bis(bromomethyl)-*o*-terphenyl (2.88 g, 6.91 mmol) in anhydrous ether (30 mL) was added to the phenyllithium reagent dropwise. The resulting mixture was stirred for 24 h and was then quenched with 1 M sulfuric acid (50 mL). The aqueous layer was extracted with ether (3 × 20 mL), and the combined organic layers were dried over anhydrous sodium sulfate and evaporated. Column chromatography on silica gel (hexanes/benzene = 9/1, R_f 0.33) followed by recrystallization from hexanes afforded the desired product **3** as long colorless needles: 0.44 g (25%); mp 215–216 °C (lit.[5] mp 217–219 °C); $C_{20}H_{16}$; MS, *m/e* 256 (M^+); UV, λ_{max} nm (log ϵ) 220 (4.7), 270 (3.2), 311 (2.1); ^1H NMR (250 MHz) δ 3.10 (s, 4 H, CH_2CH_2), 6.54 (s, 8 H, p-Ar H), 7.40–7.62 centered at 7.51 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz).

9,9-Dibromobenzo[2.2]paracyclophane (9). *N*-Bromosuccinimide (0.76 g, 4.27 mmol) and cyclophane **3** (0.36 g, 1.41 mmol) in carbon tetrachloride (35 mL) were refluxed for 48 h. The resulting succinimide was filtered when cooled, and the filtrate was evaporated. The desired product **9** was isolated (0.17 g, 29%) after silica gel column chromatography (hexanes/benzene = 9/1, R_f 0.50): mp 222–223 °C (from hexanes); $C_{20}H_{14}Br_2$; MS, *m/e* 412 (M^+); accurate mass measd 411.9462, calcd 411.9493; ^1H NMR (250 MHz) δ 4.69 (s, 2 H, CH_2) 6.57–6.60 and 6.72–6.76 centered at 6.67 (m, A_2X_2, 4 H, p-Ar H, J_{AX} = 8.2 Hz), 6.62–6.67 and 7.29–7.33 centered at 6.98 (A_2X_2, 4 H, p-Ar H, J_{AX} = 6.8 Hz), 7.44–7.64 centered at 7.54 (A_2B_2, 4 H, o-Ar H). Anal. Found: C, 56.34; H, 3.26. Calcd: C, 57.98; H, 3.41 (sample contaminated with small amount of tribromide).

1,4-Dihydro-1,4-epoxydibenzo[2.2]paracyclophane (16). To a mixture of dibromide **9** (0.73 g, 1.77 mmol) and freshly distilled furan (**12**; 50 mL, 0.69 mol) was added dropwise a suspension of potassium *tert*-butoxide (5 g, 45 mmol) in anhydrous THF (50 mL) over 1 h. After being stirred for an additional 1 h, the mixture was quenched with 1 M sulfuric acid (100 mL). The aqueous layer was extracted with chloroform (3 × 30 mL), and the combined organic layers were dried over anhydrous sodium sulfate and evaporated. Column chromatography on silica gel (benzene) of the residue afforded the desired product **16** (R_f 0.34; 0.213 g, 47%) and ketone **21** (R_f 0.60; 0.1 g, 21%).

Endoxide **16**: mp 203–205 °C; $C_{24}H_{16}O$; MS, *m/e* 320 (M^+); accurate mass measd 320.1199, calcd 320.1201; ^1H NMR (250 MHz) δ 5.82 (s, 2 H, CHO), 6.11–6.58 centered at 6.35 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.1 Hz, $J_{AX'}$ = 1.5 Hz), 6.60–6.69 centered at 6.65 (A_2X_2, 4 H, p-Ar H, J_{AX} = 7.9 Hz, $J_{AX'}$ = 1.5 Hz), 7.49 (s, 2 H, CH=CH), 7.40–7.59 centered at 7.50 (A_2B_2, 4 H, o-ArH, J = 5.5 Hz, J' = 3.4 Hz).

Ketone **21**: mp 217–219 °C (from acetone); $C_{20}H_{14}O$; MS, *m/e* 270 (M^+); accurate mass measd 270.1073, calcd 270.1045; ^1H NMR (250 MHz) δ 3.88 (s, 2 H, CH_2CO), 6.63–6.75 centered at 6.69 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.0 Hz), 6.75 (s, 4 H, p-Ar H), 7.43–7.68 centered at 7.56 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.3 Hz). Anal. Found: C, 88.78; H, 5.20. Calcd: C, 88.86; H, 5.22.

