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Cycloarenes, a New Class of Aromatic Compounds, I

Synthesis of Kekulene

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Definition and nomenclature of cycloarenes, a new class of aromatic compounds, are discussed. Cyclo[*d.e.d.e.d.e.d.e.d.e.d.e*]dodecakisbenzene ("kekulene", **1**) has been synthesized as the first representative of cycloarenes. – From the dithiaphane **11** by double sulfur extrusion, either photochemically or by pyrolysis of disulfone **12**, the carbocyclic system **13** was formed which by dehydrogenation yielded **14**. By Stevens rearrangement of **11** followed by elimination the phanediene **15** was obtained which was dehydrogenated to **18**. From **15** by photo-cyclodehydrogenation in excellent yield the octahydrokekulene **19** was obtained. The different reactivity of **15** and **18** in the photo-cyclodehydrogenation is discussed in terms of electronic and steric effects. Dehydrogenation of **19** yielded **1**.

Cycloarene, eine neue Klasse aromatischer Verbindungen, I

Synthese von Kekulen

Definition und Nomenklatur der Cycloarene, einer neuen Klasse aromatischer Verbindungen, werden diskutiert. Als erster Vertreter der Cycloarene wurde Cyclo[*d.e.d.e.d.e.d.e.d.e.d.e*]dodecakisbenzen („Kekulen", **1**) synthetisiert. – Aus dem Dithiaphan **11** wurde durch doppelte Schwefel-Extrusion, entweder photochemisch oder durch Pyrolyse des Disulfons **12**, das carbocyclische System **13** erhalten, dessen Dehydrierung **14** ergab. Durch Stevens-Umlagerung von **11** mit anschließender Eliminierung entstand das Phan-dien **15**, das zu **18** dehydriert wurde. Durch Photo-Cyclodehydrierung von **15** wurde das Octahydrokekulen **19** in ausgezeichneter Ausbeute erhalten. Die verschiedene Reaktivität von **15** und **18** bei der Photo-Cyclodehydrierung wird in Bezug zu elektronischen und sterischen Effekten diskutiert. Durch Dehydrierung von **19** wurde **1** erhalten.

Introduction

Definition and Nomenclature of Cycloarenes: We define "cycloarenes" as polycyclic aromatic compounds in which, by a combination of angular and linear annellations of benzene units, fully annellated macrocyclic systems are present enclosing a cavity into which carbon-hydrogen bonds point. A selection of conceivable examples of cycloarenes are shown in formulas **1**, **2**, **3** and **4**. Incidentally, all members of the cycloarene series have molecular masses which are multiples of 50; these "magic numbers" are 600 for **1** and **2**, 500 for **3** and 450 for **4**.

Naming of cycloarenes according to existing nomenclature rules, i.e. by selecting arbitrarily two bridge-head atoms and applying the normal rules for polycyclic systems,

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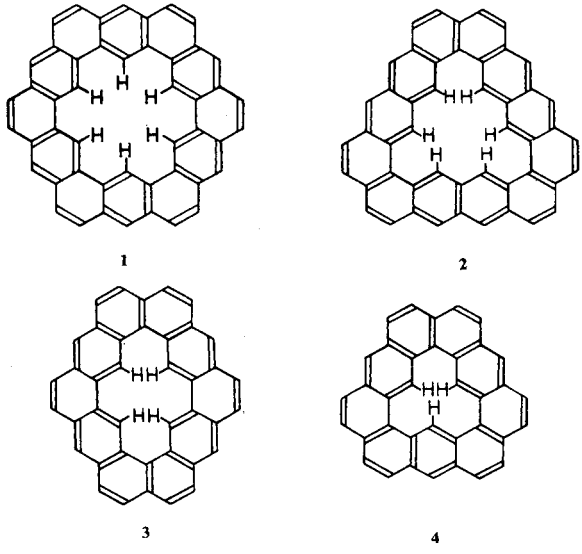
would lead to extraordinarily complicated names which do not indicate in a simple way structure and symmetry of these molecules. Therefore, a specific nomenclature for cycloarenes is suggested[1] as exemplified for **1**–**4**: According to the number of annellated benzene units present, **1** and **2** are named as cyclododecakisbenzenes, **3** as cyclodecakisbenzene and **4** as cyclononakisbenzene. In order to obtain an unambigious notation the type of annellation must be indicated. To this purpose, proceeding clock-wise through the macrocycle each annellation is related to the previous one by labelling as "*a*" the bond of fusion between two rings and then marking the bonds of the individual rings in a clock-wise version which, for the formulas shown, leads to "*d*" for linear and to "*e*" for angular annellations. Thus, for the isomers **1** and **2** which differ in the annellation sequence the names "cyclo[*d.e.d.e.d.e.d.e.d.e.d.e*]dodecakisbenzene" and "cyclo[*d.d.e.e.d.d.e.e.d.d.e.e*]dodecakisbenzene", respectively, are derived. Correspondingly, **3** is "cyclo[*d.e.d.e.e.d.e.d.e.e*]decakisbenzene", and **4** is "cyclo[*d.e.e.d.e.e.d.e.e*]nonakisbenzene".



Theoretical Relevance of Cycloarenes: In 1951 *McWeeny*[2] suggested that **1** should provide a crucial experimental test between the different predictions which Pauling's semi-classical approach and more recent MO calculations made with regard of the diamagnetic anisotropy of aromatic systems. Later, with the rise of annulene chemistry, cycloarenes became of interest in connection with the related problem of benzenoid versus annulenoid aromaticity: On the one hand, cycloarenes can be formulated as a combination of two annulene perimeters bridged by radial single bonds; these perimeters may be of [4n + 2]-type (as in **1**, **2** and **3**) or of [4n]-type (as in **4**). On the other hand, cycloarenes may be considered as regular benzenoid systems where just a specific way of annellation led to a macrocyclic structure. As a unique feature of cycloarenes, the protons in the intramolecular cavity should make it possible to decide by ^{1}H NMR

to what an extent the diatropicity in the macrocyclic system can compete with ring-current induction within the benzenoid subunits. Finally, cycloarenes are interesting aromatic systems with regard to the problem of π-bond delocalisation and as test models for *Clar's* sextet concept[3]; in this context it should be mentioned that for cycloarenes an especially high number of Kekulé structures can be formulated (e.g., for **1** no less than 200 different structures).

