concentration, percent conversion, CB-2:CP-3): 0.0 M, 4%, 76:24; 0.2 M, 33%, 94:6; 0.4 M, 36%, 95:5; 0.8 M, 53%, 97:3; 1.0 M, 74%, 98:2.

Deuterium Labeling Study. A 0.1 M solution of adduct **1** in methanol-*O-d* was photolyzed with the 450-W lamp for 30 min with use of the uranium glass filter. The resulting photoproduct mixture was analyzed by GCMS, which showed that the peak corresponding to CP-3 had incorporated deuterium to the extent of 55% after correction for the M + 1 peak.

Photolysis of Enedione 1 at Low Temperatures in Acetonitrile. Photolysis of the adduct **1** at a series of temperatures below room temperature was carried out by using the nitrogen laser. A solution of enedione **1** (0.1 M) in acetonitrile/water (50:1, v/v) was used in all cases. The desired temperature was achieved by selecting an appropriate solvent/dry ice mixture[19] or by ice and ice/salt mixtures. The adduct **1**, in a transparent dewar flask containing the coolant, was photolyzed for 5-10 min, and the products were analyzed by GC. The results obtained are shown in the upper portion of Figure 2 (text).

Crystal Photolysis of Enedione 1. When a single crystal or a polycrystalline sample of adduct **1** was photolyzed at room temperature for up to 20 min by using the nitrogen laser (5% conversion), the only product observed by GC was cyclobutanone **2**. When the irradiation was continued for longer periods of time (1-1.5 h, ca. 30% conversion), the crystal partially melted, and GC showed the formation of both photoproducts in a **2**:**3** = 30:1 ratio. Laser photolysis (50 min) of a single crystal maintained at -41 °C afforded only CB-**2**.

Variable Temperature Photolysis of Enedione 7 in Acetonitrile. As before, 0.1 M solutions of the adduct **7**, maintained at the desired temperature in an appropriate solvent/dry ice or ice/salt bath, were photolyzed for 5-10 min with the nitrogen laser. Temperatures above room temperature were achieved by immersing the photolysis sample in a refluxing organic solvent of appropriate boiling point. Since all three photoproducts had been isolated and characterized previously,[5] no attempt was made to isolate them in this study. The reaction mixtures were analyzed by GC with the results shown in the lower part of Figure 2 (text).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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[19] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; Chapter 16.

"Pagodane": The Efficient Synthesis of a Novel, Versatile Molecular Framework

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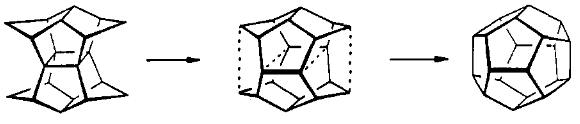
Contribution from the Institut für Organische Chemie und Biochemie, Universität Freiburg, D-7800 Freiburg, Federal Republic of Germany, and Ciba-Geigy AG, CH-4008 Basel, Switzerland. Received December 9, 1986

Abstract: The class of "pagodane" compounds constitutes a novel series of undecacyclic, strained, and chemically versatile carbon frameworks. In particular, the $C_{20}H_{20}$ [1.1.1.1]pagodane (**1**) and variously substituted derivatives thereof are principal precursors for structurally closely related dodecahedranes. The synthesis of **1** commences from isodrin **3** and consists of ca. 45 functional and structural modifications which are efficiently concentrated into 14 one-pot operations with an overall yield of 24%. Key steps in this reaction sequence are a benzo/benzo [6 + 6] photocycloaddition and a domino Diels-Alder reaction. Monochromatic irradiation (254 nm) of the dibenzo compound **18** led to a 7:3 equilibrium mixture of **18** with the *syn-o,o'*-dibenzene isomer **42**. The (unexpectedly high) thermal stability of the latter permitted the regiospecific addition of maleic anhydride to give rise to the pagodane framework **48** by two consecutive [4 + 2]-addition steps. From the diester **55** the parent hydrocarbon **1** as well as the 4,9-diketone **70** is prepared. Geometrical details of the face-to-face dibenzo compound **18**, the [6 + 6] photoisomer **42**, and the [1.1.1.1]pagodane derivative **55** are provided by X-ray structural determinations.

"Pagodane" is the trivial name we have coined for the highly complex, esthetically appealing $C_{20}H_{20}$ polyquinane **1**.[2] The obvious need for such a short-hand description can be readily understood in view of the von Baeyer/IUPAC and Chemical Abstracts nomenclature given in Chart I. Our interest in the [1.1.1.1]pagodane[3] system **1** arose primarily from its close relationship with the entirely pentagonal $C_{20}H_{20}$ structure, dodecahedrane **2**.[4]

Chart I



1

2

1: Undecacyclo[9.9.0.$0^{1,5}$.$0^{2,12}$.$0^{2,18}$.$0^{3,7}$.$0^{6,10}$.$0^{8,12}$.$0^{11,15}$.$0^{13,17}$.$3^{16,20}$]-eicosane.

2: Undecacyclo[9.9.0.$0^{2,9}$.$0^{3,7}$.$0^{4,20}$.$0^{5,18}$.$0^{6,16}$.$0^{8,15}$.$0^{10,14}$.$0^{12,19}$.$0^{13,17}$]-eicosane.[5]

1: Perhydro-2,7,8b,3,4b,6-ethanediylidinedipentaleno[1,6-*ab*:1',6'-*ef*]-pentalene.

2: Perhydro-5,2,1,6,3,4-[2,3]butanyl[1,4]diylidenedipentaleno-[2,1,6-*cde*:2',1',6'-*gha*]pentalene.

In both cases, the skeletons exhibit unusually high point group symmetries (i.e., D_{2h} vs. I_h), and each contains 12 cyclopentane units. Furthermore, as can be deduced at a glance from the IUPAC designation, both are undecacyclic with all 20 atoms making up the main ring and with all interconnections being of the same order. Consequently, the structural alterations required in going from **1** to **2** are limited to only the hydrogenolytic fission of two cyclobutane C-C bonds, with inversion of the cyclobutane

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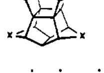
[1] (a) Universität Freiburg. (b) Ciba-Geigy AG. (c) Alexander von Humboldt Fellow, 1985-1986.

[2] (a) Fessner, W.-D.; Prinzbach, H.; Rihs, G. *Tetrahedron Lett.* **1983**, *24*, 5857-5860. (b) Fessner, W.-D. Ph.D. Dissertation, Universität Freiburg, 1986.

[3] The name "pagodane" represents the class of compounds based on the general structure (i) in which X symbolizes bridges of different nature and lengths. The length of the bridges is given in square brackets placed in front of the name, according to their order in the IUPAC numbering scheme.



i

[4] Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446-5450.

[5] Eckroth, D. R. *J. Org. Chem.* **1967**, *32*, 3362-3365.

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Chart II

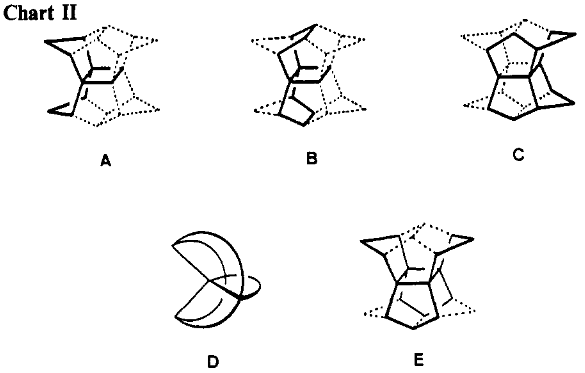
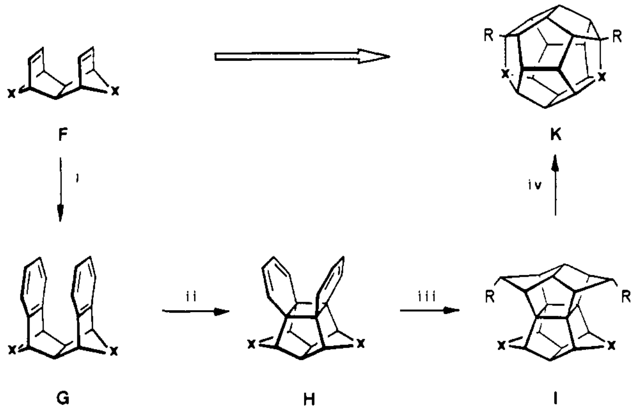


Chart III



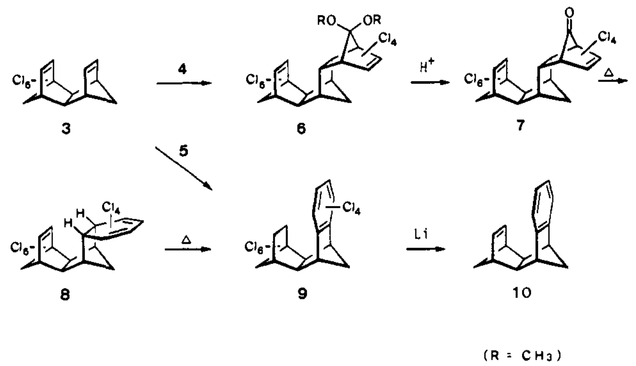
centers and concomitant opening of the molecular sphere, followed by oxidative formation of two C–C bonds between opposing methylene groups. Energetically, MM2 force field calculations[6a] place **1** ($\Delta H_f{}^\circ$ = 64.4 kcal/mol) by as much as 42.2 kcal/mol above the stabilomer **2** ($\Delta H_f{}^\circ$ = 22.2[7] kcal/mol). The difference in strain energy is of a similar magnitude. Most of this strain is taken up by the central four-membered ring, making this structural unit an obvious target for specific chemical attack.

The polycyclic framework of **1** incorporates some rather noteworthy structural peculiarities (Chart II): (i) the central cyclobutane ring forms part of several propellane substructures, as exemplified by A and B,[8] (ii) each of the quaternary carbon atoms forms the center of a [5.5.5.5]fenestrane unit C[9] which is folded around the cyclobutane ring to generate a centropentacycle D,[10] and (iii) every side of the four-membered ring is spanned by a three-carbon chain, thus constituting a [3.3.3.3]tetraannulane unit E.[11]

The complexity of the structures **1** and **2** is further demonstrated by considering the total number of possible subsidiary rings that can be derived from graph analysis. This amounts to 685 for **1**[12a] and to 1168 for **2**.[12b]

Our ultimate preparative aim lies in the efficient synthesis of **2** and other dodecahedranes which incorporate a broad substitution pattern, via pagodane **1** and appropriately substituted derivatives thereof. Our approach, as generalized in Chart III, is subdivided into four stages: (i) twofold benzoannelation of the *syn*-1,6-dienes F, (ii) [6 + 6] photocycloaddition within the face-to-face dibenzo substrates G, and (iii) elaboration of the resultant *syn-o,o′*-dibenzene moiety in H into the doubly caged pagodanes I. Depending upon the nature of the X/R groups, catalytic rearrangement[13] as well as directed stepwise procedures[14] can be envisaged for the ultimate transformation (iv) of the pagodanes into dodecahedranes, I → K.

Scheme I



In this paper, we detail expedient syntheses of the hydrocarbon **1**, the prototype for the general structures I (X = CH_2, R = H), and several 4,9-disubstituted derivatives. The cornerstone of our approach, the former insecticide isodrin (**3**)[15] (still available commercially in bulk quantities[16]), has within it 12 carbon atoms already properly arranged in four cyclopentane rings, embodying practically one-half of the pagodane skeleton **1**. Moreover, considering the long distance to be travelled, the masked C_{2v} symmetry inherent in the starting material **3** would significantly abbreviate an envisaged serial synthesis of **1** and **2**. The point must be stressed that since such a multistep sequence would need to be started on the kilogram scale, every step with a less than 90% yield had to be considered "unsatisfactory". This of course is no mean feat! In view of the rapid expansion of the project (see the Summary and Outlook section), not only the synthetic feasibility but the preparative utility of our strategic scheme had to be demonstrated.

Stage 1: Twofold Benzoannelation F → G

The benzoannelation of isodrin (**3**) to the monobenzo compound **10** has been described by Mackenzie[17] as a four-step sequence (Scheme I) with an overall yield of 38%. Thus, the cycloadduct **6** from the reaction of **3** with tetrachlorocyclopentadienone dimethyl acetal **4**[18] was cleaved with concentrated sulfuric acid at ambient temperature, and the resulting ketone **7** was isolated and decarbonylated at 110 °C to give **9** directly. Under these conditions, the intermediate cyclohexadiene **8** undergoes a very rapid transannular dyotropic hydrogen transfer.[19] Upon dehalogenation of **9** with lithium/*tert*-butyl alcohol, the double bond is regenerated to give benzoene **10**. A simplification in this scheme was recognized in a one-pot hydrolysis/thermolysis procedure due to the stability of the polyhalogenated products toward concentrated acid. By gradually heating the acetal **6**, suspended in sulfuric acid, to 140 °C, a nearly quantitative formation of **9** resulted, demon-

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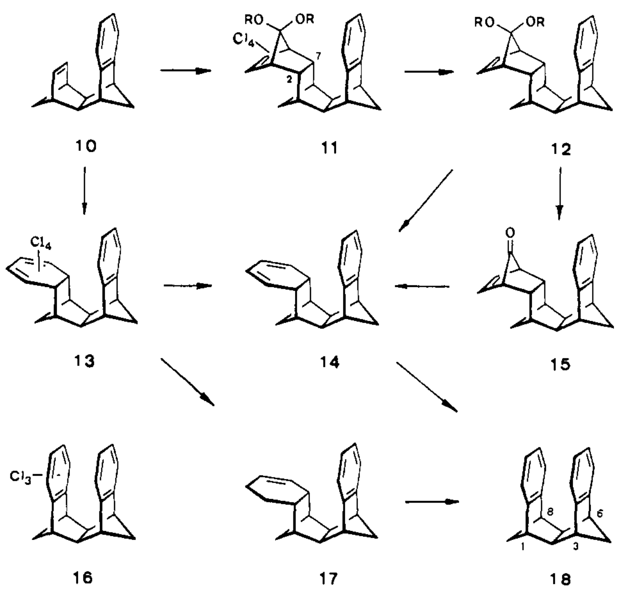
[17] Mackenzie, K. *J. Chem. Soc.* **1965**, 4646–4653.

[18] (a) Newcomer, J. S.; McBee, E. T. *J. Am. Chem. Soc.* **1949**, *71*, 946–951. (b) Gassman, P. G.; Marshall, J. L. *Org. Synth. Collect. Vol.* **1973**, *V*, 424–428.

[19] (a) Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189–2194. (b) Mackenzie, K.; Proctor, G. J.; Woodnutt, D. J. *Tetrahedron Lett.* **1984**, *25*, 977–980 and references cited therein.

Scheme II

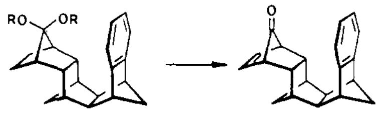


(R = CH_3)

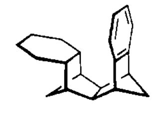
strating the insensitivity of the intramolecular hydrogen shift under these conditions. After extensive optimization, even on the kilogram scale, an overall yield of 82–85% **10** was reproducibly achieved. A further improvement was made possible by the substitution of **4** by the more reactive tetrachlorothiophene dioxide **5**,[20] as the initial cycloadduct spontaneously releases sulfur dioxide to give intermediate **8**, which then aromatizes to **9**. On the millimole scale, the one-step yield of **9** was quantitative. On a molar scale, however, the economically restrictive availability of **5** has so far precluded its further application.

The second benzoannelation[21] was executed in a manner similar to the first (Scheme II). The norbornene type character of the double bond of **10** was expected to facilitate the addition of the electron-demanding diene **4**, but in practice, rather forcing conditions were required to effect this transformation. Even with various precautions, partial decomposition of **10** could not be avoided, and an average yield of 70–80% was not improved upon. Apparently, the cycloaddition generates significant steric compression between the benzene ring and the vinylic hydrogens during rehybridization and thus hinders the formation of the adduct **11**. The respective upfield chemical shift of δ 2.19 in the product **11**, as contrasted to δ 2.73 in **6**, supports this hypothesis since it indicates a strong aromatic anisotropic effect.

Contrary to conventional acetals, the hydrolysis of halogenated acetals requires the use of concentrated mineral acid. Upon such treatment, **11** instead suffered considerable decomposition and, as a consequence, the chlorine substituents were removed beforehand. Dehalogenation of systems similar to **11** with lithium/*tert*-butyl alcohol gives rise to significant amounts of C=C double bond saturated material. It is known that the extent of overreduction can be greatly reduced by replacing lithium with sodium.[22] Nevertheless, under the best conditions so far, **12** was consistently accompanied by ca. 10% of the saturated acetal **19**. Direct separation of this material was not necessary, however, as it could be readily removed at a later stage. Two-phase hydrolysis of **12** to the norbornenone **15** with dilute sulfuric acid was straightforward, and decarbonylation of **15** occurred rapidly in boiling carbon tetrachloride. The majority of the cyclohexadiene product **14** was easily isolated by crystallization from hexane, and the remainder was separated from the accompanying norbornanone **20** by filtration through silica gel. A further simplification for the preparation of **14** was attained by a one-pot trans-acetalization/decarbonylation procedure in which a solution of **12** in butanone was heated in the presence of a catalytic amount of *p*-toluenesulfonic acid; the loss of carbon monoxide from the intermediate **15** drives the reaction to completion.



19 20



21

(R = CH_3)

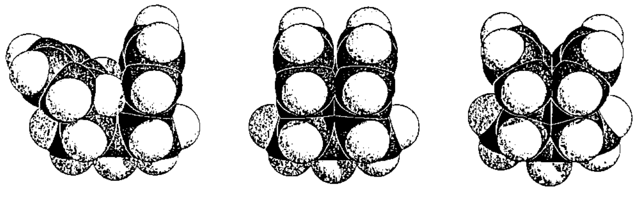


Figure 1. Space filling models of **14**, **18**, and **42** (SCHAKAL[36]).

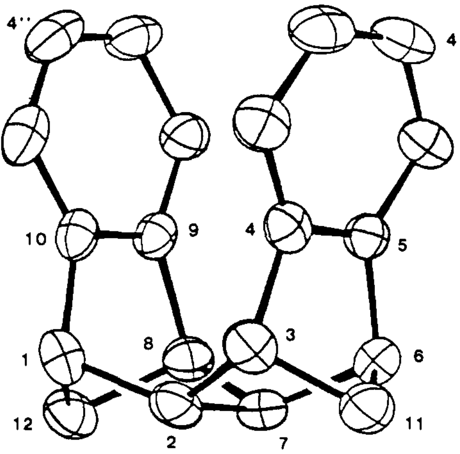
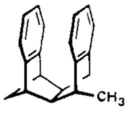
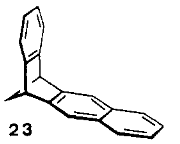


Figure 2. ORTEP diagram of one of the two crystallographically independent molecules of **18**.[33]

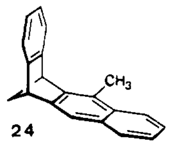
The aromatization of diene **14** to dibenzo compound **18** turned out to be a critical step which, for some time, jeopardized the whole project. The two inner hydrogen atoms to be eliminated are sterically so efficiently shielded, as is convincingly demonstrated by the space filling model in Figure 1, that they resisted numerous oxidizing reagents and procedures (e.g., O_2, MnO_2, PbO_2, chloranil, DDQ, S_8, BuLi-*t*-BuOK, NBS/base, Br_2/base).[23] Encouraging results were eventually achieved when recourse was made to dehydrogenation over 10% palladium on carbon under drastic conditions. In our early experiments, an intimate mixture of **14** and the catalyst heated at 250 °C for 30 min did indeed give **18**, but considerable amounts of cyclohexane **21** and some polymeric material were also formed. From additional minor components detected upon scaling up, three were identified as **22–24**.