Dibenzo[2.2]paracyclophane (5). Lithium aluminum hydride (0.37 g, 9.8 mmol) was added carefully to a suspension of titanium(IV) chloride (2.4 mL, 21.0 mmol) in anhydrous THF (100 mL) at 0 °C under nitrogen, followed by triethylamine (0.53 g, 5.3 mmol) in anhydrous THF (10 mL). The mixture was stirred and refluxed for 30 min and then allowed to cool to room temperature. To this reagent was added the endoxide **16** (51.4 mg, 0.16 mmol) in anhydrous THF (15 mL), and the mixture was stirred for 1 h. Saturated potassium carbonate solution (200 mL) was added. The aqueous layer was extracted with chloroform (3 × 100 mL), and the combined organic layers were dried over anhydrous sodium sulfate and evaporated. Column chromatography on silica gel (benzene, R_f 0.95) of the residue afforded the cyclophane **5**: 35 mg (72%); mp 275 °C dec (from acetone); $C_{24}H_{16}$; MS, *m/e* 204 (M^+); accurate mass measd 304.1221, calcd 304.1251; UV, λ_{max} nm (log ϵ) 222 (4.7), 266 (3.6), 295 (2.4); ^1H NMR (250 MHz) δ 6.68 (s, 8 H, p-Ar H), 7.44–7.69 centered at 7.57 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz). Anal. Found: C, 94.26; H, 5.25. Calcd: C, 94.70; H, 5.30.

9,14-Dihydro-9,14-epoxybenzonaphtho[2.2]paracyclophane (18). Isobenzofuran (**14**) was prepared by the following procedure:[11] diisopropylamine (1.5 g, 14.9 mmol) and *n*-butyllithium in *n*-hexane (8 mL, 6 M, 48 mmol) were mixed and stirred at 0 °C under nitrogen. To the lithium diisopropylamide reagent was added 1-methoxy-1,4-dihydroisobenzofuran[28] (0.24 g, 1.62 mmol), and the resulting mixture was stirred for 15 min. It was then quenched with saturated ammonium chloride solution (30 mL) and extracted with benzene (3 × 10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated to about 6 mL.

Dibromide **9** (72 mg, 0.18 mmol) was mixed with the aforementioned freshly prepared isobenzofuran (**14**), and then a suspension of potassium *tert*-butoxide (1.5 g, 13 mmol) in anhydrous THF (30 mL) was added slowly to the above mixture. The mixture was stirred for 1 h, and then 0.5 M sulfuric acid (40 mL) was added. The aqueous layer was extracted with chloroform (3 × 10 mL), and the combined organic layers were dried over anhydrous sodium sulfate and evaporated. Column chromatography on silica gel (benzene, R_f 0.77) gave the title compound **18**: 49 mg (74%); mp 247–249 °C; $C_{28}H_{18}O$; MS, *m/e* 370 (M^+); accurate mass measd 370.1337, calcd 370.1358; ^1H NMR (250 MHz) δ 6.03 (s, 2 H, CHO), 5.64–6.33 centered at 5.99 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.2 Hz), 6.59 (s, 4 H, p-Ar H), 7.05–7.08 and 7.41–7.44 centered at 7.24 (A_2B_2, 4 H, Nap H, J = 5.1 Hz, J' = 3.0 Hz), 7.31–7.35 and 7.45–7.49 centered at 7.40 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz).

Benzonaphtho[2.2]paracyclophane (6). The procedure for the preparation of **6** is similar to that for the preparation of **5**. Reagents: lithium aluminum hydride (0.37 g, 9.8 mmol), titanium(IV) chloride (2.4 mL, 21.0 mmol) in anhydrous THF (100 mL); triethylamine (0.53 g, 5.3 mmol) in anhydrous THF (10 mL); endoxide **18** (62 mg, 0.17 mmol) in anhydrous THF (10 mL). Reaction time: 5 h. Column chromatography on silica gel (benzene, R_f 0.95) afforded the cyclophane **6**: 45.7 mg (77%); mp 278 °C dec (from toluene); $C_{28}H_{18}$; MS, *m/e* 354 (M^+); accurate mass measd 354.1442, calcd 354.1409; UV, λ_{max} nm (log ϵ) 229 (4.5), 237 (4.6), 267 (3.7), 274 (3.6), 283 (3.5), 295 (3.2), 307 (2.7), 322 (2.4); ^1H NMR (250 MHz) δ 6.69–6.77 centered at 6.73 (A_2X_2, 8 H, p-Ar H, J_{AX} = 8.4 Hz), 7.46–7.49 and 7.67–7.71 centered at 7.58 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.3 Hz), 7.57–7.61 and 7.95–7.99 centered at 7.78 (A_2B_2, 4 H, Nap H, J = 6.2 Hz, J' = 3.3 Hz), 8.10 (s, 2 H, Nap H). Anal. Found: C, 94.80; H, 5.19. Calcd: C, 94.88; H, 5.12.