Earlier Attempts to Synthesize Cycloarenes: In view of the problems mentioned in the preceding section it is surprising that no cycloarene has been known prior to the synthesis of **1** which is described in this paper[4]. Already in 1965, however, *Staab*[5] reported first attempts to prepare **1** which then, at the centennial of *Kekulé*'s benzene structure, was given the name "kekulene" because of its being regarded as a "superbenzene" on account of its planar cyclic conjugation and D_{6h} symmetry. These first attempts concentrated on the strategy to build up first the inner eighteen-membered perimeter and then complete the thirty-membered periphery. As suitable precursors substituted hexa-*m*-phenylenes[6] and 3.6′;3′.6″;3″.6-triphenanthrylene[7] were envisaged. These attempts failed as did first experiments following the alternative strategy of first closing the outer ring system. In 1968, *Vögtle* and *Staab*[8] developed a new synthetic route to 3,11-bis(bromomethyl)-5,6,8,9-tetrahydrodibenzo[*a,j*]anthracene (**6**) from which by *Wurtz* coupling 5,6,8,9,21,22,24,25-octahydro[2.2](3,11)dibenzo[*a,j*]anthracenophane (**13**) as an interesting potential precursor to **1** was obtained. Yields, however, were extremely poor, and dehydrogenation experiments with **13** did not lead to isolable amounts of **1**. In view of these disappointing results of a very troublesome and long route to **1** this approach was eventually abandoned 15 years ago.

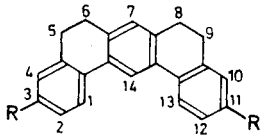
Parallel to our own efforts, *Jenny* et al.[9] had tried, too, to synthesize cycloarenes which they named "coronaphenes"[1]. In fact, as long ago as 1970 they had claimed[10] to have prepared **1**. Since reference has been made to this claim by others we are compelled to state that the authors named until now published neither a synthetic procedure leading to **1** nor any account of properties of **1**. Similarly, the pretension to a synthesis of the carbon skeleton of **3**[11] was never substantiated, and obviously was wrong[12]. More recently, *Wilcox* et al.[13] reported preliminar synthetic studies related to **4**; the synthesis of the cycloarene, however, has not yet been achieved.

Synthesis of Kekulene (1)

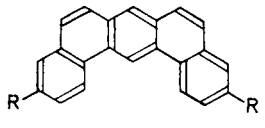
Projected Scheme of the Synthesis of **1**: When the attempts to synthesize **1** were resumed in 1976 we followed, in principle, the earlier approach[8] to build up the outer perimeter by coupling of two suitably substituted dibenzo[*a,j*]anthracene building blocks. In the meantime new efficient methods for the formation of carbon-carbon bonds in macrocyclic systems had been developed and extensively tested in the synthesis of phanes. These methods consist of the primary cyclisation of bis(bromoalkyl)- and bis(mercaptoalkyl)arenes to dithiaphanes and the subsequent sulfur extrusion with formation of carbon-carbon single or double bonds for which a variety of procedures now is available. Thus, the first key stage for the synthesis of **1** had to be the preparation of a dithia[3.3]dibenzo[*a,j*]anthracenophane (e.g., **11**). Sulfur extrusion then should lead to carbocyclic systems which contain already the carbon skeleton of **1** with the

only exception that two carbon-carbon bonds of the inner perimeter were still to be closed.

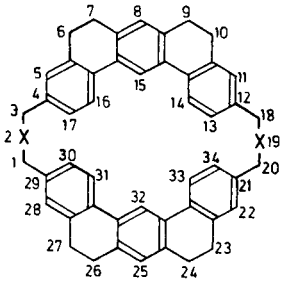
Synthesis of Dibenzo[a,j]anthracene Precursors: In view of the long synthetic route to **1** new more convenient preparative approaches to the dibenzo[*a,j*]anthracene system were sought for. These experiments were partially successful[14]; they did not lead, however, to preparative results superior to the synthesis of 5,6,8,9-tetrahydrodibenzo[*a,j*]-anthracene (**5**) by *Vögtle* and *Staab*[8], especially after this procedure had been adopted by some modifications to large-scale operation (see Experimental Part). Bromomethylation of **5** according to the procedure applied to 9,10-dihydrophenanthrene[15] resulted in the formation of the 3,11-bis(bromomethyl) derivative **6** [mp 260–265 °C (dec.); 51% yield]. Using the thiourea method **6** was converted to the 3,11-bis(mercaptomethyl) derivative **7** (mp 243 °C; 76%) as the second cyclisation component.



5: R = H
6: R = CH_2Br
7: R = CH_2SH
8: R = CH_3



9: R = CH_3
10: R = CH_2Br



11: X = S
12: X = SO_2

For spectroscopic comparison 5,6,8,9-tetrahydro-3,11-dimethyldibenzo[*a,j*]anthracene (**8**) was prepared from **6** by lithium aluminum hydride reduction (mp 214 °C; 64%). Catalytic dehydrogenation yielded 3,11-dimethyldibenzo[*a,j*]anthracene (**9**; mp 182 °C; 81%). Bromination of **9** with *N*-bromosuccinimide in tetrachloromethane led to 3,11-bis(bromomethyl)dibenzo[*a,j*]anthracene (**10**) as a further potential candidate for a cyclisation reaction (dec. 266–268 °C; 70%). Due to the considerably lower solubility of **10** as compared to **6**, however, no cyclisations starting from **10** were tried (as we later learned such cyclisations with the dehydrogenated dibenzoanthracene system would have been dead-end syntheses).

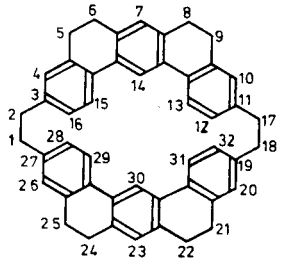
Synthesis of 6,7,9,10,23,24,26,27-Octahydro-2,19-dithia[3.3](4,12)dibenzo[a,j]anthracenophane (**11**) *and its 2,2,19,19-Tetraoxide* (**12**): Sulfur containing precursors from which by extrusion of sulfur or sulfur dioxide, respectively, the carbon skeleton of **1** was expected to be formed are the dithia[3.3]dibenzo[*a,j*]anthracenophane **11** and the disulfone **12** derived therefrom. **11** was obtained by cyclisation of the bis(bromomethyl) compound **6** and the bis(mercaptomethyl) compound **7** in the remarkably high yield of 60% (potassium hydroxide, benzene/ethanol; high dilution).

11 forms pale-yellow platelets of mp 291 °C (corr); elemental analysis and spectroscopic data are in accordance with the structure assumed. Of interest with regard to conformational mobility is the ^1H NMR spectrum [360 MHz, $CDCl_3$: δ = 2.70 (s,

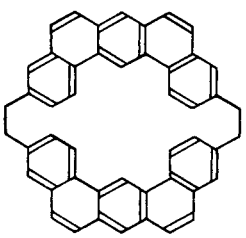
16H), 3.82 (s, 8H), 6.73 (dd, J = 8 and 1.8 Hz, 4H), 6.91 (s, 2H), 6.94 (d, J = 1.8 Hz, 4H), 7.40 (d, J = 8 Hz, 4H), 7.83 (s, 2H)]. The singlets for the methylene groups adjacent to the sulfur (1,3,18,20-H) are neither to be expected for the step-like *anti*-conformation nor for the *syn*-conformation. The experimental results favor conformational changes *anti* ⇌ *syn* ⇌ *anti* with rates fast in relation to the ^{1}H NMR time scale. Comparison of the ^{1}H NMR signals of **11** with those of the monomeric analogue **7** shows that all aromatic hydrogens of **11** are highfield-shifted for about 0.2 – 0.5 ppm. This can be explained by the assumption that to the conformational equilibrium mentioned the *syn*-conformation contributes significantly.