22



23



24

The formation of **21** led us to determine the ratio of products **18**:**21** as a function of the catalyst/substrate ratio. At a ratio Pd/C:**14** of about 4:1 this amounted to 2:1, which was enhanced to 7:1 at a loading of 20:1. For practical purposes, a compromising 10:1 ratio of Pd/C:**14** was used to provide **18** reproducibly in 70% average yield or 40% overall for the second four-step benzoannelation sequence based on **10**.

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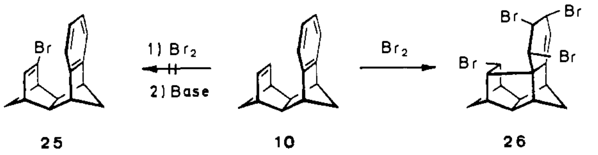
Scheme III



The production of large quantities of **18**, although somewhat restricted by technical problems, is facilitated by its proclivity toward crystallization. The costs involved are acceptable since the catalyst can be conveniently recycled. After Soxhlet extraction of the products with ethyl acetate, the catalyst is regenerated on heating in vacuo.[24] Extraction with methylene chloride irreversibly poisoned the catalyst whilst benzene did not extract the polymeric material sufficiently. Loss of activity and increasing amounts of **21** were noticed after more than 10 cycles.

Intensive efforts were made to avoid the competitive hydrogenation of diene **14**. For example, gas-phase dehydrogenation by subliming **14** through a column packed with Pd/C catalyst heated at 250–300 °C cleanly produced **18** but only at slow conversion rates. At temperatures greater than 450 °C, fragmentation of **14** into a mixture of indene, benzene, and cyclopentadiene dominated. It is yet to be investigated as to whether the presence of a stronger hydrogen-binding cocatalyst of the type recently reported by Paquette[25] will have any beneficial effect.

The higher reactivity of **5** permitted the addition to benzoene **10** to proceed under milder conditions than with **4** to give the tetrachlorocyclohexadiene **13** in 92% yield. Lithium/*tert*-butyl alcohol reduction of the latter in tetrahydrofuran solution progressed to the cyclohexene **17** in 88% yield contaminated with a small amount of the C_s positional isomer. On the other hand, when **13** was subjected to sodium/*tert*-butyl alcohol reduction in ether, overreduction to **17** was suppressed, and the diene **14** was obtained as the major component of the product mixture. Pure **17** as well as **14**/**17** mixtures could also be dehydrogenated over palladium, although a similar ratio of **18**/**21**, as that derived from **14**, was only achieved with higher quantities of the catalyst. This three-step alternative increased the overall yield for the second benzoannelation to 60%. As was expected from our experience with **14**, all attempts to aromatize **13** to **18** through HCl elimination, a methodology which has enabled the synthesis of similarly congested dibenzo compounds,[26] were fruitless. Under forcing conditions, only decomposition occurred.

An alternative synthesis of **18**, by addition of 1,4-bisacetoxybutadiene to benzoene **10** followed by ester pyrolysis of the corresponding adduct, could not be realized as under no conditions could the adduct be made. An attempt to activate the olefin moiety of **10** with a substituent that might be easily eliminated following the annelation step, exemplified by vinyl bromide **25**, was similarly unsuccessful as **10** exhibited a marked propensity toward transannular bonding in reactions with electrophiles.[21] This behavior of **10** toward homoconjugate reactions is also shared by dienes **3** and **27**.[15] Addition of bromine to **10**, for example, yielded only the tetrabromide **26** (Scheme III).

Two comments are appropriate here with respect to potential major simplifications in the construction of **18**. Firstly, **18** can be envisaged retrosynthetically as the product arising from the twofold addition of isoindene to an acetylene equivalent in an endo-type fashion. As can be anticipated from the severe benzo/benzo repulsions operative in the transition state leading to the endo,endo configuration **18**, the formation of this isomer would most likely be precluded. Indeed, in a similar case, addition of isobenzofuran to dimethyl acetylenedicarboxylate was found to deliver predominantly the sterically less hindered exo,endo as well as the exo,exo adducts.[27] Secondly, in isodrin **3**, only one of the C=C double bonds is accessible to addition by the C_4-synthons **4**/**5**, and twofold benzoannelation therefore was conducted as two consecutive series of reactions. The basic diene **27**[28] could, in principle, make a simultaneous twofold benzoannelation feasible. In reality, the reaction of **27** with excess thiophene dioxide **5** at 0 °C gave not the desired bis adduct **29** but exclusively the aromatic compound **31**, as was evident from spectral data and its conversion to the known hydrocarbon **32**.[17] The dyotropic hydrogen migration, which takes place in the intermediate **28** after the initial addition of 1 equiv of **5**, obviously proceeds too rapidly to allow the second addition. Compared with the results of Mackenzie,[17] who was able to isolate the corresponding intermediate **8**, the deviating behavior of **28** must be attributed to the higher electron density at the acceptor C=C double bond. Obviously, this competition is precluded when **29** is approached in a stepwise manner by using acetal **4** instead of **5**, in analogy to Scheme I. The diene **27** reacts with **4** smoothly to form a monoadduct, which only very reluctantly added a second equivalent of the acetal to give **30** together with much polymeric material. Since the yield of the bis adduct **30** (43%) was not at all satisfactory for our needs, this route was not further pursued (Scheme IV).

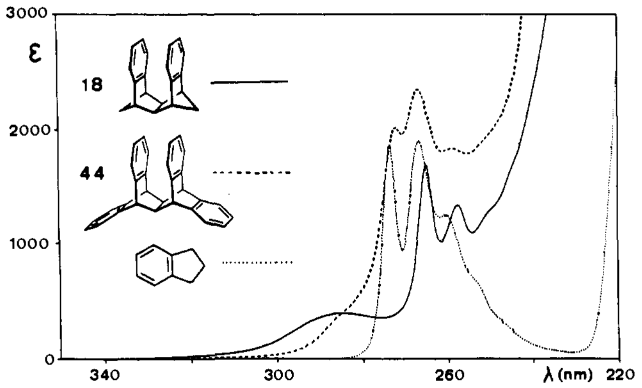
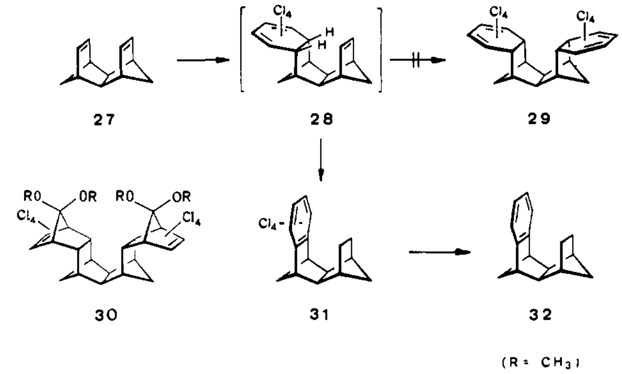


Figure 3. UV spectra of **18**, **44**, and indane in isooctane.

Scheme IV



As a consequence of the proximity of the two face-to-face-oriented benzene rings in the [3.3]orthocyclophane **18** (see the space filling model in Figure 1), characteristic spectroscopic properties arise. The signals for the aromatic protons appear at relatively high field, isochronic at δ 6.54 in $CDCl_3$ solution and as an AA′BB′ pattern at δ 6.69 and 6.59 in benzene-d_6. Similar data have been measured for [2.2]paracyclophanes,[29] the effect being primarily attributed to mutual shielding by the aromatic rings. The UV absorption curve of **18**, shown in Figure 3, is reproduced together with those of the structurally related compounds, janusene **44**[30] and indane.[31a]

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(24) Zander, M.; Grundmann, C. In *Methoden der Organischen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1981; Vol. 5/2b, pp 107–237.

(25) Paquette, L. A.; Miyahara, Y.; Doecke, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 1716–1718.

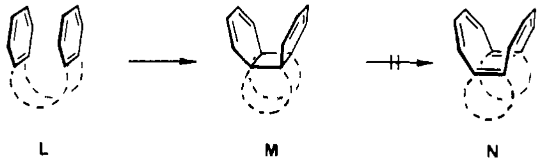
(26) Fessner, W.-D.; Sedelmeier, G.; Knothe, L.; Prinzbach, H.; Rihs, G.; Yang, Z.-z.; Kovac, B.; Heilbronner, E. *Helv. Chim. Acta*, in press.

(27) (a) Grund, C. Dissertation, Universität Freiburg, in preparation. (b) Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599–1606.

(28) Bruck, P.; Thompson, D.; Winstein, S. *Chem. Ind.* (*London*) **1960**, 405.

(29) Vögtle, F.; Neumann, P. *Top. Curr. Chem.* **1974**, *48*, 67–68 and references cited therein.

Chart IV



In both **18** and **44**, a broad absorption starting from ca. 310 nm shows a comparable extinction coefficient of about 400 at 285 nm.[32] This phenomenon, which is not observed in the UV spectrum of indane, has to be attributed to the special face-to-face orientation of the aromatic rings in **18** and **44** and is interpreted as charge-transfer bands.[30] From the PE analysis of **18** [IP = -7.8 (b_2 (π)), -8.2 (a_2 (π)), -8.8 (a_1 (π)), and -9.2 eV (b_1 (π))],[33] an averaged benzo/benzo resonance integral of $\beta = -0.5$ eV has been determined. This value corresponds to that found for [2.2]paracyclophane ($\beta = -0.5$ eV) and for other, higher order cyclophanes,[34] although the interactions within **18** are somewhat smaller than those determined for the benzo/ene analogue **10** [IP = -8.0 (a' (π)), -8.85 (a'' (π)), and -9.10 eV (π); $\beta = -0.64$ eV][33] or for the basic diene **27** [IP = -8.10 (π_-) and -9.35 eV (π_+); $\beta = -0.63$ eV].[35]

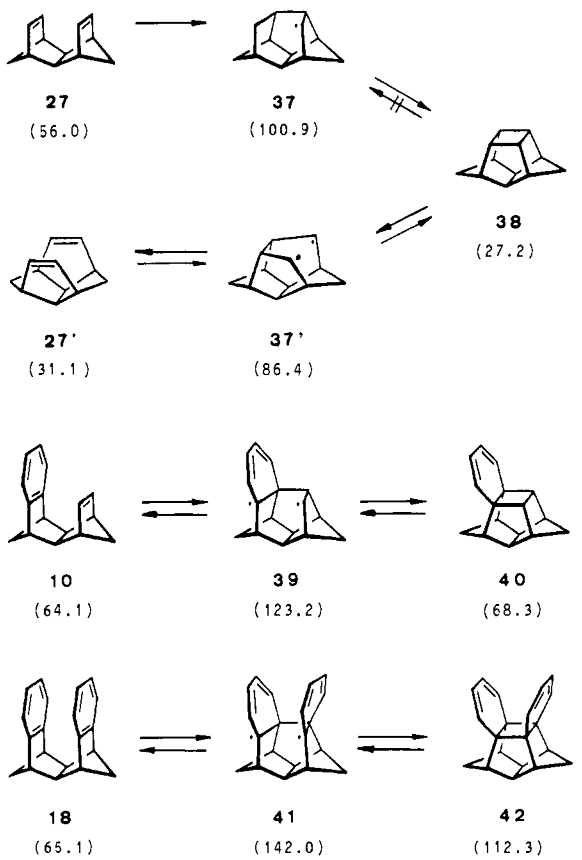
The single-crystal X-ray analysis of **18** (Figure 2) also revealed rather large proximity effects. The closest π–π distance of 3.04 Å approximates that of 2.99 Å found in a janusene derivative,[37] both of which are much shorter than the van der Waals distance for aromatic compounds.[38] Nevertheless, the two benzene rings remain planar, the π–π repulsion being levied by a ca. 4° outward pyramidalization at the annelated positions and by a widening of interplanar angles. The π–π interorbital angle of 161° approaches the ideal value of 180° for the prospected transannular bond formation (Chart III).

The transannular distances for **18** and similarly for **27**, as calculated by force field methods, are consistently shorter than the experimentally determined values.[39] These discrepancies indicate that not only van der Waals repulsions but also electronically destabilizing forces are operative between the π-clouds. After all, the steric and electronic situation in **18** and **27** approximates that of the respective transition states for the thermally symmetry-forbidden [6 + 6]- and [2 + 2]-cycloaddition reactions.

Stage 2: Benzo/Benzo Photocycloadditions G → H (18 → 43)

The second stage of Chart III required not only an efficient benzo/benzo [6 + 6] cycloaddition but a *syn*-tricyclo-[6.2.0.0^{2,7}]dodecatetraene (*syn-o,o'*-dibenzene) product H that would be kinetically stable enough to allow subsequent chemistry to be carried out. In fact, it was the discovery of exactly such a situation in the valence isomer pair **18**/**42** which had originally initiated the pagodane project.

Chart V[a]



[a] $\Delta H_f°$ values in kcal/mol.

Problems associated with the construction of *o,o'*-dibenzene building blocks M by intramolecular benzo/benzo photocycloaddition (Chart IV) arise from the fact that these reactions are highly endothermic and that the σ-coupled butadiene units within the photoproducts are quite effective light-absorbing competitors. A selective transformation upon direct excitation will most likely be the exception, whereas unpredictable positions of photoequilibria, side reactions (e.g., thermal isomerization to give N[40]), and material loss by polymerization will be the rule.[41]

The possibility for selective sensitization is limited by the lack of sensitizers suitable for the excitation of simple uncondensed benzenoid chromophors.[42] These difficulties are well known from earlier pertinent experiences with (di)benzo compounds derived from the bridged 1,4-/1,5-dienes **33**[43]/**35**.[44] In the latter, at least

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(30) Cristol, S. J.; Lewis, D. C. *J. Am. Chem. Soc.* **1967**, *89*, 1476–1483.

(31) (a) Morton, R. A.; DeGouveia, A. J. A. *J. Chem. Soc.* **1934**, 911. (b) Henri, V.; Pickett, L. *J. Chem. Phys.* **1939**, *7*, 439–440.

(32) For another [3.3]orthocyclophane with an enforced juxtaposition of two benzene rings and similar spectroscopic consequences, cf.: Mataka, S.; Takahashi, K.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M. *J. Chem. Soc., Chem. Commun.* **1985**, 973.

(33) Prinzbach, H.; Sedelmeier, G.; Krüger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 271–273.

(34) Heilbronner, E.; Kovač, B. *Helv. Chim. Acta* **1981**, *64*, 430–447 and references cited therein.

(35) (a) Martin, H.-D.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3143–3145. (b) Prinzbach, H.; Sedelmeier, G.; Martin, H.-D. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 103–104. (c) Albert, B.; Berning, W.; Burschka, C.; Hünig, S.; Martin, H.-D.; Prokschy, F. *Chem. Ber.* **1981**, *114*, 423–432.

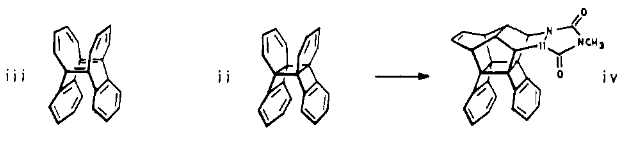
(36) Keller, E. *Chem. Unserer Zeit* **1980**, *14*, 56–60.

(37) Macintyre, W. M.; Tench, A. H. *J. Org. Chem.* **1973**, *38*, 130–133.

(38) The van der Waals distance between two parallel benzene nuclei is usually at least 3.4 Å (ref 29).

(39) (a) Murty, B. A. R. C.; Spurr, P. R.; Pinkos, R.; Grund, C.; Fessner, W.-D.; Hunkler, D.; Fritz, H.; Roth, W. R.; Prinzbach, H. *Chimia* **1987**, *41*, 32–36. (b) Ermer, O.; Bödecker, C.-D.; Preut, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 55–56.

(40) The *syn-o,o'*-dibenzene structure ii was originally proposed for the dimer of biphenylene formed upon direct irradiation at room temperature. It was recently revised (X-ray) to iii. Cf.: (a) Goldman, N. L.; Ruden, R. A. *Tetrahedron Lett.* **1968**, 3951–3954. (b) Passer, E. L.; White, J. G.; Goldman, N. L.; Lerit, A. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1856–1860. (c) Kimura, K.; Ohno, H.; Morikawa, K.; Hiramatsu, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2169–2173. The question is still open: whether ii is the precursor of iii. Our efforts to intercept ii, e.g., as triazolinedione adduct iv,[4,48] have been unsuccessful.

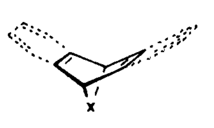


(41) For a review, see: (a) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1979**, *33*, 2459–2489. (b) Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 243.

(42) E_T: acetone 81.7 kcal/mol, xanthone 74.0 kcal/mol, xylene 82.1 kcal/mol. Cf.: Murov, S. L. *Handbook of Photochemistry*; Marcel-Dekker: New York, 1973.

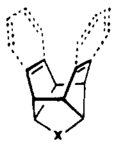
(43) Meier, H. In *Methoden der Organischen Chemie*, 4th/Ed.; Georg Thieme Verlag: Stuttgart, 1975; Vol. 4,5a, p 222.

(44) X = $(CH_2)_0$: (a) McKennis, J. S.; Brener, L.; Ward, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 4957–4958. (b) Paquette, L. A.; James, D. R.; Klein, G. *J. Org. Chem.* **1978**, *43*, 1287–1292. X = $(CH_2)_1$: (c) Marchand, A. P.; Chou, T.-C.; Ekstrand, J. D.; Helm, D. v. d. *J. Org. Chem.* **1976**, *41*, 1438–1444. (d) Eaton, P. E.; Cassar, L.; Hudson, R. A.; Hwang, D. R. *Ibid.* **1976**, *41*, 1445–1448. X = $(CH_2)_2$: (e) Martin, H.-D.; Sedelmeier, G.; Prinzbach, H. *Chimia* **1979**, *33*, 329–332.



33

34



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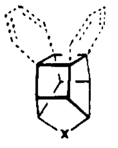


36

with one- or two-atom bridges, $[_\pi 2 + {}_\pi 2]$ cycloadditions are generally efficient processes upon either direct or sensitized excitations. In the dibenzo **33** cases studied,[45] the products resulted only from diradical or carbene intermediates formed by di-π-methane pathways. Even with the monobenzo **33** systems, no [6 + 2] cage adducts **34** were directly observed.[46] In several cases, their intermediacy could be deduced from the respective products.[47]

Apparently, no systematic study was undertaken to attempt [6 + 6]-type additions under varying conditions or to detect the potential [6 + 6]-adducts at very low temperatures. As with the dibenzo **33** substrates, no [6 + 6] or even [6 + 2] additions were realized with various mono- and dibenzo **35** compounds at reaction temperatures down to −70 °C. In direct irradiation experiments, products derived from Cope-type rearrangements prevailed.[48] Admittedly, both 1,4-/1,5-arene substrates **33**/**35** are not particularly suited for this purpose. The respective photoisomers would be expected to be highly thermodynamically instable due to the fact that, in their formation, the generation of not only a four-membered ring but of two additional small rings is involved.

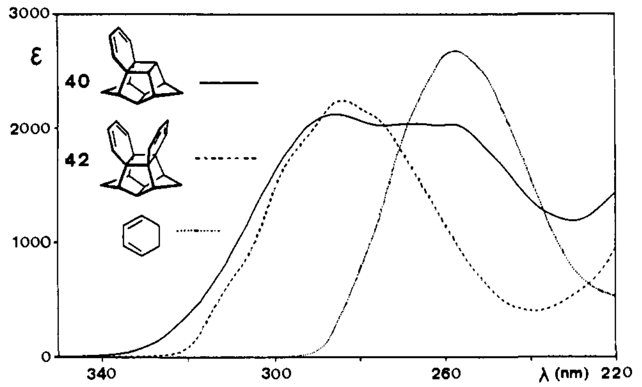
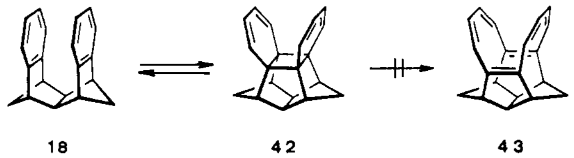


Figure 4. UV spectra of **40**, **42**, and 1,3-cyclohexadiene ($\cdot{}^1/_3$) in isooctane.