1-Methyl-1,4-dihydro-1,4-epoxydibenzo[2.2]paracyclophane (17). The procedure for the preparation of **17** is similar to that for the preparation

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of **16**. Reagents: potassium *tert*-butoxide (3.5 g, 31.2 mmol) in anhydrous THF (100 mL); dibromide **9** (700 mg, 1.7 mmol); freshly distilled 2-methylfuran (**13**; 45 mL, 0.49 mmol). Reaction time: 8 h. Column chromatography on silica gel (benzene) afforded **17** (R_f 0.34; 62.3 mg, 11%) and ketone **21** (R_f 0.60; 54.2 mg, 12%).

Endoxide **17**: mp 196–200 °C; $C_{25}H_{18}O$; MS, *m/e* 334 (M^+); accurate mass measd 334.1361, calcd 334.1358; ^1H NMR (250 MHz) δ 2.00 (s, 3 H, CH_3), 5.71 (d, 1 H, CHO, J = 1.9 Hz), 6.51–6.64 centered at 6.58 (m, 4 H, p-Ar H), 6.13–6.17 and 6.58–6.62 centered at 6.37 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.0 Hz, $J_{AX'}$ = 1.6 Hz), 7.45 (AB q, 2 H, CH=CH, J = 5.3, 1.8 Hz), 7.39–7.58 centered at 7.49 (A_2B_2, 4 H, o-Ar H, J = 5.4 Hz, J' = 3.4 Hz).

1-Methyldibenzo[2.2]paracyclophane (8). The procedure for the preparation of **8** is similar to that for the preparation of **5**. Reagents: lithium aluminum hydride (0.29 g, 4.9 mmol); titanium(IV) chloride (1.2 mL, 10.5 mmol) in anhydrous THF (50 mL); triethylamine (0.27 g, 2.7 mmol) in anhydrous THF (5 mL); endoxide **17** (60 mg, 0.18 mmol) in anhydrous THF (12 mL). Reaction time: 10 h. Column chromatography on silica gel (benzene, R_f 0.95) afforded **8**: 53.4 mg (93%); mp 280 °C dec (from heptane); $C_{25}H_{18}$; MS, *m/e* 318 (M^+); accurate mass measd 318.1410, calcd 318.1408; ^1H NMR (250 MHz) δ 2.49 (s, 3 H, CH_3), 6.60–6.75 centered at 6.68 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.3 Hz), 6.68 (s, 4 H, p-Ar H), 4.34–7.69 centered at 7.52 (m, 7 H, o-Ar H). Anal. Found: C, 94.30; H, 5.71. Calcd: C, 94.30; H, 5.70.

9,14-Diphenyl-9,14-dihydro-9,14-epoxybenzonaphtho[2.2]paracyclophane (19). The procedure for the preparation of **19** is similar to that for the preparation of **16**. Reagents: potassium *tert*-butoxide (1.0 g, 8.9 mmol) in anhydrous THF (15 mL); dibromide **9** (11 mg, 0.03 mmol) and 2,5-diphenylisobenzofuran (**15**; 95 mg, 0.35 mmol) in anhydrous THF (10 mL). Reaction time: 15 min. The excess 2,5-diphenylisobenzofuran was removed by column chromatography on silica gel (hexanes/benzene = 9/1, R_f 0.50). The desired product **19** was obtained (5.9 mg, 40%) on thick-layer chromatography (silica gel, hexanes/ethyl acetate = 4/1, R_f 0.45): mp 270 °C dec; $C_{40}H_{26}O$; MS, *m/e* 522 (M^+); accurate mass measd 522.2013, calcd 522.1984; ^1H NMR (250 MHz) δ 6.60–6.80 centered at 6.70 (m, 8 H, p-Ar H), 7.30–7.85 centered at 7.58 (m, 18 H, C_6H_5, Nap H, and the o-Ar H).