From **11** the disulfone **12** was obtained by oxidation with *m*-chloroperbenzoic acid (chloroform; 15 h at 20 °C; 81%).

5,6,8,9,21,22,24,25-Octahydro[2.2](3,11)dibenzo[a,j]anthracenophane (**13**) *and [2.2](3,11)Dibenzo[a,j]anthracenophane* (**14**): For the preparation of **13** from **11** two methods were promising in view of their successful application in the synthesis of phanes: the photochemical sulfur extrusion[16] from **11** and the sulfone pyrolysis[17] of **12**. In fact, by irradiation of **11** in trimethylphosphite **13** (mp 466 – 470 °C, under nitrogen) was obtained in 59% yield. The usual procedure of vacuum gas-phase pyrolysis was not applicable to **12** because of the extremely low volatility of **12**. However, a short-term pyrolysis in the solid phase which had been developed for other poorly volatile sulfones[18] (details see Experimental Part) turned out to be successful here, too, and led to the formation of **13** from **12** in 75% yield.



13



14

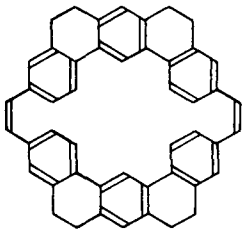
The temperature-dependent ^{1}H NMR spectra (360 MHz, [D_2]-1,1,2,2-tetrachloroethane) of **13** were of interest due to the specific conformational situation caused by strong steric interactions between the two pairs of protons 12-H/32-H and 16-H/28-H. The high upfield-shift of these four protons to δ = 5.84 (br. d, J = 7.45 Hz, at 0 °C) as compared to the neighbouring 13,15,29,31-H at δ = 7.22 (d, J = 7.45 Hz) supports an *anti*-conformation for **13** as does the finding that the remaining aromatic protons show absorptions [δ = 7.12 (br. s, 6H, 7,23-H and 4,10,20,26-H), 7.67 (s, 2H, 14,30-H)] very similar to those of the monomeric analogue **8**. The methylene absorptions of the phane bridges show at 0 °C the expected AA'XX' pattern with δ_A = 2.56 and δ_X = 3.12 whereas for the four CH_2-CH_2 groups (5,6,8,9,21,22,24,25-H) an ABCD multiplet at δ = 2.73 – 3.07 is observed. Due to these latter methylene groups the aromatic rings in the tetrahydrodibenzoanthracene units are twisted against each other

for about 18° (similarly as in 9,10-dihydrophenanthrene). As a consequence of this twisting there are two *anti*-conformations possible for **13**: the step-like conformation with 12-H and 16-H both showing upwards and 28-H and 32-H both turned down, and a centrosymmetric conformation with alternately 12-H up, 16-H down, 28-H up and 32-H down. With regard to sterical strain both conformations seem to be nearly equivalent since both have favorable up-and-down positions for the two pairs of sterically crowded hydrogens. On the basis of the NMR data mentioned above, a distinction between the two conformations is not possible, and therefore for the low-temperature form of **13** both must be considered. When the temperature of NMR measurements is raised, at 50°C a broad unresolved signal (δ = 2.32 – 3.38) appears for all 24 aliphatic protons of **13**. At 120°C the spectrum of **13** is again highly resolved: the low-temperature AA'XX' signal for 1,2,17,18-H now is simplified to a singlet at δ = 2.82, and the ABCD pattern for 5,6,8,9,21,22,24,25-H is changed to a symmetrical AA'BB' signal at δ = 2.84 – 2.96. From these results it is very likely that the flipping motions in the tetrahydrodibenzoanthracene subunits and in the macrocyclic system occur simultaneously in a correlated process; estimation of steric barriers from models support this conclusion. The *syn*-conformation does not contribute significantly to the conformational equilibrium established at higher temperature as is shown by the finding that the NMR absorptions of the aromatic protons, as compared to the low-temperature spectrum, remain essentially unchanged [δ = 5.85 (dd, J = 7.9 and 1.4 Hz, 4H), 7.03 (s, 2H), 7.04 (br. s, 4H), 7.19 (d, J = 7.9 Hz, 4H), 7.68 (s, 2H)].

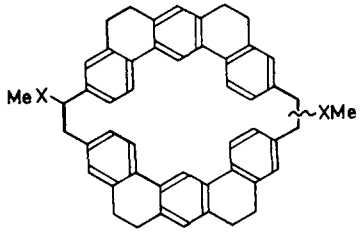
Dehydrogenation of **13** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene yielded **14** as pale-yellow needles [mp 490 – 495°C (dec.); 81%]. It is interesting to compare the internal mobility of **14** with that of the closely related **13**. In ^{1}H NMR (360 MHz, $CDCl_3$) at 45°C the protons of the methylene bridges (1,2,17,18-H) give a simple A_2X_2 pattern with δ = 2.69 ("d", $J \approx$ 9 Hz, 4H), and δ = 3.33 ("d", $J \approx$ 9 Hz, 4H). The signals of 12,16,28,32-H are, as expected, strongly shifted upfield to δ = 5.76 (dd, J = 9 and 2 Hz, 4H). The remaining aromatic protons show the following absorptions: δ = 7.68 and 7.81 (AB, J = 8 Hz, 8H), 7.72 (d, J = 2 Hz, 4H), 8.04 (d, J = 9 Hz, 4H), 8.31 (s, 2H), 9.56 (s, 2H). This absorption pattern is in accordance with a step-like *anti*-conformation. Up to 110°C (in [D_5]nitrobenzene) the spectrum remains essentially unchanged; in contrast to **13** there is no indication for a coalescence of the absorptions of the methylene protons. Thus, as a result of the planarity of the dibenzoanthracene units, **14** exists in a much more rigid and less mobile structure than **13**.