Scheme V



On the basis of the calculated data[49] compiled in Chart V for the 1,6-diene **27**, the benzoannellated structures **10** and **18**, the photoisomers **38**, **40**, and **42**, and their presumed respective diradical intermediates **37**, **39**, and **41**, there was good indication[49,50] that stable benzo/ene (**40**) and benzo/benzo cycloadducts (**42**) might be accessible. In addition, competitive pathways such as the di-π-methane or Cope rearrangements found in the 1,4-/1,5-diene systems **33**/**34**[44] are not feasible. With dienes **27** and **3**, [2 + 2] cycloaddition by direct or sensitized excitation proceeds readily.[51] The birdcage **38** is stable beyond 400 °C.[52] In a recent vapor-phase pyrolysis study, an activation enthalpy $\Delta H^{\ddagger}$ (430 °C) of ca. 59 kcal/mol was determined for the reversible metathetic cleavage to give **27′**, in good agreement with the calculated $\Delta\Delta H_f{}^\circ$ = 59.2 kcal/mol for the **38**/**37′** pair.[49]

In our model study[33] on irradiation of benzoene **10** in benzene solution with a high-pressure Hg lamp through Pyrex effected no product formation. In fact, as was shown later, the cage isomer **40** was isomerized back to **10** under these conditions as can be understood from their relative UV absorption curves (Figures 3 and 4). Direct irradiation with monochromatic 254-nm light from a low-pressure Hg lamp or sensitized excitation with acetone[42] or xanthone[42] produced ca. 2:1, 4:1, and 1:3 photoequilibrium mixtures of **10** with **40**, respectively.[27a]

Thermally, **40** was stable up to at least 250 °C in benzene solution.[27a] The E_a value (ca. 57 kcal/mol) for the thermal back reaction to **10** in the vapor phase, when compared to the calculated $\Delta\Delta H_f{}^\circ$ value (54.9 kcal/mol) for **40**/**39**,[49] again documents the reliability of the MM2 values for these systems.

The calculated endothermicity for the cyclization **18** → **42** ($\Delta\Delta H_f{}^\circ$ = 47.2 kcal/mol) was not expected to be prohibitive.[50] However, the dibenzo compound **18** was inert toward acetone-sensitized excitation, presumably since the triplet energy for the isolated chromophoric xylene units is too high.[42] With the charge-transfer absorption of **18** extending to significantly longer wavelength than that normally found for cyclohexadiene chromophores (Figure 4),[31b] an opportunity was seen for the selective excitation of **18** by using monochromatic 300-nm light. Still, after several hours of irradiation in a Rayonet reactor, no product was observed. Success was finally achieved on irradiation of **18** with monochromatic 254-nm light. The reaction, as conveniently monitored by ^{1}H NMR, slowly gave rise to a ca. 7:3 equilibrium mixture of **18** with the [6 + 6]-addition isomer **42**. The alternative C_{2v} hexaene structure **43** (N), also considered in view of the surprisingly long wavelength UV absorption of the photoproduct, was ruled out by the ^{13}C NMR data. Fortunately, in spite of a

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(45) $X = CH_2$: (a) Ipaktschi, J. *Chem. Ber.* **1972**, *105*, 1989–1995. X = CH=CH: (b) Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882–2883. (c) Rabideau, P. W.; Hamilton, J. B.; Friedman, L. *J. Am. Chem. Soc.* **1968**, *90*, 4465–4466. (d) Paddick, R. G.; Richards, K. E.; Wright, G. J. *Aust. J. Chem.* **1976**, *29*, 1008–1015. (e) Iwamura, H.; Yoshimura, K. *J. Am. Chem. Soc.* **1974**, *96*, 2652–2654. $X = CH_2CH_2$: (f) Cristol, S. J.; Aeling, E. O. *J. Org. Chem.* **1985**, *50*, 2698–2707 and references cited therein. $X = CHCH_2$ CH: (g) Hemetsberger, H.; Holstein, W.; Weres, F. *Tetrahedron* **1983**, *39*, 1151–1160 and references cited therein.

(46) (a) Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 7103–7107. (b) Trost, B. M. *J. Org. Chem.* **1969**, *34*, 3644–3645. (c) Eberbach, W.; Würsch, P.; Prinzbach, H. *Helv. Chim. Acta* **1970**, *53*, 1235–1249. (d) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3723–3733. (e) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4597–4599.

(47) X = CH=CH: (a) Brewer, J. P. N.; Heaney, H. *J. Chem. Soc., Chem. Commun.* **1967**, 811–812. (b) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 6096–6108. (c) Demuth, M.; Amrein, W.; Bender, C. O.; Braslavsky, S. E.; Burger, U.; George, M. V.; Lemmer, D.; Schaffner, K. *Tetrahedron* **1981**, *37*, 3245–3261 and references cited therein. (d) Bender, C. O.; Bengston, D. L.; Dolman, D.; Herle, C. E. L.; O'Shea, S. F. *Can. J. Chem.* **1982**, *60*, 1942–1952. X = O: (e) Ziegler, G. R.; Hammond, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 513–514. (f) Prinzbach, H.; Würsch, P.; Vogel, P.; Tochtermann, W.; Franke, C. *Helv. Chim. Acta* **1968**, *51*, 911–917. (g) Ziegler, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 446–449. (h) Murty, B. A. R. C.; Kumar, C. V.; Dabral, V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4165–4171. (i) Bartlett, P. D.; Ghosh, T. *Tetrahedron Lett.* **1985**, *26*, 2613–2616. X = NR: (j) Kaupp, G.; Perreten, J.; Leute, R.; Prinzbach, H. *Chem. Ber.* **1970**, *103*, 2288–2301. (k) Swenton, J. S.; Oberdier, J.; Rosso, P. D. *J. Org. Chem.* **1974**, *39*, 1038–1042. (l) Yamada, S.; Sato, S.; Ohashi, M. *Heterocycles* **1984**, *21*, 692. (m) Motyka, L. A. *Tetrahedron Lett.* **1985**, *26*, 2827–2830.

(48) Sedelmeier, G.; Fessner, W.-D.; Grund, C.; Spurr, P. R.; Fritz, H.; Prinzbach, H. *Tetrahedron Lett.* **1986**, *27*, 1277–1280.

(49) Doering, W. v. E.; Roth, W. R.; Breuckmann, R.; Figge, H. J.; Figge, L.; Lennartz, H.-W.; Fessner, W.-D.; Prinzbach, H., unpublished results. The modified MM2 force field, parametrized for radical species (conjugated systems), will be described by: Roth, W. R.; Klärner, F.-G.; Siepert, G.; Fleischer, U.; Lennarzt, H.-W., unpublished results.

(50) Osawa, E.; Aigami, K.; Inamoto, Y. *J. Org. Chem.* **1977**, *42*, 2621–2626.

(51) (a) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3062–3075. (b) Dong, D. C.; Edward, J. T.; *J. Org. Chem.* **1980**, *45*, 2395–2399. (c) Jones, G., II; Becker, W. G.; Chiang, S.-H. *J. Photochem.* **1982**, *19*, 245–251; *J. Am. Chem. Soc.* **1983**, *105*, 1269–1276.

(52) Fukunaga, T.; Clement, R. A. *J. Org. Chem.* **1977**, *42*, 270–275.

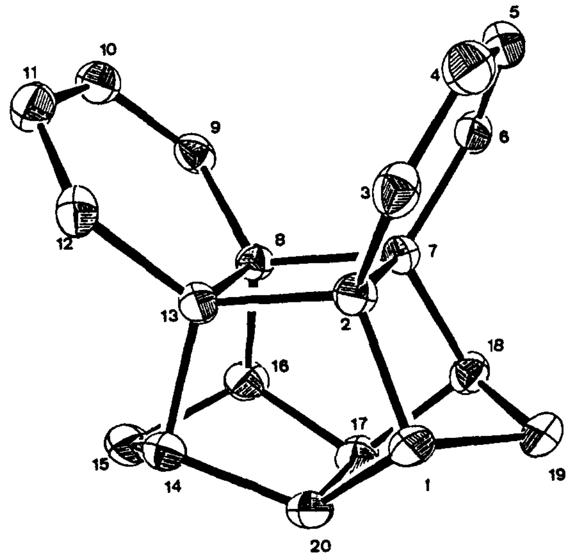


Figure 5. ORTEP diagram of one of the two crystallographically independent molecules of **42**.

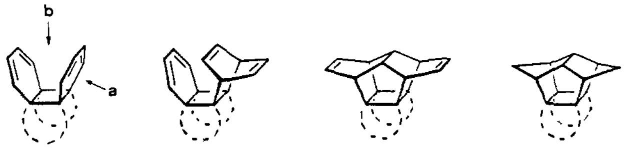
long irradiation time, no noticeable thermal or photochemical side reaction interfered. After partial crystallization of unchanged **18** from the equilibrium mixture, pure tetraene **42** could be isolated only by extensive chromatography because of their similar R_f values. For the scale-up, the necessity for adequate dilution and limitations brought about through the dependency on a high-intensity monochromatic 254-nm light source demands rather extensive labor for the production of large quantities of **42** (Scheme V).

A qualitative explanation for the position of the 7:3 equilibrium can be seen in the correlation (Figures 3 and 4) of relative extinction coefficients of **18** and **42** at 254 nm (i.e., 1100 and 2000, respectively). That the 300-nm irradiation of **18** was unproductive became clear when **42** was found to isomerize into **18** under these conditions. Decisive photomechanistic details for the intriguing intramolecular 1,2–1′,2′ benzene dimerization, supposedly only allowed from S_2 or T_1 excited states,[41] are not yet available.

A comparison of the UV curve of **42** with that of cyclohexadiene[31b] (Figure 4) revealed a red shift with the absorption beginning as high as 350 nm. The tailing stems most likely from an efficient homoconjugative coupling between the syn-oriented butadiene units. This was supported by a detailed PE analysis,[53] which showed a large through-bond ($\beta = -1.5$ eV) and a small through-space ($\beta = -0.25$ eV) contribution. The difference in contributions is in accordance to the specific geometrical arrangement and corresponds well with the $\beta = -1.5$-eV value found for the *anti-o,o′*-benzene dimer **46**.[54]

The space filling models represented in Figure 1 nicely illustrate the change in geometry during the phototransformation of **18** into **42**. For a more precise evaluation of the projected chemistry, an X-ray structural determination of the unique *syn-o,o′*-dibenzene compound **42** was undertaken. Exact structural data were also helpful for a better understanding of its UV and PE spectral idiosyncrasies. The asymmetric unit cell of a tetraene **42** crystal contains two independent molecules. Both show only minimal deviation from C_{2v} symmetry and from each other. The structure of one of these is reproduced in Figure 5. The planar cyclohexadiene rings face each other at an angle of 67.2° and form an interplanar angle of 123.6° with the cyclobutane ring, a situation which is well simulated by semiempirical SCF-MO calculations on the MNDO[6b] level. The transannular distances between opposite sp^2 carbon atoms amount to 3.058 and 4.279 Å. At 1.575 Å, the photochemically formed cyclobutane bonds are somewhat elongated in comparison to the typical value of cyclobutanes (1.55–1.56 Å),[55] an effect which is ascribed to homoconjugative destabilization.[56] For comparison, a selection of experimentally determined bond lengths and angles, averaged over both molecules, are given in Table I together with those as calculated. Considering the known tendency of MNDO to overestimate strained bond lengths, both methods reliably reflect the real situation.

Chart VI



The photoproduct **42** is a bridged derivative of the still elusive *syn-o,o′*-benzene dimer **45**. Whereas the anti isomer **46**[57] fragments readily into benzene (E_A = 26.1 kcal/mol; $\Delta H^{\ddagger}$ = 25.5 kcal/mol; $\Delta S^{\ddagger}$ = 2.3 cal/(mol·grd); $\Delta G^{\ddagger}$ = 24.8 kcal/mol),[58] **42** is extraordinarily stable, a property which is essential for the impending chemistry. In a thorough kinetic study by Roth et al.,[49] the activation parameters for the clean isomerization of **42** into **18** ($\Delta\Delta H_f^\circ$ = −47.2 kcal/mol) at 206 °C in decalin solution were determined to be $\Delta H^{\ddagger}$ = 37.8 kcal/mol and $\Delta S^{\ddagger}$ = 2.9 cal/(mol·grd). This activation barrier is ca. 8 kcal/mol higher than expected on the basis of the calculated $\Delta\Delta H_f^\circ$ for **42**/**41** (29.7 kcal/mol). It is suggested that the rigidity of the framework prohibits the stepwise radical opening and, instead, the symmetry-forbidden concerted mechanism is operative.[49]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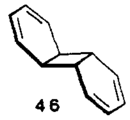
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Stage 3: Pagodanes

With the acquisition of **42**, the stage was now set for the formation of the second birdcage unit of pagodane, as formulated in Chart III. Conceptually, a domino Diels–Alder reaction[59] of an acetylene equivalent[60] to a diene unit of M (Chart VI) would ideally meet this requirement. In the primary adduct O, the inner bicyclo[2.2.2]octadiene C=C double bond is perfectly oriented for a subsequent intramolecular Diels–Alder reaction to give the [2.2]pagodane fragment P. By this multiple cycloaddition sequence, four new C–C single bonds and two more cyclopentane rings are created. Moreover, all six remaining methine groups are adjusted stereospecifically into the desired all-cis-syn-fused geometry. The last four cyclopentane rings for the [1.1.1.1]pagodane architecture (cf. Q) could then be introduced by ring contractions at the ethylene bridges. From a consideration of the specific steric relationships within **42**, as revealed by the X-ray analysis, a significant steric hindrance toward dienophile additions was expected, since not only are the inner cyclohexadiene faces mutually shielded, but their outer faces are partially obstructed by the *syn*-methylene hydrogens situated directly in front. Consequently, an uncertainty existed with respect to the relative rates of addition of dienophiles and the thermal isomerization back to **18**. Notwithstanding, an outside *domino*-type addition, along

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(53) Gleiter, R.; Zimmermann, H.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.* **1985**, *118*, 3856–3860.

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(59) (a) Paquette, L. A.; Wyvratt, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 4671–4673. (b) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *Ibid.* **1978**, *100*, 5845–5855.

(60) De Lucchi, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585–2632.

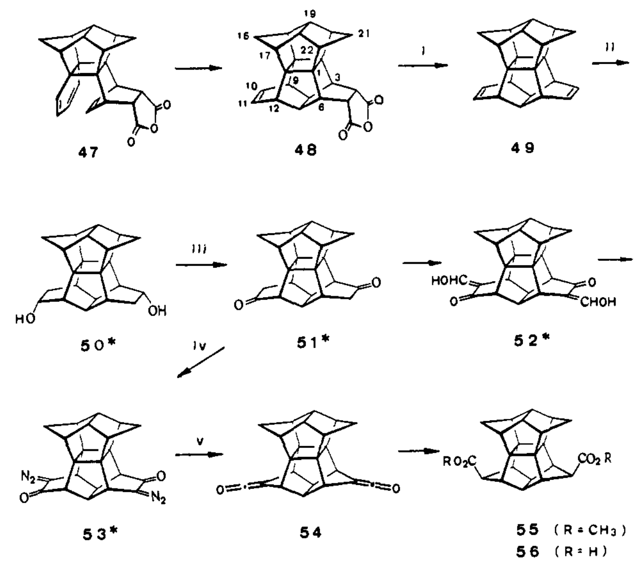
coordinate *a*, to the tetraene **42** should be far more favorable than an inside *pincer*-type addition, along coordinate *b*, which would be only possible (if at all) with sterically undemanding sp-hybridized dienophiles.

Initially, phenyl vinyl sulfoxide was considered, as the intermediate cycloadducts readily eliminate phenylsulfenic acid to directly introduce the desired double bond.[61] When heated with the tetraene **42** at 140 °C, only slow isomerization of **42** to **18** occurred, and no Diels–Alder adduct was observed. Control experiments with sterically unhindered 1,3-cyclohexadiene showed that such a cycloaddition can only be brought about at temperatures approaching 190 °C. At this temperature, the half-life of **42**, as evident from the kinetic studies, is too short to permit its efficacious preparative utilization. (*E*)- and (*Z*)-1,2-bis(phenylsulfonyl)ethylenes are also highly reactive acetylene equivalents,[62] but both failed to add to **42**, probably due to their rather low solubility as well as the steric hindrance arising from the relatively bulky phenylsulfonyl substituents and the shielded character of the diene.

With maleic anhydride as the classic dienophile, the elaboration of **42** into the pagodane framework was rendered an easy matter. On adding this reagent to a benzene solution of **42**, the lime-yellow color of a charge-transfer complex instantly developed and slowly faded when the solution was heated to 80 °C. According to TLC and ^{1}H NMR analyses, a single product was formed stereospecifically and was isolated in quantitative yield. This colorless crystalline material was characterized as a 1:1 adduct by elemental analysis for $C_{24}H_{20}O_3$. The number, shape, and relative locations of the signals in both ^{1}H and ^{13}C NMR spectra are consistent only with the formation of C_s symmetrical domino structure **48** as arising from an external attack. In particular, the presence of only one type of olefinic resonance, integrating for two hydrogen and carbon atoms each, rules out any alternative structure of lower intricacy such as **47**. Despite the complexity of the molecule, all proton resonances were sufficiently resolved to be unambiguously assigned. The two sets of 10 protons for each half of the molecule, although isolated from each other by the cyclobutane ring with respect to vicinal coupling, are interrelated by an unusual, but diagnostic, five-bond zig-zag coupling of less than 1 Hz between the bridgehead protons of the norbornane units and those of the bicyclo[2.2.2]octane moieties across the common cyclobutane bond (e.g., 3-H/22-H). The individual methylene hydrogens can be easily distinguished because only the inner (syn[63]) ones couple to the norbonane exo hydrogens (e.g., 16-syn-H/18-H). A further zig-zag coupling (<1 Hz) over six bonds between these two syn hydrogens was revealed on homonuclear decoupling experiments. This kind of relationship is typical for *endo,endo*-dimethanonaphthalene and other birdcage-type systems. The anti orientation of the anhydride moiety, as expected by an endo-type addition in accordance to the Alder rule, was elucidated by the absence of any compressional effect upon the opposite syn hydrogen.[64] Despite a thorough search for the intermediate adduct **47**, under no circumstances could its intermediacy be detected or established.

The two-step sequence of photochemical and thermal cycloadditions, which dramatically alters the molecular topology from the cyclophane **18** into the pagodane **48**, proved to be readily amenable to large-scale preparations with excellent overall efficiency. The rather laborious purification of the photoproduct **42** could be avoided, for the crude photolysis mixture could be used directly for the addition with maleic anhydride. Subsequent workup amounted only to simple column filtration of the product mixture. Unreacted dibenzo compound (**18**) was conveniently recovered for recycling by elution with carbon tetrachloride whilst further elution with methylene chloride furnished the more polar adduct **48** together with excess maleic anhydride. The latter was expeditiously removed by sublimation (Scheme VI).

Scheme VI[a]



[a] (i) Cu_2O/bipyridyl/H_2O/quinoline, 100–150 °C/6 h, reflux/30 h; (ii) B_2H_6/THF, 0 °C → room temperature/4 h, NaOH/H_2O_2, 0 °C → room temperature/2 h; (iii) Jones reagent/acetone, 0 °C → room temperature/2 h; (iv) $HCOOCH_3$/NaH/THF/catalytic MeOH, room temperature/6 h, 40 °C/16 h HOAc; *p*-TsN_3/NEt_3, room temperature/2 h; (v) CH_3OH, high-pressure Hg lamp, pyrex, room temperature/7 h. * Mixture of regioisomers.