9-Bromobenzo[2.2]paracyclophane (24).[5] A mixture of cyclophane **3** (52 mg, 0.21 mmol), *N*-bromosuccinimide (38 mg, 0.21 mmol), and a trace amount of benzoyl peroxide in carbon tetrachloride (5 mL) was irradiated by a sunlamp (500 W) for 30 min with vigorous stirring. The resulting succinimide was filtered when it cooled to room temperature. The filtrate was evaporated. Preparative layer chromatography (silica gel, hexanes/benzene = 9/1, R_f 0.3) followed by recrystallization from hexanes yielded the monobromide **24** (14 mg, 21%): mp 194–196 °C (from hexanes) (lit.[5] mp 190–193 °C); $C_{20}H_{15}Br$; MS, *m/e* 334 (M^+), 336 (M^+ + 2); ^1H NMR (250 MHz) δ 3.33 (AB q, 1 H, CH_2, J = 6.9, 14.3 Hz), 4.07 (AB q, 1 H, CH_2, J = 9.0, 14.3 Hz), 5.23 (t, 1 H, CHBr, J = 6.9, 9.0 Hz), 6.30–6.80 centered at 6.55 (m, 8 H, p-Ar H), 7.41–7.64 centered at 7.53 (A_2B_2, 4 H, o-Ar H).

Benzo[2.2]paracyclophan-9-ene (4).[5] The monobromide **24** (19.0 mg, 0.06 mmol) in anhydrous THF (2 mL) was added to a vigorously stirred potassium *tert*-butoxide (413 mg, 3.7 mmol) suspension in anhydrous THF (15 mL) in 30 min. The reaction was then quenched with 2 M hydrochloric acid (20 mL), and the aqueous layer was extracted with ether (3 × 15 mL). The combined organic layers were dried over anhydrous magnesium sulfate and evaporated. The desired product **4** was isolated (9.0 mg, 67%) after preparative layer chromatography on silica gel (hexanes/benzene = 9/1, R_f 0.66): mp 225–228 °C (from hexanes) (lit.[5] mp 227–229 °C); $C_{20}H_{14}$; MS, *m/e* 254 (M^+); UV, λ_{max} nm (log ϵ) 217 (4.8), 260 (3.9), 339 (2.9); ^1H NMR (250 MHz) δ 6.53–6.55 centered at 6.54 (A_2X_2, 8 H, p-Ar H, J_{AX} = 8.2 Hz), 7.28 (s, 2 H, CH=CH), 7.41–7.63 centered at 7.52 (A_2B_2, 4 H, o-Ar H, J = 5.6 Hz, J' = 3.4 Hz).

***cis*- and *trans*-9,10-Dibromobenzo[2.2]paracyclophanes (25).** Bromine (93 mg, 0.58 mmol) in carbon tetrachloride (15 mL) was added dropwise to the cyclophene **4** (147 mg, 0.58 mmol) in carbon tetrachloride (10 mL). The reaction was monitored by TLC and was then quenched with 40% sodium hydroxide solution (4 mL). The aqueous layer was extracted with chloroform (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate and evaporated. *cis*-**25** (62.2 mg, 26%) and *trans*-**25** (52.9 mg, 23%) were isolated by column chromatography on silica gel (hexanes/benzene = 9/1, R_f 0.12 and R_f' 0.24, respectively).

cis-**25**: mp 268 °C dec (from acetone); $C_{20}H_{14}Br_2$; MS, *m/e* 412 (M^+), 414 (M^+ + 2), 416 (M^+ + 4); accurate mass measd 415.9506, calcd 415.9424; ^1H NMR (250 MHz) δ 5.74 (s, 2 H, CHBrCHBr), 6.58 (s, 4 H, p-Ar H), 6.63–7.34 centered at 6.99 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.3 Hz), 7.44–7.63 centered at 7.54 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz). Anal. Found: C, 57.30; H, 3.38. Calcd: C, 57.98; H, 3.41.

trans-**25**: mp 275 °C dec (from acetone); $C_{20}H_{14}Br_2$; MS, *m/e* 412 (M^+), 414 (M^+ + 2), 416 (M^+ + 4); accurate mass measd 415.9478, calcd 415.9424; ^1H NMR (250 MHz) δ 5.22 (s, 2 H, CHBrCHBr), 6.49–6.90 centered at 6.70 (m, two A_2X_2, 8 H, p-Ar H, J_{AX} = 8.3 Hz, J' = 1.7 Hz), 7.43–7.62 centered at 7.53 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz).