5,6,8,9,21,22,24,25-Octahydro[2.2](3,11)dibenzo[a,j]anthracenophane-1,17-diene (**15**) *and [2.2](3,11)Dibenzo[a,j]anthracenophane-1,17-diene* (**18**): The sulfur-containing macrocycles **11** and **12** are suitable precursors not only for the introduction of carbon-carbon single bonds but also of double bonds which turned out to be crucial for the kekulene synthesis. For the conversion of **11** to **15**, the bis-sulfonium salt formed by the reaction of **11** with methyl fluorosulfonate (in dichloromethane; 92%) was subjected to a Stevens rearrangement (potassium *tert*-butoxide, tetrahydrofuran, 12 h, 20°C). A mixture of isomeric 1,17(18)-bis(methylthio) compounds **16** was obtained in 75% yield. For the introduction of the double bonds **16** was methylated with methyl fluorosulfonate (dichloromethane, 91%), and 1,2-elimination to **15** was achieved (potas-

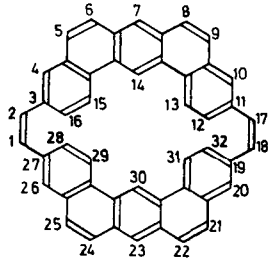
sium *tert*-butoxide, tetrahydrofuran, 12 h, 20°C) in 26% yield. Since in this reaction by-products are formed which are difficult to separate from **15**, the alternative elimination route *via* the disulfoxide **17** was attempted: **16** was oxidized with *m*-chloroperbenzoic acid to **17** (mixture of isomers) which on pyrolysis at 450°C yielded **15** in 43% yield. In contrast to these two procedures for the preparation of **15** from **11**, the application of the Ramberg-Bäcklund reaction to the disulfone **12** led to **15** only in very poor yield.



15



16: X = S
17: X = SO



18

15 crystallizes in pale-yellow plates of mp 472°C (dec., under nitrogen). Elemental analysis and relevant spectroscopic data are in full agreement with the assumed structure (see Experimental Part). The conformational situation of **15** is similar to that discussed for **13**. The ^{1}H NMR spectrum (360 MHz, $CDCl_3$) reveals that at 30°C conformational interconversions are fast resulting in a sharp singlet for the 16 methylene protons at δ = 2.883. The olefinic protons 1,2,17,18-H absorb as a singlet at δ = 6.745. The absorptions of the aromatic protons are in accordance with a predominating *anti*-conformation: δ = 6.575 (dd, J = 8.3 and 1.7 Hz, 4H, 12,16,28,32-H), 7.098 (d, J = 1.7 Hz, 4H, 4,10,20,26-H), 7.114 (s, 2H, 7,23-H), 7.365 (d, J = 8.3 Hz, 4H, 13,15,29,31-H) and 7.658 (s, 2H, 14,30-H) (the numbering of carbon atoms corresponds to formula **18**).

Dehydrogenation of **15** with DDQ (boiling benzene, 24 h; 66%) yielded [2.2](3,11)-dibenzo[*a,j*]anthracenophane-1,17-diene (**18**). **18** is scarcely soluble in most conventional solvents; it may be crystallized, however, from dimethyl sulfoxide out of which **18** is obtained as yellow needles which do not melt up to 520°C (sublimation). Elemental analysis and spectroscopic results are in accordance with the structure suggested. A V-shaped *syn*-conformation as proposed, for example, for [2](3,6)phenanthreno[2]-(2,7)naphthalenophane-1,13-diene[19] and [2.2](3,6)phenanthrenophane-1,13-diene[20] is ruled out for **18** in favour of an *anti*-conformation on the basis of ^{1}H NMR (360 MHz, [D_5]nitrobenzene, 80°C): δ = 7.075 (s, 4H, 1,2,17,18-H), 7.119 (d, J = 8.7 Hz, 4H, 12,16,28,32-H), 7.737 and 7.793 (AB, J = 8.95 Hz, 8H, 5,9,21,25-H and 6,8,22,24-H), 7.782 (br. s, 4H, 4,10,20,26-H), 8.141 (s, 2H, 7,23-H), 8.602 (d, J = 8.7 Hz, 4H, 13,15,29,31-H) and 9.742 (s, 2H, 14,30-H). These ^{1}H NMR data are of interest for comparison with kekulene (**1**) since in the series of **1**-precursors **18** is the only one with a fully conjugated π-system although, in contrast to **1**, annulenoid structures cannot be formulated for **18**. A limitation for this comparison, of course, is the non-planarity of **18**. – The mass spectrum shows M^+ with m/z = 604 as base peak, fragment ions

formed by hydrogen abstraction [m/z = 603 (30%), 602 (28), 601 (40), 600 (43)] as well as doubly charged ions [m/z = 302 (22%, M^{++}), 301 (31), 300 (40)]. In addition, an intense $(M + 2)^+$ peak appears at m/z = 606. This does not indicate, however, incomplete dehydrogenation in the reaction **15** → **18** as is shown by the complete lack of aliphatic absorptions in ^1H NMR and IR. Rather, this finding must result from hydrogen-transfer in the ion source which, due to the very low volatility of **18**, must be heated to about 280°C. Similar observations have been reported for other low-volatile compounds with olefinic double bonds like vinyl-substituted porphyrines[21] and for the structurally related [2.2.2](2,7)phenanthrenophane-1,13,25-triene[9].

Attempted Syntheses of Kekulene by Cyclodehydrogenation of **13** *and* **14**: Catalytic cyclodehydrogenation of **13** and **14** was attempted by sublimating these potential **1**-precursors in a quartz tube through zones of various dehydrogenation catalysts heated to 500 – 600°C. The experimental set-up and a typical experiment out of a series of such attempts is described in detail in the Experimental Part. Obviously, partial dehydrogenation occurred. A separation of the mixture of similar compounds which all are extremely insoluble was, however, not possible.

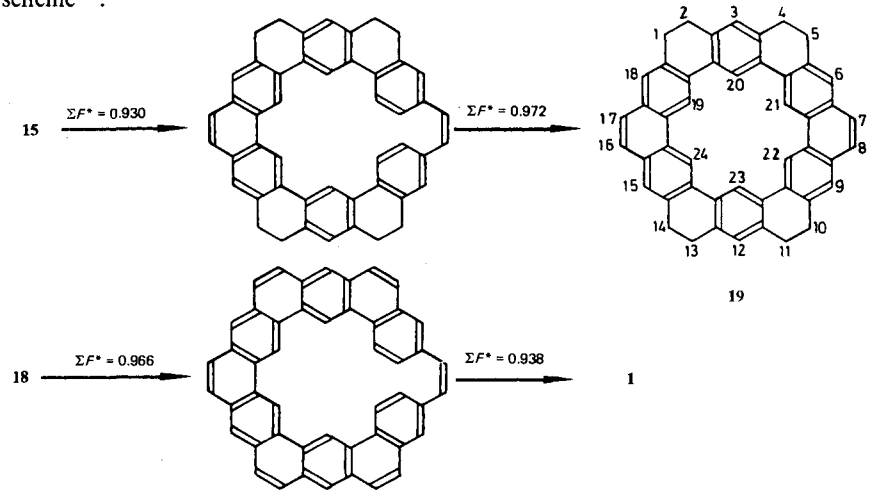
Cyclodehydrogenation in a Scholl reaction had been successfully applied to the synthesis of coronene from [2.2](2,7)naphthalenophane[22]. Under the same conditions no reaction occurred with **13**. Applying more drastic conditions to **13** (aluminum trichloride, sodium chloride; 15 min at 140°C), from the reaction mixture by sublimation (500°C/10^{-3} torr) a product was obtained the mass spectrum of which showed, besides the presence of partially dehydrogenated material and other by-products, strong peaks with m/z = 600 and 300. This indicated that **1** probably was formed. Further purification by extraction with boiling 1,2,4-trichlorobenzene left green-yellow material (17% yield) which consisted predominantly of **1** as shown by spectroscopic comparison with authentic **1** (see below). Two by-products of m/z = 628 and 614 which obviously are alkylated kekulenes could not be separated due to similar insolubility. When applying the same conditions of the Scholl reaction to **14** instead of **13** a black solid was obtained from which no substance could be sublimated at all.