With the principal [2.2.1.1]pagodane skeleton firmly established, the degradation of the anhydride functional group to an olefinic moiety was now called for to regain the economically important symmetry of the system. Direct catalytic decarboxylation of anhydrides to olefins with $Ni(CO)_2(Ph_3P)_2$ in refluxing diglyme[65] has facilitated the efficient synthesis of many unsaturated compounds that are otherwise difficult to obtain.[60] In contrast, conversion of **48** to diene **49** required far more drastic conditions than expected and consumed much more than catalytic amounts of the expensive nickel complex. On a small scale, in refluxing triglyme, less than 50% conversion took place after 13 h with 0.6 equiv of catalyst. Since this procedure was unsatisfactory for the preparation of **49** in synthetically useful quantities, an alternative method had to be sought. Standard saponification of **48** and decarboxylation of the resultant diacid with complexed Cu_2O in hot quinoline[66] afforded the diene **49** in 68% yield. On the all too simple idea that water is consumed on hydrolysis of **48** yet is eliminated on decarboxylation of the corresponding diacid, treatment of the anhydride **48** with Cu_2O in quinoline in the presence of a small amount of water delivered **49** directly in ca. 80% overall yield. In comparison, the diacid was converted to the same product in only 34% yield through conventional lead tetraacetate treatment.[67] Both ^{1}H and ^{13}C NMR spectra of the beautifully crystalline diene **49** exhibit only seven absorptions each, as expected from its inherent C_{2v} symmetry. Upon catalytic hydrogenation, the parent [2.2.1.1]pagodane **57** was obtained.

At this point, further modification of **49** to provide the [1.1.1.1]pagodane framework was limited to the removal of two of the equivalent trigonal carbon atoms. The symmetry elements

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(61) Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597–1599.

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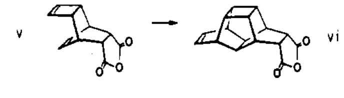
(63) The IUPAC rules do not give a definitive *and* perceptive stereochemical description for substituents at ethylene or methylene bridges of such polycycles. The syn/anti terminology is used throughout in the sense of the relative orientation with respect to the central cyclobutane ring.

(64) Further corroboration of this aspect stems from a spectral comparison with the anhydride vi,[82] which was synthesized via the known endo cyclooctatetraene–maleic anhydride adduct v: Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1–92.



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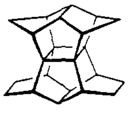
intrinsic to **49** allowed all subsequent chemical changes to be implemented concurrently at an independent pair of reaction centers and thus amounted to the manipulation of only a single type of functional group. As each nonbonded pair of unsaturated centers in **49** is interrelated by only one of *two different* symmetry operators (i.e., the C_2 axis or one of the two mirror planes), functional changes which break the molecular symmetry consequently lead to *two subgroups* of products that have either C_2, or C_s symmetry. Specifically directed introduction of one of these symmetry elements or the separation of the components was uncalled for, however, as both series return to the same C_{2v} symmetrical intermediate en route to the target molecule **1**.

Additional complications had to be considered from stereochemical ambiguities arising from syn or anti reagent approach. Attack from an anti direction seemed likely to be highly favored over a syn approach which encounters steric interference from the opposite inner methylene hydrogens. To this end, the behavior of **49** toward epoxidation was examined. With two equivalents of *m*-chloroperbenzoic acid at 0 °C, conversion to a single diepoxide occurred in excellent yield with no indication of even a trace amount of any stereoisomer. The maintenance of C_{2v} symmetry was apparent from the simple ^{1}H NMR spectrum while nuclear Overhauser correlation of the oxirane α-protons to the *syn*-methylene hydrogens confirmed the anti stereochemistry as assigned in **58**.



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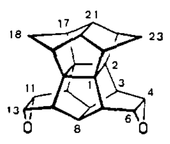
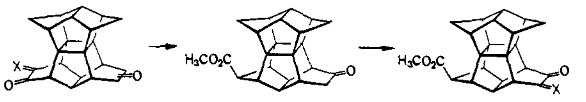


58

A most efficient and standard method for achieving ring contractions even in highly strained systems is the well-known photo–Wolff rearrangement of a diazoketone (viz., **53**). For this purpose, diene **49** was subjected to exhaustive hydroboration/oxidation to give stereochemically homogeneous *anti,anti*-diols **50** in 96% yield. The employment of a large excess of diborane was necessary to prevent the formation of insoluble polymeric alkylboranes and incomplete conversion. While milder methods such as Collins or pyridinium dichromate oxidations suffered from the low solubility of the diols in compatible solvents, essentially quantitative conversion to a 1:1 statistical mixture of C_s/C_2 isomeric diones **51** was achieved by Jones oxidation of the diols without skeletal rearrangement. The C_s isomer could be partially enriched by crystallization from ether–hexane, which enabled the complete assignment of all proton NMR signals. The number of carbon signals corresponded well to the existence of two regioisomers, 13 signals for the C_s and 12 for the C_2 isomer. Efforts were undertaken to adapt shorter, one-pot procedures for the direct oxidation of the diene **49** into **51**. Palladium-copper-catalyzed oxidation of **49** using Wacker-type methodology[68] or chromic acid oxidation in the presence of $Hg(OAc)_2$[69] was exceedingly slow and gave rise to numerous byproducts. Alternatively, immediate Jones oxidation of the alkylborane[70] obtained by hydroboration in benzene, rather than the recommended tetrahydrofuran or ether solvents which were also affected, afforded the diketones **51**, albeit in significantly lower yield (ca. 65%) as compared to the original two-step procedure.

All attempts to achieve direct diazo-group transfer[71] to diones **51** failed. The α-methylene group apparently requires activation, so the diones were transformed into bis(α-formyl) diketones **52** by condensation with an excess of methyl formate.[72] Upon treatment with *p*-toluenesulfonyl azide, smooth conversion into bisdiazodiketones **53** proceeded. From the standpoint of minimal manipulation, isolation of the bisformylated compounds was not required. After extensive experimentation, a one-pot formylation/diazotization procedure was developed whose efficiency (77% isolated yield) served best our needs. From the crude oily 1:1 mixture of regioisomers, the pure C_2 isomer could be easily isolated as deep-yellow crystals by trituration with methanol. In a pure crystalline state, the bisdiazodiketones **53** proved to be stable for months, even at room temperature, if protected from light and moisture.

Scheme VII



59 (X = CHOH)
60 (X = N_2)
61
62 (X = CHOH)
63 (X = N_2)

When a dilute methanol solution of the isomers **53** was irradiated with the Pyrex-filtered light of a high-pressure mercury lamp, the yellow color of the solution slowly faded and a single, sparingly soluble product precipitated as colorless needles and was isolated in almost quantitative yield. The ^{1}H NMR spectrum of this material shows one methoxyl singlet, one kind of methylene AB pattern, and absorptions for five different methine groups. Taken into account with the nine-line ^{13}C NMR spectrum, the product had to be a C_{2v} symmetrical [1.1.1.1]pagodane diester with either syn,syn- or anti,anti-orientated ester groups. The thermodynamically unfavorable syn,syn configuration, consistent with a kinetically controlled anti capture of methanol from intermediate ketenes (viz., **54**) to give **55**, was deduced from NOE measurements and finally confirmed by X-ray crystal structure determination (vide infra).[2] Although the photolysis could be scaled up with ease by use of an appropriate light source (Hanau TQ-2024, 2000 W), this transformation was somewhat capricious, and good yields could only be obtained when conditions of high dilution were met.

The twofold ring contraction procedure **53** to **55** could also be carried out in a sequential manner as in the bisformylation of diketone **51**, the second step (i.e., the formylation of the **59** anion) required forcing conditions. From the reaction with only slight excess of reagents at room temperature, the monoformyl diketone **59** could be isolated as the predominant product. Diazotization to monodiazodiketone **60**, followed by photolysis in methanol, led to the keto ester **61**, a representative derivative of the [2.1.1.1]-pagodane series. Repetition of the above sequence produced the corresponding formyl keto ester **62** and diazoketo ester **63**. Wolff rearrangement of the latter cleanly afforded the diester **55** (Scheme VII).

With the first [1.1.1.1]pagodane derivative successfully synthesized, the matter of gaining access to the parent hydrocarbon **1** had to be addressed. The degradation of the ester functions of **55** was effected on the corresponding diacid **56**, prepared either by hydrolysis of the diester or by irradiation of the bisdiazoketones **53** in aqueous tetrahydrofuran. Iododecarboxylation[73] of **56** produced an epimeric mixture of diiodides **64**, from which the anti,anti epimer was crystallized selectively from acetone for characterization purposes. Reduction of the iodides **64** with Na-K alloy/*tert*-butyl alcohol in tetrahydrofuran solution delivered the title compound **1** quantitatively. This procedure proved superior to the use of zinc/acetic acid because of the poor solubility of starting material and product in the latter solvent. The highly crystalline, $C_{20}H_{20}$ undecacyclic polyquinane **1** melts at 243 °C, ca. 40 °C above the melting point of the higher [2.2.1.1] homologue. It is barely soluble in most organic solvents and only moderately soluble in benzene or chloroform. Upon heating (140 °C/14 mm), the compound easily sublimes to form small, shiny

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(68) (a) Fahey, D. R.; Zuech, E. A. *J. Org. Chem.* **1974**, *39*, 3276–3277. (b) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415–2434. (c) Tsuji, J. *Synthesis* **1984**, 369–384.

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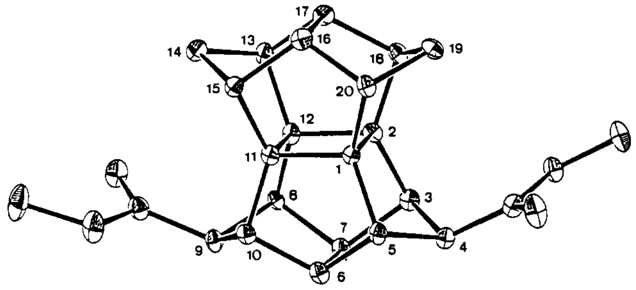
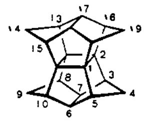


Figure 6. ORTEP diagram of **55**.

twinned crystals. The presence of a dominant molecular ion peak and almost no significant fragmentation in the mass spectrum attests to the high stability of the exceedingly rigid carbocyclic pagodane framework. Both the high-field ^{1}H and ^{13}C NMR spectra displayed only four groups of absorptions each, in response to the unusual influence of three mirror planes of the D_{2h} point group symmetry acting upon the four interwoven norbornane units. The ^{1}H–^{13}C coupling constants for the bridgehead methines of 139 and 141 Hz demonstrated their pronounced s-type character, an attribute typical for strained hydrocarbons.

		(δ, CDCl$_3$)	^{1}H-NMR	^{13}C-NMR
	C- 1,- 2,-11,-12			62.9
	C- 4,- 9,-14,-19	1.56(s)	1.60(a)	41.9
	C- 3,- 5,- 8,-10, -13,-15,-18,-20		2.24	42.7
	C- 6,- 7,-16,-17		2.60	59.6

To shed some light on the actual bonding situation prevailing in the strained polycyclic system and to enable more concise assessment of further transformations into dodecahedranes, crystals of diester **55** were subjected to X-ray structure analysis. As shown in Figure 6, the molecule adopts an axial symmetry which is only slightly offset by packing effects. Most remarkable, in respect of the projected "opening" of pagodane into the dodecahedrane sphere, is the rather unusual length of the lateral C1–C2/C11–C12 cyclobutane bonds of 1.59 Å, which is only rivaled by the exceptionally elongated outer C6–C7/C16–C17 bonds (ca. 1.62 Å). In comparison with their frontal C1–C11/C2–C12 counterparts (1.55 Å) or with those of structurally related compounds like dinitrobirdcage,[74] [4]peristylanedione,[75] or pentaprismanecarboxylic acid[76] (all around 1.56 Å), our expectations seemed justified that these pivotal bonds should bear a major part of the high molecular strain enforced by the particular arrangement of multiple bridgings. Indeed, in the comparison of the averaged experimental data with values predicted for **55** and **1** by force field and SCF-MO methods (Table II), again a quite satisfactory compatibility can be seen.

In the pursuit of a derivative of **1** which might be a helpful precursor for effecting the ultimate step for a conversion into dodecahedranes, efforts were subsequently directed toward the synthesis of [1.1.1.1]pagodane-4,9-dione (**70**). From strategic considerations, bis(α-diketone) **67** appeared to be a logical precursor, since benzilic acid type ring contraction and oxidative decarboxylation of the resulting α-hydroxy carboxylic acids have high-yielding precedents.[77] Numerous attempts were made to oxidize diones **51** with selenium dioxide under widely varied conditions. On all occasions, deep orange-yellow products were obtained which slowly deposited elemental selenium to leave a colorless intractable material. Singlet oxygen treatment of enamino ketones **65**,[78] accessible from condensation of **51** with *tert*-butoxybis(dimethylamino)methane, gave no evidence for the formation of the tetraketone **67**. Similarly, attempted ozonolytic cleavage of the α,β-unsaturated ketones **65** and **66** were all uniformly unsuccessful and always led to colorless amorphous products, presumably polymeric hydrates. Although conceptually short, this route was abandoned. Ozonolysis of the reactive ketene intermediates[79] (e.g., **54**) to prepare the diketone **70** directly was also consistently disappointing. An alternative procedure was

Table I. Selected Experimental (Av) and Calculated Structural Data for **42**

	exptl	MM2	MNDO
	Bond Lengths, Å		
1–2	1.545	1.535	1.573
1–19	1.530	1.533	1.554
1–20	1.537	1.539	1.565
2–3	1.495	1.493	1.496
2–7	1.553	1.550	1.607
2–13	1.575	1.540	1.578
3–4	1.328	1.340	1.354
4–5	1.453	1.453	1.466
17–20	1.555	1.549	1.595
	Nonbonded Distances, Å		
3–12	3.058	2.945	3.064
4–11	4.279	4.131	4.326
	Bond Angles, deg		
2–1–19	102.6	104.0	103.8
2–1–20	101.2	101.4	102.0
19–1–20	103.4	103.8	103.4
1–2–3	116.1	117.8	116.7
1–2–7	103.4	103.0	102.6
1–2–13	107.5	108.1	107.7
3–2–7	116.3	115.6	115.8
3–2–13	119.7	118.1	119.8
7–2–13	90.0	90.0	90.0
14–15–16	95.6	93.9	95.1
1–20–14	109.1	108.2	108.2
1–20–17	103.4	103.0	102.9

Table II. Selected Experimental (Av) Structural Data of **55** and Calculated Data of **1**

	exptl (**55**)	MM2 (**1**)	MNDO (**1**)
	Bond Lengths, Å		
1–2	1.589	1.549	1.614
1–11	1.552	1.521	1.570
1–20	1.536	1.522	1.548
13–14	1.558	1.535	1.558
13–17	1.544	1.552	1.577
16–17	1.625	1.565	1.604
	Nonbonded Distances, Å		
4–19	3.611	3.504	3.570
	Bond Angles, deg		
1–2–12	90.0	90.0	90.0
1–2–18	103.3	103.6	103.2
1–11–15	108.8	109.6	108.8
2–18–17	99.5	98.8	100.2
2–18–19	105.2	104.8	104.3
3–2–18	132.9	131.6	133.5
13–14–15	95.0	95.0	96.1
14–15–16	103.0	103.1	102.5
15–16–17	102.6	103.0	103.1
15–16–20	110.9	110.0	109.1
	Torsional Angles, deg		
1–2–12–13	104.1	104.4	103.9
1–11–12–13	109.4	110.2	109.4
3–2–1–20	141.1	139.6	141.3
3–2–12–13	151.3	151.1	152.2
13–17–16–20	115.1	114.4	113.5

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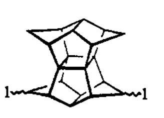
searched for, further afield. The copper-catalyzed oxidative cleavage of α-branched aldehydes is reported to give good yields of ketones having one less carbon atom.[80] With this in mind, the diester **55** was reduced with lithium aluminum hydride to the diol **68** and oxidized to the corresponding unstable dialdehyde with pyridinium dichromate. When the crude dialdehyde was subjected to the reported reaction conditions, among the miscellany of products produced, a small amount of **70** was detected. Ultimately, the desired pagodanedione **70** was obtained satisfactorily by way of **69** derived from bissulfenylation of diester **55**. The crowded environment around the ester functions in **69** inhibits their free rotation as is evident from the presence of two sets of signals in the ^{1}H NMR spectrum, one each for C_2 and C_s atropisomers. The chemical consequence of this phenomenon was encountered by the reluctance of the diester toward standard hydrolysis. When **69** was carried through the three-step sequence[81] of saponification with potassium hydroxide in refluxing glycol, oxidation to a hemithioacetal, and hydrolysis without isolation of the intermediates, overall yields of 80–90% could be achieved.

The diketone **70** crystallizes as large colorless spars and melts with decomposition at 321–323 °C. The strain inherent in the norbornanone substructure is apparent by a IR carbonyl absorption at 1755 cm^{-1} and in the mass spectrum by the ease in which **70** (*m/e* 288, 100%) loses two molecules of carbon monoxide (*m/e* 232, 70%). The C_{2v} symmetry is reflected in the simplicity of both the ^{1}H and ^{13}C NMR spectra, the relative chemical shifts of which are reminescent to those of the structurally related birdcage diketone.[82] Similar spectral correlations are also found between pagodanes **1**, **49**, and **57** and the corresponding birdcage-type systems.[82]



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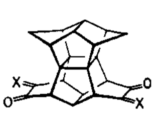
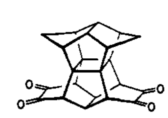
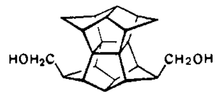


65 (X = CHN(CH$_3$)$_2$)
66 (X = CHC$_6$H$_5$)



67



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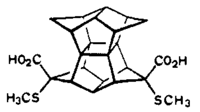

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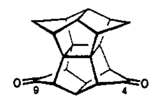

70

Summary and Outlook

Although the synthesis of [1.1.1.1]pagodane **1** from isodrin (**3**) requires a total of ca. 45 functional changes, these could be concentrated into 14 one-pot manipulations making our detailed, optimized protocol highly efficient. An overall yield of ca. 24% has thereby been obtained which implies remarkable yields of 90% per step or 97% per functional change.

The arrival at pagodane **1** and the related diketone **70** has now allowed the preparation of sufficient multigram quantities of material for us to continue our conquest of dodecahedranes. Still, two bottlenecks remain in the path from isodrin (**3**): the dehydrogenation of **15** to **18** and the photocyclization of **18** to **42**. At present, only the conversion of decagram amounts of compound can be carried out at one time, and the production of hectogram quantities **18** and **42** remains rather labor intensive.

Important extensions of this work are now being aimed at the repetition of the sequence from **3** to **1** with disubstituted derivatives of diene **27** such that [1.1.1.1]pagodanes with all four methylene units functionalized can be prepared. Stereospecific domino Diels–Alder reactions of **42** with a variety of heterodienophiles have opened up the way to heteropagodanes and heterododecahedranes.[2b,83]

In our preliminary investigations, catalytic transformation of **1** has indeed led to **2**, if only in poor yields,[2b,13] so far. The inefficacious efforts to bring about the isomerization of **1** into **2** under superacidic conditions were compensated by the discovery of a unique 2π-aromatic cyclobutanoid dication of theoretical relevance.[84] The intricacies of these one/two electron oxidations were unraveled by cyclic voltammetric, ESR, and electron-stripping studies[85] and revealed an intimate relationship between the stability of these radical cations/dications and the respective frameworks.

The possibility for broad variations of functionality within the pagodane system I (Chart III) highlights its versatility as a precursor for a multitude of polycyclic compounds featuring fascinating molecular architecture.