9-Bromobenzo[2.2]paracyclophan-9-ene (22). *trans*-**25** (38.3 mg, 0.05 mmol) and a 20-fold excess of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (0.23 g, 1.86 mmol) in benzene (20 mL) were refluxed for 63 h under nitrogen and then allowed to cool to room temperature. The product mixture was washed successively with 0.1 M sulfuric acid (4 × 20 mL) and water (2 × 20 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated. Column chromatography on silica gel (hexanes/benzene = 9/1, R_f 0.35) afforded the vinyl bromide **22** (23.4 mg, 78%). Similar treatment of *cis*-**25** (54.7 mg, 0.13 mmol) with a 10-fold excess of DBN (0.17 g, 1.33 mmol) in refluxing benzene (20 mL) for 24 h also gave the vinyl bromide **22** (28 mg, 63%) after the same workup procedure: mp 210–213 °C (from hexanes); $C_{20}H_{13}Br$; MS *m/e* 332 (M^+); accurate mass measd 332.0195, calcd 332.0201; ^1H NMR (250 MHz) δ 6.57–6.66 centered at 6.62 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.5 Hz), 6.69 (s, 4 H, p-Ar H), 7.55 (s, 1 H, CH=CBr), 7.42–7.63 centered at 7.53 (A_2B_2, 4 H, o-Ar H, J = 5.3 Hz, J' = 3.4 Hz). Anal. Found: C, 72.08; H, 3.92. Calcd: C, 72.08; H, 3.93.

Benzo[2.2]paracyclophan-9-one (21). Silver acetate (2 equiv, 5.0 mg, 0.03 mmol) in glacial acetic acid (1 mL) was mixed with the dibromide **9** (6.1 mg, 0.015 mmol), and the mixture was refluxed for 1 min. Water (0.5 mL) was added, and the yellow precipitate was filtered when cooled. The filtrate was evaporated under vacuum. Preparative layer chromatography on silica gel (benzene, R_f 0.6) gave the ketone **21**: 1.7 mg (40%); mp 217–219 °C (from acetone). The spectrometric data of the ketone **21** are identical with those of an authentic sample prepared previously.

9-Semicarbazonobenzo[2.2]paracyclophane (29). Semicarbazide hydrochloride (40 mg, 0.36 mmol) and anhydrous sodium acetate (30 mg, 0.37 mmol) were refluxed in anhydrous ethanol (5 mL) for 2 min. The precipitate was filtered and washed with anhydrous ethanol (3 × 1 mL). The filtrate containing semicarbazide was mixed with ketone **21** (97.5 mg, 0.36 mmol) in anhydrous ethanol (50 mL) and refluxed for 12 h. The product was filtered as a white precipitate upon cooling to room temperature and was washed with ethanol (3 × 10 mL). It was dried under vacuum to yield the product **29**: 67.5 mg (57%); mp 263–264 °C; $C_{21}H_{17}N_3O$; MS, *m/e* 327 (M^+); accurate mass measd 327.1361, calcd 327.1372. Anal. Found: C, 75.29; H, 5.13; N 12.95. Calcd: C, 77.04; H, 5.23; N, 12.84 (recrystallization has not been carried out due to low solubility of **29**).

1,2,3-Selenadiazolobenzo[2.2]paracyclophane (28). Semicarbazone **29** (20 mg, 0.06 mmol) and selenium dioxide (purified by sublimation) (1 g, 18 mmol) were heated in anhydrous dioxane (20 mL) at 80 °C (oil bath) for 2 h. The product mixture was quenched with water (80 mL) and extracted with chloroform (3 × 20 mL). The organic layer was washed with water (3 × 50 mL), dried over anhydrous sodium sulfate, and evaporated. Column chromatography on silica gel (benzene, R_f 0.63) afforded the selenadiazole **28**: 10.4 mg, (50%); mp 194 °C dec; $C_{20}H_{12}N_2Se$; MS, *m/e* 332 ($M^+ - N_2$); ^1H NMR (250 MHz, DMSO-d_6) δ 6.58–6.84 centered at 6.71 (m, 8 H, p-Ar H), 7.44–7.64 centered at 7.54 (A_2B_2, 4 H, o-Ar H).