Finally, in analogy to the photochemical conversion of [2.2]metacyclophane to tetrahydropyrene[23], a photochemical cyclodehydrogenation of **14** was attempted. Irradiation in the presence of benzophenone as well as iodine did not lead to the **1**-skeleton; instead, the starting material was reisolated.

Photo-cyclodehydrogenation of **15** *and* **18**; *Synthesis of Kekulene* (**1**): Photochemical cyclodehydrogenations of 1,2-diarylethenes (e.g., from stilbenes to phenanthrenes) are well-studied and widely applied reactions. If there are different positions into which the cyclisation might occur it has been shown[24] that the reaction predominates for which the sum of the free valence indices in the first excited state ΣF^* of the atoms forming the new bond is highest. It has further been suggested that ΣF^* should exceed 1.0 for a successful photo-cyclisation.

To build up the carbon skeleton of **1** starting from **15** and **18** two successive cyclisation/dehydrogenation steps are needed in both cases. From **15** they should lead to 1,2,4,5,10,11,13,14-octahydrokekulene (**19**), from **18** correspondingly to **1** itself. For both reactions from **15** and from **18**, however, the ΣF^* values for each of the two cycli-

sation steps are considerably lower than 1.0 as is seen from the figures in the following scheme[25].



From this point of view, the prospects for both reactions seemed about equally bad. In addition, it was difficult to predict how sterical effects would influence these reactions in view of the very specific sterical situation present. So far, sterical effects on photo-cyclodehydrogenations did not receive much attention. In contrast to normal 1,2-diarylethanes with relative free conformational mobility, sterical effects might, however, have a decisive role in the reactions of **15** and **18** where the reaction centers are sterically fixed by the framework of the macrocyclic systems.

With regard to both problems mentioned, the photochemical experiments with **15** and **18** had surprising results: When **15** was irradiated (300 W Osram-Ultra-Vitalux lamp) in benzene in the presence of iodine a precipitate was formed within minutes. After 10 min no starting material could be detected in the solution any more (TLC). From the precipitate after recrystallization from nitrobenzene in 70% yield octahydrokekulene **19**, the first compound with the carbon skeleton of **1**, was obtained in yellow needles, mp > 620 °C (analytical and spectroscopic data see below). Thus, in spite of the unfavourable ΣF^* values the two successive cyclisation/dehydrogenation steps proceeded with excellent results.

In contrast to the rapid photoconversion of **15** to **19**, the photo-cyclodehydrogenation of **18** which should lead directly to **1** was much less satisfying. Irradiation under the same conditions as for **15** led to the quantitative recovery of the starting material even when the irradiation was extended to 5 h. Only under much more drastic conditions – irradiation with a mercury high-pressure lamp for 13 h – **18** could no longer be detected in the solution (TLC). When working up this reaction a dark material was obtained which beside **1** (MS) contained large quantities of polymeric and partially oxidized products. These unwanted main products of the reaction did not arise from photochemical decomposition of primarily formed **1** during the long irradiation; when later pure **1** was irradiated for 13 h under the same conditions, unchanged **1** was quantitatively recovered.

The extraordinary difference in the photoconversion of **15** and **18** cannot be rationalized on the basis of electronic effects (similar $\Sigma F^* < 1.0$). Instead, it must be explained by the different conformational flexibility in these two systems which has been discussed already in view of ^{1}H NMR data (see above). Due to the methylene bridges in the tetrahydrodibenzo[*a,j*]anthracene units **15** has a much larger conformational mobility than **18** which as a consequence of the planar dibenzo[*a,j*]anthracene systems is considerably more rigid. Obviously, **15** can adopt more easily the most favourable cyclisation geometry allowing optimal interaction of the reacting centers[26]. So we are faced in these reactions with a clear case of sterical control of photo-cyclodehydrogenations which, obviously, can even overule poor electronic conditions for these reactions.

The structure of 1,2,4,5,10,11,13,14-octahydrokekulene (**19**) is unambiguously confirmed by analytical data. The mass spectrum (temperature of inlet system and ion source: 350 and 280°C, resp.) contains the following peaks: m/z = 608 (20%, M^+), 607 (8), 606 (14), 605 (5), 604 (14), 603 (9), 602 (35), 601 (55), 600 (100), 300 (82), 200 (7). This means that from the molecular ion there are successive hydrogen abstractions up to the base peak m/z = 600 corresponding to kekulene of which also the doubly and triply charged ions are observed. The non-appearance of other fragment ions reflects the high stability of the ring system. The ^{1}H NMR spectrum [arsenic trichloride/[D_5]nitrobenzene (3:1), 50°C] is likewise in full accordance with the assumed structure: δ = 3.11 – 3.27 (AA'BB', 16H, 1,5,10,14-H and 2,4,11,13-H), 7.26 (s, 2H, 3,12-H), 7.74 and 7.77 (s, 4H each, 7,8,16,17-H and 6,9,15,18-H), 9.19 (s, 2H, 20,23-H) and 9.67 (s, 4H, 19,21,22,24-H) (cf. formula **19** for numbering of atoms).

The dehydrogenation of **19** to **1** met with considerable difficulties as a consequence of the extreme low volatility as well as solubility. Dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone did succeed, however, using the unusual solvent 1,2,4-trichlorobenzene and a reaction time of 3 days at 100°C. After washing the precipitate formed extensively with ethyl acetate and chloroform nearly pure **1** was obtained in 91% yield. Further purification had to take into account that **1** with regard to insolubility is certainly unsurpassed among hydrocarbons of comparable size[27]. For example, 350 ml of 1-methylnaphthalene at the boiling point 245°C dissolve 10 mg of **1**, 100 ml of boiling 1,2,4-trichlorobenzene (bp 214°C) dissolve about 1 mg of **1**. Recrystallisation from boiling triphenylene (bp 425°C) by slowly cooling to 300°C yielded **1** in greenish-yellow needles. For X-ray structure analysis[28] **1** was best crystallized from pyrene (purified by zone melting) by cooling slowly from 450 to 350°C in a tube sealed under vacuum. Pure **1** may also be obtained, although with partial decomposition, by sublimation under rather drastic conditions (500°C/10^{-3} torr, 1 d for 15 mg).