Experimental Section

(1α,2α,3β,6β,7α,8α,9β,10α,13α,14β)-3,4,5,6,10,11,12,13,17,17-Decachlorohexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-4,11-dien-16-one Dimethyl Acetal (6).[17] A mixture of isodrin **3** (600.0 g, 1.64 mol) and tetrachlorocyclopentadienone dimethyl acetal **4** (480.0 g, 1.82 mol) was heated at 110 °C for 48 h. The resulting crystalline solid was allowed to cool to 70–80 °C and dissolved in hot chloroform (2.2 L). Upon dilution with methanol (3.5 L) and cooling to 0 °C, with mechanical stirring, the adduct crystallized as fine, colorless needles which were filtered off, washed with methanol (400 mL), and dried under vacuum. The mother liquors were concentrated to afford a second crop of slightly colored crystals; total yield 975.0 g (94%); mp 184 °C [lit.[17] 189 °C]; ^{1}H NMR (250 MHz) δ 3.61 (s, OCH$_3$), 3.52 (s, OCH$_3$), 3.16 (m, 9-, 14-H), 2.75 (m, 1-, 8-H), 2.73 (s, 2-, 7-H), 1.81 (dm, 15s-H), 1.19 (dm, 15a-H); ^{13}C NMR (20.2 MHz) δ 131.9, 129.8 (C-4, -5, -11, -12), 113.9 (C-16), 109.4 (C-17), 79.1, 76.8 (C-3, -6, -10, -13), 56.2 (C-9, -14), 52.6 (OCH$_3$), 51.6 (OCH$_3$), 51.2 (C-2, -7), 39.4 (C-15), 38.0 (C-1, -8).

(1α,2β,3α,6α,7β,8α,9β,10β)-1,8,9,10,11,11-Hexachloro-4,5-(tetrachlorobenzo)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (9).[17] **A. Hydrolysis and Thermolysis of 6.** A mechanically stirred suspension of finely crystallized or pulverized **6** (315.0 g, 0.50 mol) in concentrated sulfuric acid (600 mL) was heated at 80 °C for 2 h at which time the temperature was gradually raised to 140 °C over 4 h with vigorous stirring. **Caution**: evolution of carbon monoxide caused the syrupy mixture to increase in volume! Heating at 140 °C was continued for 1 h, and then the slurry was cooled and carefully poured on to crushed ice (ca. 5 kg). The precipitated product was collected by suction filtration through a sintered glass filter funnel, and the residue was washed successively with water and methanol to give, after drying in vacuo, pure **9** as a colorless microcrystalline solid (267.0 g, 96%).

B. Cycloaddition of 3 with 5. A solution of isodrin **3** (10.0 g, 27.4 mmol) in carbon tetrachloride (100 mL) was refluxed with tetrachlorothiophene 1,1-dioxide **5** (7.4 g, 29.1 mmol) under nitrogen for 2 h during which sulfur dioxide was evolved and a microcrystalline solid deposited. Ethanol (200 mL) was added and, after concentration to 50 mL, the precipitate was isolated by suction filtration. Washing with cold ethanol and drying in vacuo provided pure **9**: 15.2 g, 100%; mp 295 °C [lit.[17] 298 °C]; IR (KBr) 3045, 2975, 2940, 2880, 1370, 1345, 1275, 1215, 1020, 915, 875, 745, 700 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.91 (m, 3-, 6-H), 3.76 (s, 9-, 10-H), 3.65 (m, 2-, 7-H), 2.25 (dt, 12s-H), 1.97 (dt, 12a-H); ^{13}C NMR (20.2 MHz) δ 143.0 (C-4, -5), 132.1, 128.2 (C-3′, -4′, -5′, -6′), 100.4 (C-11), 75.3 (C-1, -8), 58.4 (C-9, -10), 57.5 (C-12), 52.5 (C-2, -7), 46.0 (C-3, -6).

(1α,2β,3α,6α,7β,8α)-4,5-Benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (10).[17] To a hot, vigorously stirred mixture of **9** (300.0 g, 0.54 mol), *tert*-butyl alcohol (1.0 kg, 13.49 mol), and dry tetrahydrofuran (2.0 L) under a nitrogen atmosphere was added granular lithium (110.0 g, 15.85 mol) in 3–5-g portions such that the reaction mixture remained at gentle reflux. The mixture was refluxed for a further 15 h, cooled to room temperature, diluted with petroleum ether (800 mL), and decanted on to crushed ice (ca. 2 kg). The organic phase was washed with water several times and dried. Concentration and distillation (92–95 °C at 0.1 mm) of the resulting yellow oil furnished pure **10** (105.0 g, 93%) with an intense characteristic odor. The colorless viscous oil solidified on cooling to −20 °C: ^{1}H NMR (250 MHz) δ 6.98 and 6.91 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 4.70 (m, 9-, 10-H), 3.07 (m, 3-, 6-H), 2.96 (m, 2-, 7-H), 2.52 (m, 1-, 8-H), 1.93 (unresolved AB, 12-H), 1.48 (dm, 11s-H), 1.40

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(dm 11a-H); ^{13}C NMR (20.2 MHz) δ 146.2 (C-4, -5), 128.9 (C-9, -10), 125.7 (C-4′, -5′), 122.0 (C-3′, -6′), 56.7 (C-12), 56.3 (C-11), 47.8 (C-2, -7), 46.1 (C-3, -6), 44.1 (C-1, -8).

(1α,2α,3β,6β,7α,8α,9β,10α,13α,14β)-11,12-Benzo-3,4,5,6-tetrachlorohexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-4,11-dien-16-one Dimethyl Acetal (11). A mixture of **10** (300.0 g, 1.44 mol), **4** (420.0 g, 1.59 mol), and xylene (200 mL) was refluxed for 12 h under a nitrogen atmosphere. After cooling to 80 °C, the mixture was diluted with methanol (500 mL) and further cooled to 0 °C with stirring. The precipitated crystals were isolated by filtration, washed with methanol, and dried in vacuo to give pale-yellow crude **11** (537.0 g, 79%). An analytical sample was obtained as colorless crystals by sublimation (160 °C, 20 mm): mp 163–164 °C; IR (KBr) 3040, 3020, 2980, 2950, 2800, 1600, 1460, 1215, 1190, 1115, 995, 810, 780, 755 cm^{-1}; UV (CH$_3$CN) $\lambda_{\max}$ (ε) 278 (620), 271 (670), 264 (490), 220 nm (9200); ^{1}H NMR (250 MHz) δ 7.22 and 7.13 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 3.34 (s, OCH$_3$), 3.23 (m, 10-, 13-H), 3.13 (s, OCH$_3$), 2.70 (m, 9-, 14-H), 2.39 (m, 1-, 8-H), 2.19 (m, 2-, 7-H), 2.01 (dm, 17s-H), 1.91 (dm, 17a-H), 1.63 (dm, 15s-H), 1.24 (dm, 15a-H); ^{13}C NMR (25.2 MHz) δ 147.5 (C-11, -12), 129.5 (C-4, -5), 125.6 (C-4′, -5′), 122.8 (C-3′, -6′), 113.5 (C-16), 77.4 (C-3, -6), 60.7 (C-17), 52.1 (OCH$_3$), 51.5 (OCH$_3$), 50.9 (C-2, -7), 48.2 (C-9, -14), 46.1 (C-10, -13), 41.8 (C-15), 38.9 (C-1, -8).

Anal. Calcd for $C_{23}H_{22}Cl_4O_2$ (472.24): C, 58.51; H, 4.70; Cl, 30.03. Found: C, 58.24; H, 4.79; Cl, 30.11.

(1α,2α,3β,6β,7α,8α,9β,10α,13α,14β)-11,12-Benzohexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-4,11-dien-16-one Dimethyl Acetal (12). Sodium (221.0 g, 9.61 mol) in toluene (1.3 L) was heated under a nitrogen atmosphere until the metal melted. The molten mass was cooled with vigorous stirring to give course granules which were rinsed with dry tetrahydrofuran (250 mL) after decanting off the toluene. A solution of the crude adduct **11** (377.8 g, 0.80 mol) in tetrahydrofuran (2.0 L) was added, and upon heating to gentle reflux, *tert*-butyl alcohol (297.0 g, 4.00 mol) was added over 45 min with efficient stirring. After 30 min, further *tert*-butyl alcohol (297.0 g) was added in one portion. The mixture was refluxed until the remaining sodium had fused to a single globule (ca. 24 h), then cooled to room temperature, and decanted on to crushed ice (ca. 4 kg). After addition of petroleum ether (500 mL), the aqueous layer was separated and extracted with petroleum ether (total 500 mL). The combined organic layers were washed thoroughly with water, dried, and evaporated after filtration through silica gel (ca. 50 g) to yield crude **12** (253.0 g, 95%) as a tan solid which was contaminated with its 4,5-dihydro derivative **19** (ca. 10% by ^{1}H NMR). Chromatography on silica gel (methylene chloride elution) and sublimation (130 °C, 20 mm) afforded an analytical sample: mp 126–127 °C; IR (KBr) 3060, 2940, 2930, 2880, 2830, 1465, 1460, 1445, 1265, 1150, 1105, 1070, 1040, 760, 740 cm^{-1}; UV (CH$_3$CN) $\lambda_{\max}$ (ε) 277 (550), 270 (600), 263 (500), 220 nm (5500); ^{1}H NMR (250 MHz) δ 7.19 and 7.06 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 5.94 (m, 4-, 5-H), 3.15 (m, 10-, 13-H), 2.91 (s, OCH$_3$), 2.69 (s, OCH$_3$), 2.65 (dm, 15s-H), 2.56 (m, 9-, 14-H), 2.51 (m, 3-, 6-H), 2.18 (m, 1-, 8-H), 1.97 (dm, 17s-H), 1.88 (dm, 17a-H), 1.74 (m, 2-, 7-H), 0.89 (dm, 15a-H); ^{13}C NMR (25.2 MHz) δ 148.3 (C-4, -5), 134.3 (C-11, -12), 124.9 (C-4′, -5′), 121.0 (C-16), 122.3 (C-3′, -6′), 61.1 (C-17), 51.9 (OCH$_3$), 50.3 (C-2, -7), 49.7 (OCH$_3$), 49.1 (C-10, -13), 46.4 (C-3, -6), 44.3 (C-15), 42.1 (C-1, -8), 40.5 (C-9, -14).

Anal. Calcd for $C_{23}H_{26}O_2$ (334.46): C, 82.61; H, 7.84. Found: C, 82.68; H, 8.04.

(1α,2α,3β,6β,7α,8α,9β,10α,13α,14β)-11,12-Benzohexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-4,11-dien-16-one (15). A solution of crude **12** (67.0 g, ca. 0.20 mol) in methylene chloride (500 mL) was vigorously stirred with 30% sulfuric acid (500 mL) for 16 h. The aqueous layer was separated and extracted with methylene chloride. The combined organic layers were washed successively with water and saturated sodium bicarbonate solution and dried. Evaporation at room temperature left crude **15** (55.0 g, 95%) as a light-brown solid which was recrystallized from methanol–chloroform (10:1) at −20 °C to give colorless crystals: mp 135 °C dec; IR (KBr) 3000, 2960, 2940, 2900, 1790, 1760, 1465, 1455, 765, 740 cm^{-1}; UV (CH$_3$CN) $\lambda_{\max}$ (ε) 278 (620), 272 (670), 264 (500), 220 nm (5800); ^{1}H NMR (250 MHz) δ 7.14 and 7.00 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 6.24 (m, 4-, 5-H), 3.19 (m, 10-, 13-H), 2.63 (m, 3-, 6-H), 2.57 (m, 9-, 14-H), 2.35 (m, 1-, 8-H), 2.01 (dm, 17s-H), 1.86 (dm, 17a-H), 1.70 (m, 2-, 7-H), 0.96 (dm, 15a-H); ^{13}C NMR (25.2 MHz) δ 199.4 (C-16), 147.6 (C-11, -12), 131.9 (C-4, -5), 125.3 (C-4′, -5′), 122.8 (C-3′, -6′), 60.3 (C-17), 51.7 (C-3, -6), 50.6 (C-9, -14), 46.1 (C-10, -13), 44.2 (C-2, -7), 43.1 (C-15), 38.4 (C-1, -8).

Anal. Calcd for $C_{21}H_{20}O$ (288.39): C, 87.45; H, 6.99. Found: C, 87.40; H, 7.23.

(1α,2β,3α,6α,7β,8α,9α,14α)-4,5-Benzopentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadeca-4,10,12-triene (14). A. Decarbonylation of 15. A solution of crude **15** (144.0 g, ca. 0.50 mol) in carbon tetrachloride (800 mL) was refluxed until the evolution of carbon monoxide ceased (5 h). After cooling, the brown solution was filtered through silica gel (ca. 200 g) and concentrated to a colorless oil which solidified on standing. Recrystallization from hexane and chromatography of the mother liquors with petroleum ether on silica gel afforded colorless needles of **14** (104.0 g, 80%).

B. One-Pot Transacetalization/Decarbonylation of 12. Pure acetal **12** (100.0 g, 0.30 mol), obtained by digestion of crude material with warm methanol, *p*-toluenesulfonic acid (2.0 g), and water (5.0 mL) were dissolved in butanone (250 mL). The mixture was heated at reflux for 16 h and then cooled, with stirring, to yield a fine crystalline mass of **14** (ca. 60 g) which was filtered and washed with cold butanone. Concentration of the filtrate afforded more product and chromatography of the mother liquors with carbon tetrachloride an additional amount of **14**: total yield 75.5 g, 97%, mp 139–140 °C; IR (KBr) 2995, 2910, 2870, 2840, 1580, 1455, 1445, 1260, 1240, 1210, 1170, 750, 740, 690, 615 cm^{-1}; UV (isooctane) $\lambda_{\max}$ (ε) 289 (1780), 278 (3980), 267 (4035), 259 (3095), 250 nm (sh, 1990); ^{1}H NMR (250 MHz) δ 7.17 and 7.03 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 5.43 ($\underline{\mathrm{AA}'}$BB′, 11-, 12-H), 5.10 (AA′$\underline{\mathrm{BB}'}$, 10-, 13-H), 3.23 (m, 3-, 6-H), 2.76 (m, 2-, 7-H), 2.03 (dm, 16s-H), 1.99 (m, 1-, 8-H), 1.92 (dm, 16a-H), 1.90 (m, 9-, 14-H), 1.84 (dm, 15s-H), 1.58 (dm, 15a-H); ^{13}C NMR (25.2 MHz) δ 146.9 (C-4, -5), 129.0 (C-10, -13), 125.3 (C-4′, -5′), 122.9 (C-3′, -6′), 120.9 (C-11, -12), 60.4 (C-16), 49.2 (C-9, -14), 48.9 (C-2, -7), 46.6 (C-3, -6), 42.8 (C-15), 36.0 (C-1, -8).

Anal. Calcd for $C_{20}H_{20}$ (260.38): C, 92.25; H, 7.75. Found: C, 91.93; H, 7.94.

(1α,2β,3α,6α,7β,8α,9α,14α)-4,5-Benzo-10,11,12,13-tetrachloropentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadeca-4,10,12-triene (13). A solution of benzoene **10** (3.6 g, 17.3 mmol) and **5** (4.8 g, 18.9 mmol) in toluene (15 mL) was heated at reflux for 1 h under a slow stream of nitrogen. Methanol (50 mL) was added and the mixture cooled to −20 °C for 2 h. The precipitated product was separated by suction filtration, washed with cold methanol, and dried in vacuo to yield colorless crystals of **13**: 6.4 g, 92%; mp 169–170 °C; IR (KBr) 3050, 3030, 3005, 2955, 2880, 2865, 1605, 1450, 1200, 1075, 805, 770, 755, 650 cm^{-1}; UV (isooctane) $\lambda_{\max}$ (ε) 316 (3315), 302 (5550), 289 (5055), 278 (4060), 270 (2900), 243 nm (sh, 2740); ^{1}H NMR (250 MHz) δ 7.20 and 7.11 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 3.33 (m, 3-, 6-H), 2.82 (m, 2-, 7-H), 2.70 (m, 1-, 8-H), 2.40 (d, 9-, 14-H), 2.10 (dm, 16s-H), 1.97 (dm, 16a-H), 1.81 (dm, 15a-H), 1.64 (dm, 15s-H); ^{13}C NMR (20.2 MHz) δ 146.5 (C-4, 5), 126.0, 123.4 (C-3′, -4′, -5′, -6′), 132.1, 122.7 (C-10, -11, -12, -13), 60.4 (C-16), 48.4, 47.2, 46.3, 45.5 (C-1, -2, -3, -6, -7, -8, -9, -14), 42.3 (C-15).

Anal. Calcd for $C_{20}H_{16}Cl_4$ (398.16): C, 60.33; H, 4.05; Cl, 35.62. Found: C, 60.09; H, 3.74; Cl, 35.70.

(1α,2β,3α,6α,7β,8α,9α,14α)-4,5-Benzopentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadeca-4,10-diene (17). To a boiling tetrahydrofuran solution (100 mL) of **13** (3.0 g, 8.2 mmol) and *tert*-butyl alcohol (6.2 g, 83.6 mmol) was added granular lithium (0.7 g, 100.9 mmol) in small portions with vigorous stirring over 1 h, and heating was continued for a further 12 h. The mixture was decanted into ice water (300 mL) and extracted with petroleum ether. The extracts were washed with water prior to drying and filtration through silica gel (ca. 20 g). The solvent was removed to leave **17** (1.9 g, 88%) as a colorless oil which was crystallized from ethanol, mp 89–90 °C; IR (KBr) 3055, 3030, 3005, 2920, 2860, 2820, 1460, 1450, 1265, 1165, 745, 695, 620 cm^{-1}; ^{1}H NMR (250 MHz) δ 7.10 and 6.98 (2 m, 3′-, 4′-, 5′-, 6′-H), 5.62 (m, 11-H), 5.25 (m, 10-H), 3.22 (m, 3-, 6-H), 2.69 (m, 2-, 7-H), 2.03 (dm, 16-H), 1.99–1.88 (m, 1-, 8-, 16-H), 1.70 (m, 9-H), 1.58 (dm, 15-H), 1.45–1.15 (overlapping m, 12-, 13-, 15-H), 0.70 (m, 14-H).

Anal. Calcd for $C_{20}H_{22}$ (262.40): C, 91.55; H, 8.45. Found: C, 91.25; H, 8.20.

Reduction of 13 with Sodium/*tert*-Butyl Alcohol in Ether. To an etheral solution (400 mL) of 13 (9.5 g, 23.9 mmol) and *tert*-butyl alcohol (18.3 g, 246.9 mmol) under nitrogen was added finely cut sodium (6.7 g, 291.6 mmol), and the mixture was heated at reflux with vigorous stirring for 16 h. Workup as above gave a colorless oil which crystallized on standing. This crude product could be used directly in the next step.

Chromatographical purification on silica gel (200 g, petroleum ether eluent) provided a mixture of **17**, its C_s-symmetrical positional isomer (1.5 g, 23%; R_f 0.48), and pure diene **14** (4.0 g, 64%; R_f 0.38).

(1α,2β,3α,6α,7β,8α)-4,5:9,10-Dibenzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene and (1α,2β,3α,6α,7β,8α,9α,14α)-4,5-Benzopentacyclo[6.6.1.1.^{3,6}.0^{2,7}.0^{9,14}]hexadec-4-ene (18 and 21). A. Dehydrogenation of 14. An intimate mixture of diene **14** (16.0 g, 61.4 mmol) and 10% palladium on carbon (144.0 g; Engelhard) was placed into four thick-walled ampules (3 × 25 cm) which were sealed and lowered for 30 min into a preheated oil bath maintained at 250 °C. On cooling, the bottles were carefully opened, and the contents extracted with ethyl acetate overnight by using a Soxhlet apparatus. Evaporation of the extract left a dark green-brown oil (ca. 15.5 g) which was taken up in carbon tetrachloride and filtered through silica gel (ca. 100 g). After removal of the solvent, the solid residue (ca. 14 g) was recrystallized from hexane to provide pure **18** (9.0–10.0 g, 57–63%, varying from run to run) as colorless needles. The mother liquors were purified by chromatography on silica gel (petroleum ether eluent) to give 2.4–4.5 g of **21** (15–28%; R_f 0.65) and an additional amount of **18** (R_f 0.34), total yield 10.3–12.7 g (65–80%).