1,2,3,4-Tetraphenyldibenzo[2.2]paracyclophane (31). The selenadiazole **28** (4 mg, 0.01 mmol) and tetraphenylcyclopentadienone (tetracyclone; 12 mg, 0.03 mmol) were refluxed in dried dimethyl sulfoxide (1 mL) at 230 °C (oil bath) for 10 min. When the mixture was cooled to room temperature, chloroform (10 mL) was added and the organic layer was washed with water (3 × 5 mL), dried over anhydrous magnesium sulfate, and evaporated. Preparative layer chromatography on silica gel (benzene, R_f 0.90) yielded the tetraphenyl-substituted cyclophane **31**: 0.5 mg (8%); mp >300 °C; $C_{48}H_{32}$; MS, *m/e* 608 (M^+); accurate mass measd 608.2501, calcd 608.2504; ^1H NMR (250 MHz) δ 6.65–6.71 centered at 6.68 (A_2X_2, 8 H, p-Ar H, J_{AX} = 8.1 Hz), 6.84–7.18 centered at 7.01 (m, 20 H, C_6H_5), 7.38–7.59 centered at 7.49 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz).

1,2,3,4-Tetrahydro-1,4-epoxydibenzo[2.2]paracyclophane (32). The endoxide **16** (273 mg, 0.85 mmol) was hydrogenated in benzene/ethanol (1/1, 20 mL) over 5% Pd–C under atmospheric pressure at 25 °C, hydrogen was taken up from a graduated gas burette at the rate of 0.1 mL/s. After the reaction was complete, the catalyst was filtered and washed with chloroform (3 × 5 mL). Column chromatography on silica gel (hexanes/benzene = 2/1, R_f 0.31) gave **32**: 264 mg (97%); mp 213 °C dec (from heptane); $C_{24}H_{18}O$; MS, *m/e* 322 (M^+), 294 ($M^+ - C_2H_4$); accurate mass measd 322.1367, calcd 322.1358; ^1H NMR (250 MHz) δ 1.60–1.79 centered at 1.70 (m, 2 H, CH_2), 2.10–2.22 centered at 2.16 (m, 2 H, CH_2), 5.45 (dd, 2 H, CHO, J = 2.8 Hz, J' = 1.4 Hz), 6.28–6.60

centered at 6.44 (A_2X_2, 4 H, p-Ar H, J_{AX} = 8.0 Hz), 6.66 (s, 4 H, p-Ar H), 7.41–7.60 centered at 7.51 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz). Anal. Found: C, 89.51; H, 5.62. Calcd: C, 89.41; H, 5.63.

Benzofurano[*c*][2.2]paracyclophane (7). Powdered endoxide **32** (263 mg, 0.82 mmol) was heated at 220 °C for 5 min under vacuum (0.5 mmHg) with occasional shaking. The reaction was monitored by TLC. Column chromatography on silica gel (benzene) yielded the furano product **7** (R_f 0.95; 71 mg, 92%) together with unreacted starting material **32** (R_f 0.34; (181 mg, 0.56 mmol). Compound **7**: mp 275 °C dec (from heptane); $C_{22}H_{14}O$; MS, *m/e* 294 (M^+); accurate mass measd 294.1046, calcd 294.1045; ^{1}H NMR (250 MHz) δ 6.62–6.72 centered at 6.67 (A_2X_2, 8 H, p-Ar H, J_{AX} = 8.4 Hz), 7.57 (s, 2 H, furanyl H), 7.43–7.64 centered at 7.54 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz); UV, λ_{max} nm (log ϵ) 200 (4.7), 219 (4.6), 267 (3.3), 274 (3.1), 287 (2.5). Anal. Found: C, 88.84; H, 4.79. Calcd: C, 89.77; H, 4.79.