Properties of Kekulene (1)

The molecular structure of **1** based on an X-ray structure analysis and structure-related spectroscopic properties of **1** will be discussed in detail in the following paper[28]. Here only those data are given which are relevant for the characterisation and the proof of structure of **1**.

Crystals of **1** do not melt up to 620°C (under nitrogen) from where on slow decomposition occurs. Beside the elemental analysis (see Experimental Part) the accurate

elemental composition was also provided by high-resolution mass spectrometry: M^+ Calcd. for $C_{48}H_{24}$: 600.1858; Found: 600.1878. The mass spectrum (temperature of inlet system and ion source >400°C)[29] shows only the molecular peak at m/z = 600 (100%, M^+) and the doubly and triply charged molecular ions m/z = 300 (52) and 200 (7). The complete lack of fragmentations demonstrates the high stability of the molecule which is also shown by its thermal stability. The mass spectra do not show any impurity up to m/z = 2000. To make sure that the dehydrogenation of **19** to **1** was indeed complete the intensities of the (M + 1)- and (M + 2)-peaks were measured (mean intensities taken from 10 mass spectra) and compared with the intensities to be expected for ^{13}C-peaks corresponding to C_{48}; there was agreement within the limits of error.

The number of vibration absorptions of **1** in the IR spectrum is, in accordance with the high molecular symmetry, very small with reference to the 72 atoms present in the molecule: ν = 3020, 3007, 1522, 1404, 1285, 1230, 1174, 959, 889, 879, 864, 781, 742, 705, 430 cm^{-1} (in KBr). – Electronic spectra in absorption and emission will be discussed in the following paper[28].

Recording of an ^1H NMR spectrum of **1** was, due to the extremely low solubility of **1**, extraordinarily difficult[30]. Despite long accumulation times measurements in common high-temperature solvents like [D_6]dimethylformamide, [D_6]dimethyl sulfoxide, [D_{18}]hexamethylphosphoric triamide, [D_5]nitrobenzene or in arsenic trichloride did not give signals. After a long and troublesome search for suitable solvents a successful recording of ^1H NMR spectra of **1** was finally possible in [D_3]-1,3,5-trichlorobenzene (mp 63°C, bp 208°C; for preparation and purification see Experimental Part) and [D_2]-1,2,4,5-tetrachlorobenzene[31] (mp 138°C, bp 243–246°C). The first usable spectrum was obtained for a saturated solution of **1** in [D_3]-1,3,5-trichlorobenzene at about 200°C (80 MHz, 50000 scans, cyclosilane as external standard, given δ-values refer to TMS): three singlets were observed at δ = 7.94, 8.37, and 10.45 with the intensity ratio 2:1:1. Optimal spectra were later recorded in [D_2]-1,2,4,5-tetrachlorobenzene at 155°C (360 MHz, 15000 scans; cyclosilane as internal standard, given δ-values refer to TMS): three singlets in the intensity ratio 2:1:1 were observed at δ = 8.010, 8.447, and 10.470 which are assigned to the three different groups of protons in **1** (1,2,4,5,7,8,10,11,13,14,16,17-H, 3,6,9,12,15,18-H and 19,20,21,22,23,24-H, respectively; numbering of atoms as in formula **19**). A detailed discussion of these results with regard to the diatropicity problem mentioned in the Introduction will be given in the following paper[28].

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Experimental Part

5,6,8,9-Tetrahydrodibenzo[a,j]anthracene (**5**): a) 400 g (470 ml, 3.77 mol) of *m*-xylene was added dropwise with stirring to 1120 ml of ice-cooled fuming nitric acid. After complete addition stirring was continued for 1.5 h at 20°C and for 8 h at 90–100°C. After cooling the reaction mixture was added slowly under vigorous stirring to 5 l of ice-water. The precipitate formed was collected by filtration, washed with 1.5 l of saturated sodium carbonate solution and 2 l of water,

and recrystallized from 3 l of methanol: 665 g (89%) of a 3:1 mixture (^{1}H NMR) of 4,6-dinitro-*m*-xylene and 2,4-dinitro-*m*-xylene (mp of isomer mixture: 59–62°C). 658 g (3.39 mol) of this mixture was heated with 724 ml (6.96 mol) of benzaldehyde and 30 ml of piperidine to 135–140°C. After stirring at this temperature for 2.5 h the reaction water formed was removed by distillation. 30 ml of piperidine was added, and stirring at 135–140°C was continued for 10 h. Upon addition of 500 ml of ethanol to the stirred warm reaction mixture the precipitate was collected by filtration, washed with ethanol and crystallized from 3 l of toluene: 521 g (37%, referred to *m*-xylene) of 4,6-dinitro-1,3-distyrylbenzene, yellow-brown crystals, mp 187°C (lit.[32] 187°C).

b) 150 g (0.40 mol) of 4,6-dinitro-1,3-distyrylbenzene in 1200 ml of ethanol/ethyl acetate (1:1) were hydrogenated in the presence of palladium catalyst (10% Pd on activated charcoal) at 90 atm hydrogen pressure for 3 h at 20°C and 12 h at 50°C. The catalyst was filtered off, and the solvents were evaporated in vacuo. The oily residue was dissolved in ethanol, and 108 g (1.1 mol) of concentrated sulfuric acid was added. The crude precipitates of three such reactions were collected and recrystallized from 3.3 l of ethanol/water (9:1): 381 g (62%) of 4,6-diammonio-1,3-bis(2-phenylethyl)benzene dihydrogensulfate, colourless needles, mp > 220°C (dec.).

c) To a suspension of 361 g (0.71 mol) of the aforementioned product and 13.5 g of copper powder ("Naturkupfer C") in 4 l of ethanol and 180 ml of concentrated sulfuric acid under stirring 242 ml (1.8 mol) of isoamylnitrite was added dropwise within 6 h. After one more hour of stirring the solution was evaporated in vacuo to a volume of 1 l; 2 l of toluene was added, and the mixture was extracted with 600 ml of water. The water extract was extracted twice with 300 ml of toluene; the combined organic phases were washed with saturated sodium carbonate solution and with water, and were dried on sodium sulfate. The oil left behind by evaporation of the solvent in vacuo was chromatographed on silica (2.5 kg) with cyclohexane/toluene (3:1). Upon addition of ligroin (60–70°C) to the eluate crystals of **5** were obtained which were recrystallized from benzene/ethanol (1:1): 23.0 g (12%) of **5**, colourless crystals, mp 161°C (lit.[8] 162°C). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.86 (s, 8H), 7.10 (s, 1H), 7.15–7.50 (m, 6H), 7.85 (d, *J* = 8.4 Hz, 2H), 8.13 (s, 1H).