B. Dehydrogenation of 17. By analogous treatment of **17** (4.0 g, 15.3 mmol) with 10% palladium on charcoal (76.0 g), there was obtained 2.4–2.9 g of **18** (61–74%) and 0.9–1.3 g of **21** (22–32%).

For **18**: mp 181–182 °C (from hexane); IR (KBr) 3010, 2930, 2850, 1455, 1445, 1265, 750, 732, 715 cm^{-1}; UV (isooctane) λ_{max} (ϵ) 284 (390), 265 (1650), 258 (1270), 250 (sh, 1220), 227 nm (4270); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.54 (s, 3′-, 3″-, 4′-, 4″-, 5′-, 5″-, 6′-, 6″-H), 3.17 (2-, 7-H), 3.15 (m, 1-, 3-, 6-, 8-H), 1.99 (d, 11s-, 12s-H), 1.79 (d, 11a-, 12a-H); ^{1}H NMR (400 MHz, C_6D_6) δ 6.69 and 6.59 (AA′BB′, 3′-, 3″-, 4′-, 4″-, 5′-, 5″-, 6′-, 6″-H), 3.00 (m, 1-, 3-, 6-, 8-H), 2.88 (m, 2-, 7-H), 1.77 (narrow AB, 11-, 12-H); ^{13}C NMR (25.2 MHz) δ 144.4 (C-4, -5, -9, -10), 125.3 (C-4′, -4″, -5′, -5″), 123.5 (C-3′, -3″, -6′, -6″), 58.6 (C-11, -12), 46.6 (C-1, -3, -6, -8), 45.9 (C-2, -7).

Anal. Calcd for $C_{20}H_{18}$ (258.36): C, 92.99; H, 7.01. Found: C, 92.70; H, 7.27.

For **21**: mp 92–93 °C (from ethanol); IR (KBr) 2960, 2920, 2890, 2860, 1465, 755, 625 cm^{-1}; ^{1}H NMR (250 MHz) δ 7.13 and 6.99 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 3.19 (m, 3-, 6-H), 2.66 (m, 2-, 7-H), 2.02 (dm, 16s-H), 1.92 (dm, 16a-H), 1.85 (m, 1-, 8-H), 1.77 (dm, 15s-H), 1.31 (m, 9-, 14-, 15a-H), 0.82–0.70 (m, 10-, 11-, 12-, 13-H); ^{13}C NMR (20.2 MHz) δ 148.0 (C-4, -5), 124.6 (C-4′, -5′), 122.9 (C-3′, -6′), 60.4 (C-16), 48.1 (C-2, -7), 46.6 (C-3, -6), 46.5 (C-1, -8), 41.2 (C-15), 35.8 (C-9, -14), 23.3 (C-10, -13), 19.3 (C-11, -12).

Anal. Calcd for $C_{20}H_{24}$ (264.41): C, 90.85; H, 9.15. Found: C, 90.27; H, 9.13.

(1α,4β,5α,6β,9β)-4,5,6,9-Tetrabromohexacyclo[8.5.1.0^{2,7}.0^{7,14}.0^{8,12}.0^{13,16}]hexadec-2-ene (26). To a stirred solution of benzoene **10** (1.0 g, 4.8 mmol) in dry methylene chloride (25 mL), cooled to −78 °C, was added bromine (770 mg, 4.8 mmol), dropwise in the same solvent (5 mL). The solvent was evaporated at ambient temperature and the oily residue triturated with cold hexane to induce crystallization. The precipitated **26** was washed with hexane and recrystallized from methylene chloride–carbon tetrachloride to afford colorless needles (1.2 g, 94% based on bromine). Chromatography of combined mother liquors/hexane washings on silica gel (petroleum ether eluent) gave ca. 500 mg (50%) of the starting material **10** and 35 mg of a mixture of olefins which was not further characterized.

Analogous reaction with 1.8 equiv of bromine (1.40 g, 8.8 mmol) provided a 2.15-g (93%) yield of the tetrabromide **26**: mp 125 °C dec; IR (KBr) 2960, 2940, 2915, 2880, 2860, 1660, 1330, 1280, 1240, 1350, 1325, 970, 850, 730, 560, 555 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.68 (d, 1 H), 5.26 (d, 1 H), 5.23 (m, 1 H), 4.94 (d, 1 H), 4.91 (dd, 1 H), 3.14 (dm, 1 H), 2.73 (m, 1 H), 2.70–2.61 (m, 2 H), 2.55 (dm, 1 H), 2.48 (m, 1 H), 2.45–2.35 (m, 2 H), 1.81 (dm, 1 H), 1.77 (dm, 1 H), 1.67 (dm, 1 H); ^{1}H NMR (250 MHz, C_6D_6) δ 5.15 (m, 3-H), 5.00 (m, 5-H), 4.94 (br d, 4-H), 4.76 (m, 9s-H), 4.37 (br d, 6-H), 2.93 (dm, 8-H), 2.59 (dm, 11s-H), 2.37 (m, 14-H), 2.18 (m, 12-H), 2.12 (m, 10-H), 2.03 (m, 1-H), 1.80 (m, 13-, 16-H), 1.48 (dm, 15s-H), 1.45 (dm, 11a-H), 1.27 (dm, 15a-H), $J_{3,4} = 3.7$, $J_{3,5} = 1.0$, $J_{4,5} = 0.7$, $J_{5,6} = 2.5$, $J_{8,12} = 5.8$, $J_{9,10} = J_{9,12} = 2.0$, $J_{15a,15s} = 10.0$, $J_{11a,11s} = 10.5$ Hz; ^{13}C NMR (20.2 MHz) δ 42.5 (t), 42.6 (t), 44.3 (d), 44.8 (d), 45.3 (d), 46.2 (d), 46.3 (d), 48.2 (d), 51.3 (d), 52.3 (d), 53.7 (d), 53.7 (s), 58.7 (d), 59.1 (d), 110.6 (d), 149.1 (s).

Anal. Calcd for $C_{16}H_{16}Br_4$ (527.94): C, 36.40; H, 3.05; Br, 60.54. Found: C, 36.01; H, 2.77; Br, 60.40.

(1α,2β,3α,6α,7β,8α)-4,5-(Tetrachlorobenzo)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (31). A solution of diene **27** (500 mg, 3.2 mmol) in methylene chloride (10 mL), through which a slow stream of nitrogen was bubbled, was treated at 0 °C with solid **5** (1.8 g, 7.1 mmol) in one portion. The mixture was allowed to warm to room temperature and stirred for 14 h. The solvent was evaporated, and chromatography of the oily residue on silica gel (petroleum ether eluent) provided **31** (1.1 g, 100%) as a colorless oil which was crystallized from *n*-pentane. Excess **5** was recovered by further elution with methylene chloride. **31**: mp 138 °C; IR (KBr) 2975, 2940, 2900, 2860, 1470, 1370, 1335, 1290, 1245, 1215, 755, 745, 665 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.50 (m, 3-, 6-H), 2.75 (m, 2-, 7-H), 2.27 (m, 1-, 8-H), 2.07 (dm, 12s-H), 1.66 (dm, 11a-H), 1.94 (dm, 12a-H), 1.37 (dm, 11s-H), 1.00 (m, 9a-, 10a-H), 0.46 (m, 9s-, 10s-H); ^{13}C NMR (20.2 MHz) δ 146.4 (C-4, -5), 128.8, 127.3 (C-3′, -4′, -5′, -6′), 59.3 (C-12), 47.4, 46.9 (C-2, -3, -6, -7), 46.8 (C-11), 39.8 (C-1, -8), 23.2 (C-9, -10).

Anal. Calcd for $C_{16}H_{14}Cl_4$ (348.10): C, 55.21; H, 4.05; Cl, 40.74. Found: C, 54.97; H, 3.89; Cl, 40.71.

(1α,2β,3α,6α,7β,8α)-4,5-Benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodec-4-ene (32).[17] **A. Dehalogenation of 31.** A solution of **31** (800 mg, 2.3 mmol) in tetrahydrofuran (30 mL) containing *tert*-butyl alcohol (1.70 g, 22.9 mmol) was heated to reflux under nitrogen and treated with granular lithium (190 mg, 27.6 mmol). After vigorous stirring for 14 h, the mixture was hydrolyzed with ice water (200 mL) and extracted with petroleum ether. The extracts were washed with water, dried, and then filtered through silica gel (10 g) and concentrated to yield **31** (410 mg, 85%) as a clear oil which crystallized on standing at −20 °C.

B. Hydrogenation of 10. A sample of **10** (600 mg, 2.9 mmol) in ethyl acetate (20 mL) was hydrogenated over 10% palladium on carbon at atmospheric pressure. The catalyst was separated by filtration through Celite, and the filtrate was evaporated to give **32** (595 mg, 98%) as a colorless oil. Further purification by vapor-phase chromatography (10% SE-30, 120 °C) provided analytically pure **32** as colorless waxy crystals: mp 24–26 °C; IR (neat) 3060, 3040, 3000, 2940, 2860, 1470, 1465, 1455, 1450 sh, 1250, 755, 740, 610 cm^{-1}; ^{1}H NMR (250 MHz) δ 7.15 and 7.01 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 3.17 (m, 3-, 6-H), 2.63 (m, 2-, 7-H), 2.16 (m, 1-, 8-H), 2.01 (dm, 12s-H), 1.91 (dm, 12a-H), 1.61 (dm, 11a-H), 1.28 (dm, 11s-H), 0.78 (m, 9x-, 10x-H), 0.63 (m, 9n-, 10n-H); ^{13}C NMR (25.2 MHz) δ 147.9 (C-4, -5), 124.8 (C-4′, -5′), 123.0 (C-3′, -6′), 60.6 (C-12), 47.4 (C-2, -7), 46.7 (C-11), 46.6 (C-3, -6), 40.2 (C-1, -8), 24.2 (C-9, -10).

(1α,2β,3α,4α,5β,8β,9α,10α,11β,12α,13α,14β,17β,18α)-5,6,7,8,14,15,16,17-Octachlorooctacyclo[10.6.1.1^{3,10}.1^{5,8}.1^{14,17}.0^{2,11}.0^{4,9}.0^{13,18}]docosa-6,15-diene-21,22-dione Bis(dimethyl acetal) (30). A solution of diene **27** (2.0 g, 12.6 mmol) and **4** (8.0 g, 30.3 mmol) in toluene (10 mL) was heated at reflux under nitrogen until no more olefin signals were seen in the ^{1}H NMR spectrum (24 h). The solvent was removed and the brown, oily residue was filtered through silica gel with carbon tetrachloride. Crystallization from carbon tetrachloride–methanol (2:1) afforded colorless spars of **30** (3.4 g, 43%): mp 239–241 °C; IR (KBr) 3035, 2970, 2930, 2900, 2830, 1595, 1590, 1185, 1110, 990, 975, 840, 825, 745, 630 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.67 (s, OCH_3), 3.55 (s, OCH_3), 3.41 (m, 4-, 9-, 13-, 18-H), 2.53 (m, 1-, 3-, 10-, 12-H), 2.14 (m, 2-, 11-H), 1.70 (dm, 19s-, 20s-H), 1.09 (dm, 19a-, 20a-H).

Anal. Calcd for $C_{26}H_{26}C_{18}$ (622.12): C, 50.20; H, 4.21; Cl, 45.59. Found: C, 49.93; H, 4.05; Cl, 45.44.

Heptacyclo[8.5.1.0^{2,9}.0^{3,8}.0^{3,14}.0^{8,12}.0^{11,15}]hexadeca-4,6-diene (40). A solution of benzoene **10** (1.00 g, 4.8 mmol) in a dry benzene–acetone mixture (2:1, 450 mL) was purged with nitrogen and irradiated through Pyrex for 16 h with a HANAU TQ-150 mercury lamp. The solvents were removed at 30 °C, and the clear oily residue (78:22 mixture of **10**/**40** by ^{1}H NMR) was purified by column chromatography on silica gel (100 g; petroleum ether eluent). Prior to recovery of unreacted **10** (720 mg, 72%; R_f 0.56), there was obtained 210 mg of **40** (21%; R_f 0.72), a colorless oil: IR (neat) 3010, 2930, 2850, 1570, 1450, 1280, 780, 760, 710, 675 cm^{-1}; UV (isooctane) λ_{max} (ϵ) 313 sh (510), 297 sh (1730), 284 (2240), 277 sh (2115), 229 nm (sh, 570); ^{1}H NMR (250 MHz) δ 5.60 ($\underline{\mathrm{A}}$A′BB′, 5-, 6-H), 5.44 (AA′$\underline{\mathrm{B}}$B′, 4-, 7-H), 2.82 (m, 2-, 9-H), 2.49 (m, 11-, 15-H), 2.46 (m, 1-, 10-H), 2.12 (m, 12-, 14-H), 1.86 (dm, 13a-H), 1.77 (dm, 13s-H), 1.71 (dm, 16a-H), 1.31 (dm, 16s-H); ^{13}C NMR (20.2 MHz) δ 127.5 (C-5, -6), 122.1 (C-4, -7), 56.8, 54.7, 54.4 (C-1, -10, -11, -12, -14, -15), 53.2 (C-3, -8), 46.2 (C-2, -9), 39.8, 39.2 (C-13, -16).

Anal. Calcd for $C_{16}H_{16}$ (208.30): C, 92.26; H, 7.75. Found: C, 92.06; H, 7.83.

Photolysis of 40. A sample of pure diene **40** (100 mg, 0.5 mmol) was dissolved in a benzene–acetone mixture (2:1, 150 mL) and irradiated as above for 2 h to give a 78:22 mixture of **10**/**40** (^{1}H NMR).

Octacyclo[12.5.1.0^{2,7}.0^{2,13}.0^{7,18}.0^{8,13}.0^{8,16}.0^{17,20}]eicosa-3,5,9,11-tetraene (42). A solution of **18** (15.0 g, 58.1 mmol) in 2,2,4-trimethylpentane (1.1 L, spectroscopic grade) was divided into six quartz tubes (3 × 50 cm) and deoxygenated with nitrogen for 15 min. After being capped, the tubes were placed in a Rayonet apparatus and irradiated with 253.7-nm light for 16 h. The slightly yellow solution was filtered through silica gel (10 g) to remove colored impurities and the solvent distilled off under reduced pressure at a bath temperature of 60 °C. According to the ^{1}H NMR spectrum, the colorless crystalline residue (14.8 g, 98.7%) contained ca. 25–30% of the photoproduct **42**, the remainder being unreacted **18**. This material was used directly for the following experiment.

For isolation of **42**, 2.00 g of this mixture was chromatographed on a silica gel column (800 g; petroleum ether eluent) to give recovered **18** (1.46 g, 73%; R_f 0.34), after isolation of pure **42** (520 mg, 26%; R_f 0.40) which was recrystallized from ethanol: mp 184–185 °C (preheated oil bath); IR (KBr) 3050, 3010, 2990, 2950, 2930, 2850, 1570, 1445, 1280, 835, 740, 685, 675, 490 cm^{-1}; UV (isooctane) λ_{max} (ϵ) 286 (2130), 268 (2030), 258 nm (2020); ^{1}H NMR (250 MHz) δ 5.73 (*AA*′BB′, 4-, 5-, 10-, 11-H), 5.30 (AA′*BB*′, 3-, 6-, 9-, 12-H), 2.59 (m, 17-, 20-H), 2.28 (m, 1-, 14-, 16-, 18-H), 1.85 (dm, 15a-, 19a-H), 1.76 (dm, 15s-, 19s-H); ^{13}C NMR (20.2 MHz) δ 126.0 (C-4, -5, -10, -11), 123.3 (C-3, -6, -9,

-12), 63.1 (C-2, -7, -8, -13), 55.0 (C-17, -20), 54.9 (C-1, -14, -16, -18), 37.9 (C-15, -19).

Anal. Calcd for $C_{20}H_{18}$ (258.36): C, 92.99; H, 7.01. Found: C, 92.69; H, 7.25.

Photolysis of 42. A nitrogen-saturated solution of pure tetraene **42** (50 mg, 0.2 mmol) in 2,2,4-trimethylpentane (20 mL) was irradiated with 253.7-nm light for 2 h to give a 7:3 mixture of **18**/**42** (^{1}H NMR).

Undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docos-10-ene-4-*anti*,5-*anti*-dicarboxylic Anhydride (**48**). **A. From Pure 42.** To a solution of **42** (200 mg, 0.8 mmol) in dry benzene (1 mL) was added freshly sublimed maleic anhydride (MA; 200 mg, 2.0 mmol) in one portion. The mixture was heated at 80 °C until the deep-yellow color faded (total conversion by TLC, 12 h). After concentration in vacuo, excess MA was removed by sublimation at 80 °C/15 mm to leave 275 mg (100%) of pure adduct **48**.

B. From a 18/42 Mixture. A **18**/**42** photoequilibrium mixture (25:75 by ^{1}H NMR; 28.6 g, 27.7 mmol of **42**) was prepared as described above. Dry benzene (20 mL) and freshly sublimed MA (6.0 g, 61.2 mmol) were added, and the mixture was stirred at 80 °C for 12 h. On evaporation of the solvent, the residue was taken up in carbon tetrachloride (200 mL) and loaded on to a silica gel column (4.5 × 25 cm). Elution with carbon tetrachloride (1.5 L) gave the starting dibenzo compound **18** (21.4 g) which was recycled. Continued elution with methylene chloride (800 mL) yielded the adduct **48** and unreacted MA which was removed by sublimation. The crude adduct **48** was crystallized from methanol as colorless, fine needles (9.7 g, 98%): mp 183–184 °C; IR (KBr) 3040, 2940, 2925, 2855, 1860, 1770, 1230, 1220, 1020, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.06 (m, 10-, 11-H), 2.99 (4-, 5-H), 2.77 (m, 9-, 12-H), 2.73 (m, 18-, 19-H), 2.43 (3-, 6-H), 2.32 (m, 20-, 22-H), 2.21 (m, 15-, 17-H), 2.00 (m, 7-, 8-H), 1.75 (dm, 21a-H), 1.44 (dm, 16a-H), 1.41 (dm, 21s-H), 1.27 (dm, 16s-H); ^{13}C NMR (20.2 MHz) δ 174.0 (C=O), 129.6 (C-10, -11), 59.9 (C-18, -19), 60.1, 55.9 (C-1, -2, -13, -14), 44.6, 43.9, 41.9 (C-7, -8, -15, -17, -20, -22), 41.7, 40.1 (C-16, -21), 38.5, 38.4, 33.3 (C-3, -4, -5, -6, -9, -12).

Anal. Calcd for $C_{24}H_{20}O_3$ (356.42): C, 80.88; H, 5.66. Found: C, 81.05; H, 5.50.

Undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10-diene (**49**). A mixture of anhydride **48** (17.82 g, 50 mmol), 2,2′-bipyridyl (8.44 g, 54 mmol), copper(I) oxide (15.40 g, 108 mmol), water (3 mL), and quinoline (90 mL) was stirred vigorously and heated to reflux over 4 h. Heating at this temperature was continued for 12 h during which excess water was allowed to distill away. After a further 24 h at reflux, the dark mixture was cooled, diluted with ether–petroleum ether (1:1; 300 mL), and filtered through a pad of Celite. The yellow filtrate was washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and dried. The solvent was evaporated and the residue was chromatographed over a short column of silica gel with methylene chloride–petroleum ether (1:1) to give pure **49** (11.09 g, 78%) which was crystallized from hexane as colorless needles: mp 204–205 °C; IR (KBr) 3040, 2930, 2915, 2855, 1605, 1375, 1280, 690, 660 cm^{-1}; ^{1}H NMR (250 MHz) δ 6.09 (m, 4-, 5-, 10-, 11-H), 2.72 (m, 3-, 6-, 9-, 12-H), 2.59 (m, 18-, 19-H), 2.12 (m, 15-, 17-, 20-, 22-H), 1.82 (m, 7-, 8-H), 1.43 (dm, 16a-, 21a-H), 1.36 (dm, 16s-, 21s-H); ^{13}C NMR (20.2 MHz) δ 130.8 (C-4, -5, -10, -11), 60.2 (C-18, -19), 59.6 (C-1, -2, -13, -14), 51.2 (C-7, -8), 43.3 (C-15, -17, -20, -22), 41.0 (C-16, -21), 38.1 (C-3, -6, -9, -12); MS, *m*/*e* (relative intensity) 284 (M$^+$, 100), 203 (21), 167 (28), 165 (22), 153 (37), 152 (28), 142 (36), 141 (47), 128 (25), 116 (42), 115 (42).