Dimethyl 1,4-Dihydro-1,4-epoxydibenzo[2.2]paracyclophane-2,3-dicarboxylate (33). The furanocyclophane **7** (22 mg, 0.07 mmol) and dimethyl acetylenedicarboxylate (DMAD) (1 mL, 7 mmol) were refluxed in toluene (10 mL) for 3 h at 150 °C (oil bath). The mixture was then cooled to room temperature. Excess DMAD and toluene were evaporated under vacuum. Column chromatography on silica gel (hexanes/ethyl acetate = 2/1) gave the title compound **33** (R_f 0.78; 24 mg, 83%) together with the unreacted starting material **7** (R_f 0.95; 3.8 mg, 0.01 mmol). Compound **33**: mp 191 °C; $C_{28}H_{20}O_5$; MS, *m/e* 436 (M^+); accurate mass measd 436.1312, calcd 436.1311; ^{1}H NMR (250 MHz) δ 3.91 (s, 6 H, CO_2CH_3), 6.04 (s, 2 H, CHO), 6.10–6.60 centered at 6.35 (A_2X_2, 4 H, p-Ar H, J = 7.9 Hz, J' = 1.7 Hz), 6.60–6.72 centered at 6.66 (A_2X_2, 4 H, p-Ar H, J = 8.1 Hz, J' = 1.7 Hz), 7.41–7.60 centered at 7.51 (A_2B_2, 4 H, o-Ar H, J = 5.5 Hz, J' = 3.4 Hz).

Dimethyl Dibenzo[2.2]paracyclophane-2,3-dicarboxylate (34). Lithium aluminum hydride (15 mg, 0.40 mmol) was added carefully to a suspension of titanium(IV) chloride (0.1 mL, 0.85 mmol) in anhydrous THF (2 mL) at 0 °C under nitrogen, followed by triethylamine (21 mg, 0.21 mmol) in anhydrous THF (0.5 mL). The mixture was stirred and refluxed for 30 min and then allowed to cool to room temperature. To this reagent was added the endoxide **33** (24 mg, 0.05 mmol) in anhydrous THF (4 mL), and the mixture was stirred for 2 h. To the mixture was added saturated potassium carbonate solution (80 mL). The aqueous layer was extracted with chloroform (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate and evaporated. Column chromatography on silica gel (benzene, R_f 0.26) afforded the title compound **34**: 16 mg, (70%); mp 273 °C dec (from heptane); $C_{28}H_{20}O_4$; MS, *m/e* 420 (M^+); accurate mass measd 420.1361, calcd 420.1362; ^{1}H NMR (250 MHz) δ 4.00 (s, 6 H, CO_2CH_3), 6.63–6.73 centered at 6.68 (A_2X_2, 8 H, p-Ar H, J_{AX} = 8.2 Hz), 7.46–7.69 centered at 7.58 (A_2B_2, 4 H, o-Ar H, J = 5.6 Hz, J' = 3.4 Hz), 8.03 (s, 2 H, protons ortho to carboxylate). Anal. Found: C, 79.95; H, 4.83. Calcd: C, 79.98; H, 4.79.

9,10,23,24-Tetrahydro-5,8:11,14:19,22:25,28-tetraethenodibenzocyclotetracosene (35). Phenyllithium[27] was prepared by adding bromobenzene (2.33 g, 16 mmol) in anhydrous ether (25 mL) dropwise to a stirring suspension of finely divided lithium (224 mg, 32 mmol) in anhydrous ether (25 mL). 4,4″-Bis(bromomethyl)-*o*-terphenyl (5.00 g, 12 mmol) in anhydrous ether (150 mL) was added to the reagent in 30 min. The resulting mixture was stirred for another 20 h and then 1 M sulfuric acid (100 mL) was added. The aqueous layer was extracted with chloroform (2 × 100 mL). The combined organic layers were dried over anhydrous sodium sulfate and evaporated. Column chromatography on silica gel (hexanes/benzene = 9/1) furnished the title compound **35** (R_f 0.14; 209 mg, 7%) and cyclophane **3** (R_f 0.33; 1.23 g, 40%). Compound **35**: mp 245–246 °C (from heptane); $C_{40}H_{32}$; MS, *m/e* 512 (M^+); accurate mass measd 512.2501, calcd 512.2504; ^{1}H NMR (250 MHz) δ 2.90 (s, 8 H, CH_2CH_2), 6.74–6.99 centered at 6.87 (A_2X_2, 16 H, p-Ar H, J_{AX} = 8.1 Hz), 7.36–7.47 centered at 7.42 (AA′BB′, 8 H, o-Ar H, J_A = 7.01 Hz, J_B = 0.57 Hz, J = 7.83 Hz, J' = 1.34 Hz). Anal. Found: C, 93.70; H, 6.29. Calcd: C, 93.71; H, 6.29.