3,11-Bis(bromomethyl)-5,6,8,9-tetrahydrodibenzo[a,j]anthracene (**6**): To a mixture of 18 g (63 mmol) of **5**, 7.75 g (258 mmol) of paraformaldehyde, 15.2 ml of phosphoric acid (89%), 26.3 ml of acetic acid and 22.1 ml of hydrobromic acid (48%) hydrogen bromide was introduced slowly at 80°C until no further absorption of hydrogen bromide occurred (about 6.5 h). After heating for 2 h to 120°C the crude product was filtered off, washed several times with water, and dried (80°C, 20 torr). Recrystallisation from 800 ml of toluene yielded 15.2 g (51%) of **6**, colourless platelets, mp 260–265°C (dec.). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.87 (s, 8H), 4.52 (s, 4H), 7.10 (s, 1H), 7.27 (d, *J* = 1.8 Hz, 2H), 7.33 (dd, *J* = 8 and 1.8 Hz, 2H), 7.79 (d, *J* = 8 Hz, 2H), 8.08 (s, 1H).

$C_{24}H_{20}Br_2$ (468.3) Calcd. C 61.56 H 4.31 Br 34.13 Found C 61.68 H 4.32 Br 34.21

5,6,8,9-Tetrahydro-3,11-bis(mercaptomethyl)dibenzo[a,j]anthracene (**7**): 4.0 g (8.5 mmol) of **6** and 1.62 g (22.5 mmol) of thiourea in 50 ml ethanol were heated under reflux for 48 h. After standing at 20°C for 12 h the isothiuronium salt was separated by filtration, dissolved in a solution of 2 g of sodium hydroxide in 50 ml of water and refluxed under nitrogen for 3 h. After cooling and acidification with 2 N hydrochloric acid the formed precipitate was filtered off, dried and crystallized from toluene: 2.45 g (76%) of **7**, pale-yellow platelets, mp 243°C (corr.). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.80 (t, *J* = 7.6 Hz, 2H), 2.88 (s, 8H), 3.77 (d, *J* = 7.6 Hz, 4H), 7.10 (s, 1H), 7.23 (d, *J* = 1.8 Hz, 2H), 7.28 (dd, *J* = 8 and 1.8 Hz, 2H), 7.79 (d, *J* = 8 Hz, 2H), 8.08 (s, 1H).

$C_{24}H_{22}S_2$ (374.6) Calcd. C 76.96 H 5.92 S 17.12 Found C 76.85 H 5.97 S 17.24

5,6,8,9-Tetrahydro-3,11-dimethyldibenzo[a,j]anthracene (**8**): 3.65 g (7.8 mmol) of **6** was added gradually under nitrogen at 20°C to a solution of 0.63 g (16.5 mmol) of lithium aluminum hydride in 250 ml of tetrahydrofuran. After refluxing for 3 h and further stirring at 20°C for 12 h the mixture was hydrolysed by adding water followed by sulfuric acid (20%), and extracted with chloroform. The chloroform extract was washed with water and dried over sodium sulfate. Evaporation of the solvent in vacuo and crystallisation of the residue from benzene/ethanol (1:1) yielded 1.54 g (64%) of **8**, long needles, mp 214°C (lit.[8] 215°C). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.35 (s, 6H), 2.83 (s, 8H), 7.08 (br. s, 3H), 7.13 (dd, *J* = 8.2 and 2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 8.07 (s, 1H).

3,11-Dimethyldibenzo[a,j]anthracene (**9**): 1.0 g (3.2 mmol) of **8**, well mixed with 0.2 g of palladium catalyst (10% Pd on activated charcoal), were heated 1 h in a CO_2-atmosphere to 300°C. After cooling chloroform was added, the catalyst was filtered off, the filtrate was evaporated in vacuo, and the residue was crystallized from benzene/ethanol (1:1): 800 mg (81%) of **9**, pale-yellow needles, mp 182°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.55 (s, 6H), 7.49 (dd, *J* = 8.1 and 2 Hz, 2H), 7.63 (d, *J* = 2 Hz, 2H), 7.59 and 7.76 (AB, *J* = 8.8 Hz, 4H), 8.23 (s, 1H), 8.80 (d, *J* = 8.1 Hz, 2H), 9.84 (s, 1H).

$C_{24}H_{18}$ (306.4) Calcd. C 94.08 H 5.92 Found C 93.86 H 5.97

3,11-Bis(bromomethyl)dibenzo[a,j]anthracene (**10**): 100 mg (0.327 mmol) of **9** and 117 mg (0.657 mmol) of *N*-bromosuccinimide in 20 ml of tetrachloromethane in the presence of a catalytic amount of dibenzoylperoxide were heated under reflux for 1 h. The succinimide formed was filtered off from the hot solution and washed three times with 20 ml of hot tetrachloromethane each. The combined filtrates were concentrated by evaporation to about 40 ml, the precipitate formed was isolated by filtration and recrystallized from toluene: 105 mg (70%) of **10**, mp 266–268°C (dec.). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 4.74 (s, 4H), 7.65–8.0 (m, 8H), 8.38 (s, 1H), 8.98 ("d", *J* = 8.8 Hz, 2H), 9.96 (s, 1H).

$C_{24}H_{16}Br_2$ (464.2) Calcd. C 62.10 H 3.47 Br 34.43 Found C 61.95 H 3.50 Br 34.08

6,7,9,10,23,24,26,27-Octahydro-2,19-dithia[3.3](4,12)dibenzo[a,j]anthracenophane (**11**): The solutions of 2.50 g (5.3 mmol) of **6** and of 2.00 g (5.3 mmol) of **7** in 1 l of benzene each, heated for solubility reasons to 75°C, were added dropwise and simultaneously within 24 h under nitrogen to a boiling mixture of 1 l benzene and 1 l ethanol (95%) to which 4 g potassium hydroxide was added. After cooling to room temperature the reaction mixture was neutralised by adding 150 ml of acetic acid, the solvents were evaporated in vacuo, and the solid residue was washed extensively with water and dried (100°C, 18 torr). Chromatography on silica from toluene followed by recrystallisation from toluene yielded 2.18 g (60%) of **11**, pale-yellow platelets, mp (corr.) 291°C. – ^{1}H NMR: see above; MS: M^+ calcd. 680.2571, found 680.2569.

$C_{48}H_{40}S_2$ (681.0) Calcd. C 84.66 H 5.92 S 9.42 Found C 84.42 H 6.10 S 9.60

6,7,9,10,23,24,26,27-Octahydro-2,19-dithia[3.3](4,12)dibenzo[a,j]anthracenophane-2,2,19,19-tetraoxide (**12**): A solution of 1.36 g (2 mmol) of **11** and 1.72 g (10 mmol) of *m*-chloroperbenzoic acid in 100 ml of chloroform was stirred at room temperature for 15 h. The resulting precipitate was filtered off, washed with dichloromethane and ethanol, and crystallized from boiling nitrobenzene: 1.2 g (81%), colourless microcrystals, scarcely soluble in all solvents, dec. >460°C (under nitrogen). – MS: *m/z* = 744 (1%, M^+), 680 (0.3), 616 (12), 310 (80), 308 (100).