Anal. Calcd for $C_{22}H_{20}$ (284.40): C, 92.91; H, 7.09. Found: C, 93.12; H, 6.95.

Undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosane (**50**). **Diene 49** (300 mg, 1.6 mmol) was hydrogenated in ethyl acetate (100 mL) over 10% palladium on carbon at atmospheric pressure. After filtration through Celite, the solvent was evaporated and the residue crystallized from ethanol. There was obtained 300 mg (100%) of **57** as transparent needles which were sublimed at 140 °C/14 mm: mp 201–202 °C; IR (KBr) 2900, 2850, 1460, 1285, 1275, 1220, 900 cm^{-1}; ^{1}H NMR (250 MHz) δ 2.69 (m, 18-, 19-H), 2.27 (m, 7-, 8-H), 2.15 (m, 15-, 17-, 20-, 22-H), 1.63 (dm, 16s-, 21s-H), 1.61 (m, 3-, 6-, 9-, 12-H), 1.56 (m, 4s-, 5s-, 10s-, 11s-H), 1.53 (dm, 16a-, 21a-H), 1.40 (m, 4a-, 5a-, 10a-, 11a-H); ^{13}C NMR (20.2 MHz) δ 59.8 (C-18, -19), 57.5 (C-1, -2, -13, -14), 48.5 (C-7, -8), 43.5 (C-15, -17, -20, -22), 40.9 (C-16, -21), 34.0 (C-3, -6, -9, -12), 18.3 (C-4, -5, -10, -11).

Anal. Calcd for $C_{22}H_{24}$ (288.43): C, 91.61; H, 8.39. Found: C, 91.54; H, 8.46.

***anti*,*anti*-5,12-Dioxatridecacyclo[11.9.0.0^{1,7}.0^{2,16}.0^{2,22}.0^{3,9}.0^{4,6}.0^{8,14}.0^{10,16}.0^{11,13}.0^{15,19}.0^{17,21}.0^{20,24}]tetracosane** (**58**). To a solution of diene **49** (100 mg, 0.35 mmol) in methylene chloride (5 mL) at 0 °C was added a solution of 85% *m*-chloroperbenzoic acid (150 mg, 0.74 mmol) in the same solvent (3 mL). After 2 h of stirring at room temperature, the reaction mixture was washed with 10% aqueous sodium sulfite and saturated sodium bicarbonate solution, dried, and evaporated to leave **58** as a colorless oil. Crystallization from hexane furnished colorless needles: 105 mg, 94%; mp 258–260 °C; IR (KBr) 3015, 2945, 2925, 2900, 2855, 1420, 1215, 1030, 840 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.08 (m, 4-, 6-, 11-, 13-H), 2.75 (m, 20-, 21-H), 2.66 (m, 8-, 9-H), 2.28 (m, 17-, 19-, 22-, 24-H), 2.22 (m, 3-, 7-, 10-, 14-H), 1.70 (dm, 18a-, 23a-H), 1.52 (dm, 18s-, 23s-H).

Anal. Calcd for $C_{22}H_{20}O_2$ (316.40): C, 83.52; H, 6.37. Found: C, 83.21; H, 6.26.

Undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4-*anti*,10(11)-*anti*-diols (50, Isomeric Mixture). A solution of diene **49** (8.3 g, 29 mmol) in dry tetrahydrofuran (200 mL) was cooled to 0 °C with stirring, and 1.0 M diborane in tetrahydrofuran (65 mL, 65 mmol) was added dropwise via syringe over a period of 30 min. The mixture was stirred at room temperature for 4 h and recooled to 0 °C, and 15% sodium hydroxide solution (100 mL) followed by 30% aqueous hydrogen peroxide (65 mL) was added slowly. After stirring at 0 °C for 1 h and at room temperature for a further 10 h, the aqueous phase was saturated with potassium carbonate (100 g), and tetrahydrofuran was evaporated at 25 °C. The granular precipitate was isolated by suction filtration, washed to neutrality with cold water, and dried in vacuo. Crystallization from methanol provided 9.0 g (96%) of diols **50** as colorless rosettes: mp 240–246 °C; IR (KBr) 3330, 2920, 2880, 2850, 1450, 1435, 1075, 1065, 985 cm^{-1}; ^{1}H NMR (250 MHz, CD_3OD) δ 4.88 (s, OH), 3.83 (m, 4-, 10(11)-H), 2.73 (m, 18-, 19-H), 2.83 (dd), 2.58 (m) and 2.34 (dd, 7-, 8-H), 2.22 (m) and 2.17 (m, 15-, 17-, 20-, 22-H), 1.89 (m, 5s-, 10(11)s-H), 1.78 (m) and 1.69 (m, 3-, 6-, 9-, 12-H), 1.66 (br d, 16a-, 21a-H), 1.44 (m, 5a-, 10(11)a-, 16s-, 21s-H).

Anal. Calcd for $C_{22}H_{24}O_2$ (320.43): C, 82.46; H, 7.55. Found: C, 82.49; H, 7.60.

Undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-diones (51, Isomeric Mixture). To a suspension of diols **50** (10.0 g, 31.2 mmol) in acetone–water (3:1, 400 mL) was added a solution of chromium trioxide (8.5 g, 85.0 mmol) in water (20 mL) and concentrated sulfuric acid (10 mL). The solids dissolved within 30 min, and stirring was continued for a further 2 h. Methylene chloride (400 mL) was added, the layers were separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic phases were washed with saturated sodium bicarbonate solution, dried, and concentrated to a colorless oil which solidified on standing. Recrystallization from ether–hexane furnished colorless needles of diones **51**: 9.6 g, 97%; mp 264–268 °C; IR (KBr) 2940, 2860, 1710, 1395, 1225, 1190, 1165, 495, 455 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.02 (ddd, 8*-H), 2.83 (m) and 2.79 (m, 7-, 8-, 18-, 19-, 18*-, 19*-H), 2.58 (ddd, 7*-H), 2.56 (m, 3-, 12-H), 2.49 (d, 3*-, 9*-H), 2.44 (m, 6*-, 12*-H), 2.41–2.34 (m, 6-, 9-, 15-, 17-, 20-, 22-, 15*-, 17*-, 20*-, 22*-H), 2.35 (dd, 5s*-, 11s*-H), 2.34 (dd, 5s-, 10s-H), 2.21 (dd, 5a*-, 11a*-H), 2.20 (dd, 5a-, 10a-H), 1.70 (dm, 16a-, 21a-H), 1.39 (dm, 16s-, 21s-H), $J_{3,8} = 3.0$, $J_{5s,5a} = 20.0$, $J_{5s,6} = J_{5a,6} = 3.0$, $J_{7,8} = 9.0$, $J_{16s,16a} = 10.5$ Hz (* denotated signals refer to the C_s isomer); ^{13}C NMR (20.2 MHz) δ 214.0, 213.5, 61.8, 61.5, 60.0, 59.9, 59.7, 57.4, 57.2, 51.3, 50.7, 48.5, 47.6, 46.7, 43.5, 43.2, 43.0, 42.7, 40.7, 40.6, 37.1, 36.8, 36.2 (2×).

Anal. Calcd for $C_{22}H_{20}O_2$ (316.40): C, 83.52; H, 6.37; Found: C, 83.71; H, 6.30.

5,11(10)-Bis(hydroxymethylene)undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-diones (52, Isomeric Mixture). A suspension of sodium hydride (50% in mineral oil; 8.0 g, 167 mmol) under nitrogen was washed 3 times with hexane and slurried in a solution of **51** (12.6 g, 40 mmol) in anhydrous tetrahydrofuran (300 mL). Following the addition of dry methyl formate (20 mL), the exothermic reaction was initiated with methanol (0.3 mL). The reaction mixture was stirred at ambient temperature for 4 h and then, after the addition of more methyl formate (20 mL), at 40 °C for 16 h. Methanol (10 mL) was carefully added to destroy excess hydride, and the mixture was acidified by addition of 10% hydrochloric acid (ca. 30 mL) until the color changed from reddish-brown to yellow. Water (100 mL) was added to dissolve the solids, and the two-phase mixture was concentrated at 30 °C to remove the organic solvent. The tan granular precipitate was isolated by suction filtration, washed with water, and dried in vacuo. This crude material (14.8 g, ca. 100%) can be used directly for the next step.

A sample was chromatographed on silica gel with benzene–ethyl acetate (1:1) and recrystallized from ether to give analytically pure **52**: mp 227 °C dec; IR (KBr) 3430, 2935, 2855, 1710, 1655, 1580, 1420, 1185, 1165 cm^{-1}; ^{1}H NMR (250 MHz) δ 11.0 (br s, =CHO*H*), 7.21 (s, =C*H*OH), 2.78 (m, 18-, 19-H), 2.56 (m, 3-, 6-, 7-, 8-, 9-, 12-H), 2.35 (m) and 2.28 (m, 15-, 17-, 20-, 22-H), 1.62 (dm, 16s-, 21s-H), 1.29 (dm, 16a-, 21a-H).

Anal. Calcd for $C_{24}H_{20}O_4$ (372.42): C, 77.40; H, 5.41. Found: C, 77.31; H, 5.63.

5,11(10)-Bis(diazo)undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-diones (53, Isomeric Mixture). A. Diazotization of 52. Crude hydroxymethylene ketones **52** (11.2 g, ca. 30 mmol) were dissolved in dry tetrahydrofuran (600 mL) and treated under nitrogen with *p*-toluenesulfonyl azide (11.9 g, 60 mmol) and triethylamine (12.2 g, 121 mmol). The solution was stirred at room temperature in the dark until a ferric chloride test proved negative (6–8 h) and then diluted with water (1 L) and thoroughly extracted with methylene chloride. The extracts were washed with 10% hydrochloric acid and saturated sodium bicarbonate solution prior to drying. Evaporation of the solution afforded an orange oil which was triturated with methanol (50 mL). The yellow precipitate was filtered, washed with ether, and dried in vacuo to provide pure C_2 **53** (4.2 g, 41%). Chromatography of the mother liquors on silica gel (5 × 40 cm; chloroform–methanol 40:1 eluent) afforded an additional mixture of bisdiazo diketones **53** (5.0 g, total yield 90%).

B. One-Pot Formylation/Diazotization of 51. Diketones **51** (12.6 g, 40 mmol) in tetrahydrofuran solution were allowed to react with sodium hydride and methyl formate as described above. The resulting brown slurry was treated dropwise with glacial acetic acid (12 mL, 210 mmol) and diluted with methylene chloride (100 mL). Triethylamine (25 mL, 179 mmol) and *p*-toluenesulfonyl azide (15.8 g, 80 mmol) were added, and the mixture was stirred in the dark until a ferric chloride test proved negative (ca. 6 h) and then diluted with ether–methylene chloride (2:1, 300 mL) and washed with saturated sodium bicarbonate solution, water, and brine. The organic layer was dried and evaporated, and the residue was triturated with methanol at −20 °C. Filtration afforded 7.85 g of product as a yellow solid, and chromatography of the filtrate on silica gel (ethyl acetate–cyclohexane 2:1) afforded an additional 3.60 g (total yield 12.05 g, 82%). This isomeric mixture of diazo diketones **53** was used directly for the next step.

For C_2 **53**: deep-yellow crystals (from chloroform) which explode on heating at ca. 200 °C; IR (KBr) 2950, 2920, 2855, 2075, 1635, 1360, 1195, 695 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.16 (m, 6-, 9-H), 2.90 (m, 3-, 12-H), 2.83 (m, 7-, 8-, 18-, 19-H), 2.41 (m, 15-, 17-, 20-, 22-H), 1.72 (dm, 16s-, 21s-H), 1.53 (dm, 16a-, 21a-H).

Anal. Calcd for $C_{22}H_{16}N_4O_2$ (368.40): C, 71.73; H, 4.38; N, 15.21. Found: C, 71.64; H, 4.13; N, 15.07.

5-(Hydroxymethylene)undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-diones (59, Isomeric Mixture). To a solution of **51** (640 mg, 2.0 mmol) in dry tetrahydrofuran (5 mL) under nitrogen was added oil-free sodium hydride (50 mg, 2.1 mmol), methyl formate (1 mL), and a catalytic amount of methanol. The reaction mixture was stirred at room temperature for 24 h, quenched with 10% hydrochloric acid (5 mL), and concentrated in vacuo to remove the organic solvent. The precipitated oily product was extracted into methylene chloride, washed with brine, dried, and evaporated to yield crude **59**. Chromatography on silica gel with methylene chloride–ethyl acetate (9:1) as eluent afforded **59** as an oil (600 mg, 87%) which solidified on standing and was used directly for the next step: IR (KBr) 3410, 2940, 2860, 1710, 1650, 1590, 1185 cm^{-1}; ^{1}H NMR (250 MHz) δ 7.36 (s, 1 H), 7.24 (br s, 1 H), 3.05 (ddd, 1 H), 2.85–2.65 (m, 6 H), 2.60–2.10 (compl m, 7 H), 1.70 (dm, 1 H), 1.59 (dm, 1 H), 1.38 (dm, 1 H), 1.26 (dm, 1 H).

5-Diazoundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-diones (60, Isomeric Mixture). A solution of the foregoing hydroxymethylene diketone **59** (520 mg, 1.5 mmol), *p*-toluenesulfonyl azide (300 mg, 1.5 mmol), and triethylamine (200 mg, 3 mmol) in anhydrous tetrahydrofuran (10 mL) was stirred at ambient temperature for 6 h. The mixture was diluted with methylene chloride and washed with 5% hydrochloric acid and water. The organic phase was dried and evaporated to leave a yellow oil which was purified by crystallization from ether: yield 470 mg, 92%; mp 163 °C dec; IR (KBr) 2945, 2860, 2065, 1710, 1640, 1370, 1200 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.13 (m, 1 H), 2.97–2.83 (overlapping m, 1 H), 2.79 (m, 2 H), 2.76–2.65 (compl m, 2 H), 2.56 (d, 1 H) and 2.45 (m), 2.41–2.29 (m, 5 H), 2.28 (dm, 1 H, J = 20.5 Hz), 2.14 (dm, 1 H, J = 20.5 Hz), 1.68 (dm, 1 H), 1.65 (dm, 1 H), 1.47 (dm, 1 H), 1.35 (dm, 1 H).

Anal. Calcd for $C_{22}H_{18}N_2O_2$ (342.40): C, 77.17; H, 5.30; N, 8.18. Found: C, 76.93; H, 5.12; N, 7.96.

Methyl Undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]heneicosan-9-one-4-*syn*-carboxylate (61). A pale-yellow solution of **60** (500 mg, 1.5 mmol) in anhydrous methanol (400 mL) was purged with nitrogen and irradiated with a HANAU TQ-150 mercury lamp through Pyrex until complete decolorization occurred (1 h). The solvent was removed and the solid residue recrystallized from ether–hexane to provide colorless crystals of **61** (490 mg, 97%): mp 190–191 °C; IR (KBr) 2940, 2860, 1720, 1425, 1270, 1240, 1215, 1180, 1050 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.62 (s, 3 H), 2.90 (m, 1 H), 2.82 (m, 2 H), 2.79 (ddd, 1 H), 2.71 (m, 2 H), 2.62 (ddd, 1 H), 2.51 (d, 1 H), 2.37 (m, 2 H), 2.24 (m, 3 H), 2.17 and 2.09 (AB, 2 H), 1.67 (dm, 1 H), 1.56 (dm, 1 H), 1.41 (dm, 1 H), 1.14 (dm, 1 H).

Anal. Calcd for $C_{26}H_{22}O_3$ (346.43): C, 79.74; H, 6.40. Found: C, 79.64; H, 6.29.

Methyl 10-(Hydroxymethylene)undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]heneicosan-9-one-4-*syn*-carboxylate (62). To a slurry of sodium hydride (200 mg, 8.3 mmol), washed free from mineral oil, in anhydrous tetrahydrofuran (3 mL) under nitrogen was added 400 mg (1.2 mmol) of **61** followed by dry methyl formate (3 mL) and a catalytic amount of sodium methoxide. The mixture was stirred at room temperature for 20 h and then acidified with 10% hydrochloric acid and diluted with water (20 mL). Extraction with methylene chloride, washing of the organic phase with brine, drying, and evaporation gave crude **62**. Recrystallization from ether furnished colorless crystals: 420 mg, 97%; mp 216–217 °C; IR (KBr) 3430, 2960, 2945, 2875, 1725, 1650, 1215, 1185, 1140 cm^{-1}; ^{1}H NMR (250 MHz) δ 10.8 (br s, =CHO*H*), 7.02 (s, =C*H*OH), 3.61 (s, OCH$_3$), 2.90 (m, 4a-H), 2.81 (m, 8-, 11-H), 2.76–2.65 (overlapping m, 3-, 5-, 6-, 17-, 18-H), 2.56 (m, 7-H), 2.36 (m, 19-, 21-H), 2.24 (m) and 2.17 (m, 14-, 16-H), 1.59 (20a-H), 1.56 (dm, 15a-H), 1.31 (dm, 15s-H), 1.15 (dm, 20s-H).

Anal. Calcd for $C_{24}H_{22}O_4$ (374.44): C, 76.99; H, 5.92. Found: C, 77.13; H, 6.10.

Methyl 10-Diazoundecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]heneicosan-9-one-4-*syn*-carboxylate (63). A solution of **62** (350 mg, 0.9 mmol) in dry tetrahydrofuran (20 mL) was treated with *p*-toluenesulfonyl azide (200 mg, 1.0 mmol) and triethylamine (200 mg, 2.0 mmol) and stirred at ambient temperature in the dark until a ferric chloride test proved negative (4 h). The mixture was diluted with water (200 mL) and extracted with methylene chloride. The extracts were washed with 10% hydrochloric acid and saturated sodium bicarbonate solution prior to drying and evaporation. The resulting yellow oil was chromatographed on silica gel (chloroform eluent) and crystallized from ether to give pure **63** (310 mg, 89%) as yellow crystals which decomposed on heating at ca. 300 °C with gas evolution: IR (KBr) 2940, 2875, 2075, 1725, 1640, 1370, 1215 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.61 (s, OCH$_3$), 3.11 (m, 11-H), 2.91 (m, 4a-H), 2.86–2.79 (overlapping m) and 2.71 (m, 3-, 5-, 6-, 7-, 8-, 17-, 18-H), 2.37 (m, 19-, 21-H), 2.29 (m, 14-, 16-H), 1.67 (dm, 15a-H), 1.57 (dm, 20a-H), 1.54 (dm, 15s-H), 1.15 (dm, 20s-H).

Anal. Calcd for $C_{23}H_{20}N_2O_3$ (365.48): C, 74.18; H, 5.41; N, 7.52. Found: C, 73.99; H, 5.22; N, 7.34.

Dimethyl Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]eicosane-4-*syn*,9-*syn*-dicarboxylate (55). A. Photolysis of 53. A solution of diazoketones **53** (6.0 g, 17.5 mmol) in methylene chloride (60 mL) was added over ca. 6 h in 5-mL portions to analytical grade methanol (2.0 L) which was continuously purged with nitrogen and irradiated with a HANAU TQ-2024 mercury lamp (2000-W) through Pyrex. Filtration of the resultant colorless suspension afforded the diester **55** (ca. 3.0 g). Evaporation of the solvent and trituration of the residue with methylene chloride–methanol followed by chromatography of the filtrate on silica gel (methylene chloride elution) yielded additional diester (total yield 5.8 g, 95%). For analysis, a sample was recrystallized from chloroform–methanol. Crystals for X-ray analysis were grown from chloroform solution by slow evaporation of the solvent as long flat needles.