9,10,23,24-Tetradehydro-5,8:11,14:19,22:25,28-tetraethenodibenzocyclotetracosene (36). Cyclophane **35** (88 mg, 0.17 mmol) was brominated with *N*-bromosuccinimide (123 mg, 0.69 mmol) in carbon tetrachloride (100 mL) with the aid of a trace amount of benzoyl peroxide and irradiation with a sunlamp (500 W) for 30 min with stirring. The resulting succinimide was filtered and washed with carbon tetrachloride (2 × 10 mL) when cooled to room temperature. The filtrate was evaporated, and the residue was evacuated for complete removal of moisture.

Without purification, the product obtained above in anhydrous THF (5 mL) was added dropwise to a suspension of potassium *tert*-butoxide (1 g, 8.9 mmol) in anhydrous THF (5 mL) under nitrogen. The mixture was stirred for 12 h and then quenched with 2 M hydrochloric acid (20 mL). The product mixture was extracted with chloroform (3 × 20 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated. Preparative layer chromatography on silica gel (hexanes/benzene = 9/1, R_f 0.00) followed by column chromatography on silica gel (chloroform, R_f 0.90) gave **36**: 10 mg (12%); mp >300 °C (from chloroform); $C_{40}H_{24}$; MS, *m/e* 504 (M^+); accurate mass measd 504.1876, calcd 504.1878; ^{1}H NMR (250 MHz δ 6.85–7.24 centered at 7.05 (A_2X_2 16 H, p-Ar H, J_{AX} = 8.2 Hz), 7.44–7.54 centered at 7.49 (AA′BB′, 8 H, o-Ar H, J_A = 7.13 Hz, J_B = 0.36 Hz, J = 7.72 Hz, J' = 1.36 Hz); UV, λ_{max} nm (log ϵ) 291 (3.7), 296 (3.7), 305 (3.6). Anal. Found: C, 95.26; H, 4.74. Calcd: C, 95.21; H, 4.79.

Acknowledgment. We express our sincere thanks to Y. H. Law, C. W. Fung, and K. W. Kwong for their assistance in measuring all the 250-MHz proton NMR spectra and high-resolution mass spectra. Thanks are also given to Drs. C. H. L. Kennard and G. Smith for their assistance in microanalyses, which were carried out at the Queensland Institute of Technology, Queensland, Australia. C.W.C. is grateful to the Croucher Foundation (Hong Kong) for the award of a Croucher Studentship.

Registry No. 3, 4432-72-8; **4**, 212-77-1; **5**, 97315-26-9; **5**·TCNE, 111615-73-7; **6**, 97315-27-0; **7**, 111615-65-7; **8**, 111615-66-8; **9**, 97315-28-1; **10**, 111615-67-9; **12**, 110-00-9; **13**, 534-22-5; **14**, 270-75-7; **15**, 5471-63-6; **16**, 97315-29-2; **17**, 111615-68-0; **18**, 97315-30-5; **19**, 97315-31-6; **21**, 97315-32-7; **22**, 111615-69-1; **24**, 64586-12-5; *cis*-**25**, 111615-70-4; *trans*-**25**, 111688-45-0; **28**, 111615-71-5; **29**, 111615-72-6; **31**, 111615-74-8; **32**, 111615-75-9; **33**, 111615-76-0; **34**, 111615-77-1; **35**, 111615-78-2; **36**, 111615-79-3; C_6H_5-*o*-$C_6H_4C_6H_5$, 84-15-1; 4,4″-BrC_6H_4-*o*-$C_6H_4C_6H_4Br$, 17788-94-2; 4,4″-$HOCH_2C_6H_4$-*o*-$C_6H_4C_6H_4CH_2OH$, 63476-04-0; 4,4″-$BrCH_2C_6H_4$-*o*-$C_6H_4C_6H_4CH_2Br$, 55759-13-2; 1-methoxy-1,3-dihydroisobenzofuran, 67536-29-2; tetraphenylcyclopentadienone, 479-33-4.