B. Photolysis of 63. By irradiation of **63** (350 mg, 0.9 mmol) in methanol (400 mL) and usual workup there was obtained 340 mg (96%) of pure crystalline **55**: mp 269 °C; IR (KBr) 2940, 2880, 1720, 1430, 1270, 1220, 1200, 1190, 1035, 1010 cm^{-1}; ^{1}H NMR (400 MHz) δ 3.59 (s, OCH$_3$), 2.84 (m, 4a-, 9a-H), 2.78 (m, 6-, 7-H), 2.67 (m, 3-, 5-, 8-, 10-H), 2.61 (m, 16-, 17-H), 2.26 (m, 13-, 15-, 18-, 20-H), 1.52 (dm, 14a-, 19a-H), 1.15 (dm, 14s-, 19s-H); ^{13}C NMR (100.6 MHz) δ 173.5 (C=O), 63.5 (C-1, -2, -11, -12), 59.6 (C-16, -17), 58.3 (C-6, -7), 57.9 (C-4, -9), 51.3 (CH$_3$), 43.9 (C-3, -5, -8, -10), 42.0 (C-13, -15, -18, -20), 40.9 (C-14, -19).

Anal. Calcd for $C_{24}H_{24}O_4$ (376.45): C, 76.57; H, 6.43. Found: C, 76.64; H, 6.23.

Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]eicosane-4-*syn*,9-*syn*-dicarboxylic Acid (56 and Epimeric Mixture). A. Hydrolysis of 55. A suspension of diester **55** (4.90 g, 13 mmol) in ethanol (400 mL) was treated with a solution of potassium hydroxide (10 g, 178 mmol) in water (100 mL), and the mixture was heated at reflux for 16 h. After concentration, the semisolid residue was taken up in warm (60 °C) water (250 mL). The stirred solution was slowly acidified to pH 1 with concentrated hydrochloric acid and cooled in an ice bath. The precipitate was isolated by suction filtration, washed with ice-cold water, and dried, to give a mixture of epimeric diacids (4.45 g, 98%) as a pale-tan solid.

B. Photolysis of 53. A pale-yellow solution of **53** (200 mg, 0.6 mmol) in a tetrahydrofuran–water mixture (1:1, 300 mL), containing sodium bicarbonate (1.0 g), was purged with nitrogen and irradiated with a

HANAU TQ-150 mercury lamp through a Vycor filter until complete decolorization occurred (2 h). The solution was concentrated to 50 mL and acidified with concentrated hydrochloric acid to pH 1. The precipitate was filtered and dried over phosphorus pentoxide to yield 190 mg (90%) of diacid **56** as an amorphous solid which slowly decomposed above 280 °C without melting: IR (KBr) 3430, 2950, 2870, 1695, 1275 cm^{-1}; ^{1}H NMR (250 MHz, Me$_2$SO-d_6) δ 3.35 (br s, 2 H), 2.82 (m, 2 H), 2.75 (m, 2 H), 2.59 (m, 2 H), 2.47 (m, 4 H), 2.17 (m, 4 H), 1.53 (dm, 2 H), 1.45 (dm, 2 H).

Anal. Calcd for $C_{22}H_{20}O_4$ (348.40): C, 75.84; H, 5.79. Found: C, 75.59; H, 5.92.

4,9-Diiodoundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]eicosane (64, Epimeric Mixture). A mechanically stirred suspension of diacids **56** (2.0 g, 5.7 mmol) and finely ground lead tetraacetate (dried in vacuo) in dry carbon tetrachloride (300 mL) under a nitrogen atmosphere was placed above a 500-W tungsten lamp. As the mixture reached reflux, a solution of iodine (3.0 g, 11.8 mmol) in the same solvent (150 mL) was slowly added dropwise until the violet color persisted. After cooling and filtration, the solution was washed with 5% aqueous sodium thiosulfate, 10% aqueous sodium hydroxide, and water. After the solution was dried, the solvent was removed and the clear oily residue was crystallized from ether–hexane to give 2.35 g (80%) of diiodides **64**. Recrystallization from acetone furnished colorless needles which consisted mainly of the bis-anti epimer: mp 270–276 °C; IR (KBr) 2965, 2950, 2920, 2855, 1450, 1270, 1170, 705, 645, 625 cm^{-1}; ^{1}H NMR (250 MHz, epimeric mixture, relative intensity of multiplets) δ 4.19–3.94 (15), 3.54 (4), 3.14–3.04 (17), 2.78–2.57 (41), 2.52–2.45 (7), 2.36–2.24 (30), 1.79–1.50 (25); signals of bis-anti epimer δ 3.98 (m, 4s-, 9s-H), 3.54 (m, 6-, 7-H), 2.65 (m, 3-, 5-, 8-, 10-H), 2.60 (m, 16-, 17-H), 2.34 (m, 13-, 15-, 18-, 20-H), 1.72 (dm, 14a-, 19a-H), 1.53 (dm, 14s-, 19s-H).

Anal. Calcd for $C_{20}H_{18}I_2$ (512.16): C, 46.90; H, 3.54; I, 49.55. Found: C, 46.93; H, 3.27; I, 49.48.

Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]eicosane (1). To a solution of diiodides **64** (1.66 g, 3.2 mmol) in anhydrous tetrahydrofuran (100 mL) was added ca. 1 g of a sodium–potassium alloy (1:1, w:w), followed by *tert*-butyl alcohol (1.0 g, 13.5 mmol). The mixture was vigorously stirred overnight under an argon atmosphere and then cautiously treated with methanol and poured into water (300 mL). The mixture was extracted with methylene chloride, and the organic layer was washed with water, dried, and evaporated to furnish pure pagodane **1** (0.84 g, 100%) as a colorless solid which was sublimed at 140 °C/14 mm to give transparent prisms: mp 243 °C (sealed capillary); IR (KBr) 2940, 2925, 2855, 1460, 1275, 1235, 1200, 1175, 910, 755, 430 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.60 (m, 6-, 7-, 16-, 17-H), 2.24 (m, 3-, 5-, 8-, 10-, 13-, 15-, 18-, 20-H), 1.60 (dm, 4a-, 9a-, 14a-, 19a-H), 1.56 (dm, 4s-, 9s-, 14s-, 19s-H), $J_{4s,4a}$ = 10.0 Hz; ^{13}C NMR (100.6 MHz) δ 62.9 (C-1, -2, -11, -12), 59.6 (C-6, -7, -16, -17), 42.7 (C-3, -5, -8, -10, -13, -15, -18, -20), 41.9 (C-4, -9, -14, -19), $J_{\text{C-6,H}}$ = 139, $J_{\text{C-4,H}}$ = 130, $J_{\text{C-3,H}}$ = 141 Hz; MS, *m/e* (relative intensity) 260 (M^{+}, 100), 259 (9), 179 (6), 165 (6), 129 (7), 128 (8), 115 (10), 91 (5), 39 (6).

Anal. Calcd for $C_{20}H_{20}$ (260.38): C, 92.26; H, 7.74. Found: C, 92.20; H, 7.66.

5,11(10)-Bis((dimethylamino)methylene)undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-dione (65, Isomeric Mixture). A mixture of diones **51** (1.0 g, 3.2 mmol) and *tert*-butoxybis(dimethylamino)methane was heated at 60 °C under nitrogen for 24 h. The resulting off-white solid mass was used directly in further experiments. For analysis, a sample was recrystallized from chloroform to furnish the C_2 isomer of **65** as colorless needles: mp >300 °C; IR (KBr) 2935, 2855, 2800, 1655, 1560, 1430, 1385, 1315, 1265, 1225, 1200, 1095, 1060, 640 cm^{-1}; ^{1}H-NMR (250 MHz) δ 7.32 (s, 4′-, 11′-H), 3.34 (m, 3-, 12-H), 3.07 (s, CH$_3$), 2.73 (m, 18-, 19-H), 2.58 (m, 6-, 9-H), 2.55 (m, 7-, 8-H), 2.30 (m) and 2.23 (m, 15-, 17-, 20-, 22-H), 1.58 (dm, 16a-, 21a-H), 1.45 (dm, 16s-, 21s-H).

Anal. Calcd for $C_{28}H_{30}N_2O_2$ (426.56): C, 78.84; H, 7.09; N, 6.57. Found: C, 78.77; H, 7.13; N, 6.61.

5,11(10)-Bis(benzylidene)undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-dione (66, Isomeric Mixture). To a solution of diones **51** (1.0 g, 3.2 mmol) and benzaldehyde (0.8 g, 7.5 mmol) in ethanol (10 mL) was added a potassium hydroxide pellet (50 mg), and the mixture was stirred at ambient temperature for 24 h. After cooling in an ice bath, the precipitated product was isolated by suction filtration, washed with cold ethanol, and dried in vacuo. Concentration of the mother liquors gave a second crop of **66**, total yield 1.4 g (90%). An analytical sample was obtained by recrystallization from ethanol: mp 180–189 °C; IR (KBr) 3060, 3015, 2945, 2855, 1690, 1610, 1250, 1190, 855, 750, 725, 690, 525, 495 cm^{-1}; ^{1}H NMR (250 MHz) δ 7.62 (s) and 7.61 (s, 5′-, 10′(11′)-H), 7.46–7.30 (m, phenyl), 3.59 (m, 6-, 9(12)-H), 3.08 (ddd), 2.91 (m), 2.85 (m), 2.82 (m), 2.79 (d) and 2.68 (ddd, 3-, 7-, 8-, 9(12)-, 18-, 19-H), 2.50 (m) and 2.44 (m, 15-, 17-, 20-, 22-H), 1.69 (m, 16a-, 21a-H), 1.42 (m, 16s-, 21s-H).

Anal. Calcd for $C_{36}H_{28}O_2$ (492.62): C, 87.78; H, 5.73. Found: C, 87.80; H, 5.68.

4-*syn*,9-*syn*-4,9-Bis(hydroxymethyl)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]eicosane (68). To a slurry of lithium aluminum hydride (100 mg, 2.6 mmol) in anhydrous tetrahydrofuran (20 mL) was added solid diester **55** (150 mg, 0.4 mmol) in one portion. The mixture was heated under reflux for 2 h, cooled in an ice bath, and treated with water (0.1 mL), 15% aqueous sodium hydroxide (0.1 mL), and water (0.3 mL). Stirring was continued for a further 30 min, and anhydrous magnesium sulfate (1 g) was added to aid filtration. The solids were leached with tetrahydrofuran, and the combined filtrates were evaporated to provide crude **68** (125 mg, 98%) as a colorless solid which was recrystallized from chloroform: mp 259 °C; IR (KBr) 3260, 2975, 2925, 2875, 2860, 1270, 1095, 1035, 1010 cm^{-1}; ^{1}H NMR (250 MHz) δ 3.49 (d, CH$_2$O), 2.78 (m, 6-, 7-H), 2.67 (m, 16-, 17-H), 2.21 (m, 3-, 4a-, 5-, 8-, 9a-, 10-, 13-, 15-, 18-, 20-H), 1.76 (dm, 14s-, 19s-H), 1.62 (dm, 14a-, 19a-H), 1.49 (br s, OH).

Anal. Calcd for $C_{22}H_{24}O_2$ (320.43): C, 82.46; H, 7.55. Found: C, 82.20; H, 7.64.

4-*anti*,9-*anti*-Bis(methylthio)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]eicosane-4,9-dicarboxylic Acid (69). Solid diester **55** (3.77 g, 10 mmol) was added to a solution of lithium diisopropylamide, prepared from diisopropylamine (3.5 mL, 25 mmol) and *n*-butyllithium (10.5 mL of a 2.1 M solution in hexane, 22 mmol), in tetrahydrofuran (150 mL) at −78 °C. The suspension was allowed to warm to room temperature over 1 h and stirred at this temperature for an additional 3 h; it was then cooled to −20 °C, and dimethyl disulfide (2.0 mL, 22 mmol) was added in one portion. A transient clear solution was observed before the product began to precipitate. The mixture was stirred to ambient temperature over 1 h, concentrated to a volume of ca. 75 mL, and diluted with chloroform (200 mL). After extraction with 5% HCl, the solution was dried and evaporated to a volume of ca. 100 mL whereupon the product crystallized. Filtration yielded 3.56 g of **69** as white flakes. Further concentration afforded an additional 0.55 g of product (1:1 mixture of meso and dl atropisomers): total yield 4.11 g, 87%; mp 271–272 °C; IR (KBr) 2950, 2920, 2880, 1710, 1475, 1275, 1240, 1220, 1190, 1040 cm^{-1}; ^{1}H NMR (400 MHz) δ 3.64 (s, OCH$_3$), 3.62 and 3.49 (2 m, 6*-, 7*-H), 3.55 (m, 6-, 7-H), 2.79 and 2.63 (2 m, 3*-, 5*-, 8*-, 10*-H), 2.78 and 2.64 (2 m, 3-, 5-, 8-, 10-H), 2.60 (m, 16-, 17-H), 2.27 and 2.23 (2 m, 13-, 15-, 18-, 20-H), 2.15 (s, SCH$_3$), 1.52 (dm, 14a-, 19a-H), 1.21 (dm, 14s-, 19s-H) (* denotated signals refer to the meso isomer); ^{13}C NMR (100.6 MHz) δ 171.5 (CO), 171.4, 69.7 (C-4, -9), 64.2, 64.0, 63.6, 63.4 (C-1, -2, -11, -12), 59.5, 59.45, 59.4 (C-16, -17), 58.8, 57.7, 56.6 (C-6, -9), 51.7 (OCH$_3$), 47.9, 47.6, 47.5, 46.9, 46.8 (C-3, -5, -8, -10), 42.0, 41.9, 41.8, 41.7 (C-13, -15, -18, -20), 40.5 (C-14, -19), 14.4 (SCH$_3$); MS, *m/e* (relative intensity) 468 (M^{+}, 100), 453 (28), 421 (25), 141 (20), 128 (29), 115 (26), 59 (45), 45 (28).

Anal. Calcd for $C_{26}H_{28}O_4S_2$ (468.62): C, 66.64; H, 6.02. Found: C, 66.34; H, 5.88.

Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]eicosane-4,9-dione (70). A mixture of **69** (0.94 g, 2 mmol) and potassium hydroxide (0.45 g, 8.0 mmol) in ethylene glycol (15 mL) was heated at reflux for 24 h. The solution was distilled to ca. one-half of its volume and cooled to ambient temperature. Glacial acetic acid (0.5 mL, 8.0 mmol) and methanol (40 mL) were added followed by, after 10 min of stirring, sodium bicarbonate (1.26 g, 15.0 mmol). After 15 min, methylene chloride (20 mL) and *N*-chlorosuccinimide (1.07 g, 8.0 mmol) were added, and stirring was continued for 4 h. The mixture was concentrated and partitioned between methylene chloride (50 mL) and 50% brine (75 mL). The aqueous phase was back-extracted with methylene chloride (25 mL), and the combined organic phases were washed with 50% brine (25 mL) and saturated sodium bicarbonate (25 mL). On concentration of the solvent to ca. 25 mL, concentrated hydrochloric acid (10 mL) was added, and the two-phase mixture was stirred for 16 h. The organic layer was separated, washed with water (25 mL), dried, and evaporated to give the diketone **70** (0.52 g, 90%). Recrystallization from chloroform–cyclohexane produced white crystalline spars: mp 321–323 °C dec; IR (KBr) 2940, 2860, 1755, 1165, 565 cm^{-1}; ^{1}H NMR (400 MHz) δ 3.30 (m, 6-, 7-H), 2.94 (m, 16-, 17-H), 2.51 (m, 13-, 15-, 18-, 20-H), 2.24 (dd, 3-, 5-, 8-, 10-H), 1.80 (dm, 14a-, 19a-H), 1.54 (dm, 14s-, 19s-H); ^{13}C NMR (100.6 MHz) δ 210.4 (C-4, -9), 62.0 (C-1, -2, -11, -12), 60.2 (C-16, -17), 47.7 (C-6, -7), 45.9 (C-3, -5, -8, -10), 42.4 (C-13, -15, -18, -20), 41.3 (C-14, -19); MS, *m/e* (relative intensity) 288 (M^{+}, 100), 232 (70), 167 (22), 166 (80), 165 (40), 115 (31), 55 (27), 44 (24), 43 (41), 41 (30).

Anal. Calcd for $C_{20}H_{16}O_2$ (288.35): C, 83.31; H, 5.59. Found: C, 83.07; H, 5.60.

X-ray Crystallographic Analysis of 42. The tetraene crystallized in a monoclinic system, space group $P2_1/n$ (centrosymmetric, racemate), with $a = 14.305$ Å, $b = 12.995$ Å, $c = 14.595$ Å, $\beta = 93.16°$, $V = 2709$ Å^3, and $Z = 8$.

A total of 4165 reflections were recorded on a Philips PW 1100 diffractometer in the θ–2θ scan mode with $2\theta = 6$–$46°$ using Mo Kα monochromatized radiation ($\lambda = 0.70926$ Å).

The unique reflections were used to solve the structure with MULTAN 78 programs. The 40 non-hydrogen atoms were anisotropically refined with block diagonal least squares ($R = 0.110$). All 36 hydrogen atoms were localized on a F map. The conventional R factor for the 3401 reflections considered observed with $I > 2\sigma(I)$ was 0.052.

X-ray Crystallographic Analysis for 55. The dimethyl ester crystallized in a monoclinic system, space group $P2_1/n$ (No. 14, centrosymmetric, racemate), with $a = 17.251$ Å, $b = 6.073$ Å, $c = 16.512$ Å, $\beta = 92.24°$, $V = 1729$ Å^3 and $Z = 4$.

A total of 3898 reflections were recorded on a Philips PW 1100 diffractometer in the θ–2θ scan mode with $2\theta = 6$–$52°$ using Mo Kα monochromatized radiation ($\lambda = 0.70926$ Å).

The unique reflections were used to solve the structure with MULTAN 77 programs. The 28 non-hydrogen atoms were anisotropically refined with block diagonal least squares ($R = 0.109$). All 24 hydrogen atoms were localized on a F map. The conventional R factor for the 2337 reflections considered observed with $I > 2\sigma(I)$ was 0.062.

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An MC–SCF Study of the Mechanisms for 1,3-Dipolar Cycloadditions

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Abstract: MC–SCF gradient calculations are reported for three different 1,3-dipolar cycloaddition reactions—fulminic acid plus acetylene, fulminic acid plus ethylene, and nitrone plus ethylene. At the STO-3G and 4-31G basis set level, the concerted pathway is preferred over the concerted pathway involving a diradical intermediate. An alternative pathway leading to the oxime has also been studied, and these results give further support to the conjecture that the concerted mechanism is preferred.

The utility of 1,3-dipolar cycloaddition reactions in synthetic organic chemistry is well established; however, considerable controversy still surrounds the mechanism of these reactions.[1–4] Although 1,3-dipolar cycloadditions were introduced more than 25 years ago, experimental studies have been unable to choose conclusively between the synchronous, concerted mechanism proposed by Huisgen[1,3] and the stepwise, diradical path favored by Firestone.[2,4]

A variety of theoretical calculations have been performed on these systems over the past two decades. These have concerned themselves with problems of regioselectivity[5–15] or have treated only one mechanism.[12,13,16–18] Ab initio studies, which have treated both mechanisms, have also been unsuccessful in resolving this problem because of inadequate methodology.[19] In previous calculations, the closed-shell species involved in the concerted process and the open-shell (diradical) species encountered in the nonconcerted path could not be compared fairly, since the available methods artificially favored one path over the other. Unlike closed-shell, restricted Hartree–Fock (RHF) and open-shell, unrestricted Hartree–Fock (UHF) methods, the multiconfiguration

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