$C_{48}H_{40}S_2O_4$ (745.0) Calcd. C 77.39 H 5.41 S 8.61 Found C 77.04 H 5.29 S 8.25

5,6,8,9,21,22,24,25-Octahydro[2.2](3,11)dibenzo[a,j]anthracenophane (**13**): a) *By Photolysis of* **11**: A suspension of 225 mg (0.33 mmol) of **11** in 500 ml of trimethylphosphite was irradiated at 20°C under nitrogen for 2 h with a 450 W mercury high-pressure lamp. The trimethylphosphite

was evaporated under reduced pressure, ethanol was added to the residue, the resulting solid product was isolated by filtration and washed with ethanol and ether. Chromatography on silica from tetrachloromethane yielded 120 mg (59%) of **13**, which was crystallized from chlorobenzene; the crystals contain in a 1:1 ratio chlorobenzene. Pure **13** was obtained by sublimation at 400°C/10^{-3} torr: mp 466–470°C (under nitrogen). – ^{1}H NMR: see above; MS: m/z = 616 (50%, M^+), 615 (12), 614 (21), 613 (3), 612 (6), 309 (76), 308 (92), 307 (100).

$C_{48}H_{40}$ (616.9) Calcd. C 93.46 H 6.54 Found C 93.47 H 6.55

b) *By Pyrolysis of* **12**: A sublimation apparatus with 350 mg (0.47 mmol) of **12** at a vacuum of 10^{-3} torr was dipped in an air bath preheated to 500°C. After 30 min the sublimate on the cooling finger was removed and chromatographed from tetrachloromethane on silica: besides 20 mg of **8**, 219 mg (75%) of **13** was obtained, identical with the product obtained by photolysis of **11** (mp, MS, IR).

[2.2](3,11)Dibenzo[a,j]anthracenophane (**14**): A solution of 220 mg (0.35 mmol) of **13** and 635 mg (2.8 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 50 ml of toluene were refluxed under nitrogen for 24 h. After evaporation of the solvent the residue was chromatographed from chloroform on neutral alumina. The yellow product was recrystallized from nitrobenzene: 175 mg (81%) of **14**, pale-yellow needles, mp 490–495°C (dec.); **14** may also be purified by sublimation at 450°C/10^{-3} torr. – ^{1}H NMR: see above; MS: m/z = 608 (100%, M^+), 607 (4), 606 (4), 304 (54).

$C_{48}H_{32}$ (608.8) Calcd. C 94.70 H 5.30 Found C 94.48 H 5.47

5,6,8,9,21,22,24,25-Octahydro-1,17(18)-bis(methylthio)[2.2](3,11)dibenzo[a,j]anthracenophanes (**16**): 2.0 g (2.94 mmol) of **11** and 1.66 g (14.7 mmol) of methyl fluorosulfonate ("magic methyl") in 50 ml of dichloromethane were stirred at 20°C under nitrogen for 6 h. After addition of ethyl acetate the precipitate was filtered off, washed with ethyl acetate and dried. The bis-sulfonium salt [2.45 g (92%); dec. > 195°C] was, without further purification, suspended in 50 ml of tetrahydrofuran to which at 20°C under nitrogen 1.68 g (15 mmol) of potassium *tert*-butoxide was added. After stirring for 12 h at room temperature the solution was poured into 100 ml of 2 N hydrochloric acid, 100 ml of water was added, and the precipitate formed was collected by filtration, washed with water and dried (100°C, 20 torr). Filtration over a short silica column from toluene yielded 1.43 g (75%) of **16** as a mixture of isomers which was used without further purification in the reaction to **15**. For analytical purposes **16** was precipitated from a solution in boiling toluene/ethyl acetate by slow addition of methanol: pale-yellow microcrystals, mp 384–392°C (dec., under nitrogen). MS: m/z = 708 (20%, M^+), 612 (100).

$C_{50}H_{44}S_2$ (709.0) Calcd. C 84.70 H 6.26 S 9.04 Found C 84.36 H 6.16 S 8.77

5,6,8,9,21,22,24,25-Octahydro[2.2](3,11)dibenzo[a,j]anthracenophane-1,17-diene (**15**): a) *By 1,2-Elimination from* **16**: 1.65 g (2.33 mmol) of **16** and 1.32 g (11.65 mmol) of methyl fluorosulfonate in 50 ml of dichloromethane were stirred at 20°C under nitrogen for 6 h. After addition of ethyl acetate the precipitate was filtered off, washed with ethyl acetate and dried. Of the bis-sulfonium salt [1.98 g (91%); dec. > 185°C] obtained in this way, 1.8 g (1.92 mmol) was suspended in 50 ml of tetrahydrofuran. After addition of 2.16 g (19.2 mmol) of potassium *tert*-butoxide the reaction mixture was stirred under nitrogen at 20°C for 12 h and then added to 100 ml of 2 N hydrochloric acid and 100 ml of water. The precipitate formed was collected by filtration, washed with water and filtered through a short silica column from chloroform. Chromatography of the obtained product on silica (column length 1.2 m) from tetrachloromethane yielded 300 mg (26%) of **15** with R_F = 0.55 (solutions and chromatography columns must be protected from light). Crystallisation from toluene gave **15** in pale-yellow plates, mp 472°C (dec.,

under nitrogen). – ^{1}H NMR: see above; MS: m/z = 612 (100%, M^+), 611 (29), 610 (38), 609 (18), 608 (20), 306 (43, M^{++}).

$C_{48}H_{36}$ (612.8) Calcd. C 94.08 H 5.92 Found C 94.06 H 6.12

b) *By Pyrolysis of the Disulfoxide* **17**: To a solution of 141.6 mg (0.2 mmol) of **16** in 20 ml of dichloromethane at –20°C 70 mg (0.40 mmol) of *m*-chloroperbenzoic acid was added. After stirring at –20°C for 10 min further dichloromethane was added, and the reaction mixture was extracted with concentrated sodium hydrogencarbonate solution and with water, dried over sodium sulfate and evaporated in vacuo. The isolated **17** (140 mg, 95%) was given into a sublimation apparatus which at 10^{-3} torr was dipped in an air-bath preheated to 450°C. The sublimate obtained in 30 min reaction time was chromatographed on silica from tetrachloromethane: 49 mg (43%) of **15**, identical with the product obtained by elimination of **16** (mp, MS, IR).

c) *By Ramberg-Bäcklund Reaction of the Disulfone* **12**: To 200 mg (0.27 mmol) of **12** in a solution of 10 ml of *tert*-butanol and 5 ml of tetrachloromethane under nitrogen at room temperature 2 g of powdered potassium hydroxide was added. After stirring the exothermic reaction mixture for 2 h, 2 N hydrochloric acid and water were added. The resulting precipitate was filtered and dried. Preparative TLC on silica from tetrachloromethane yielded 2 mg (1.2%) of **15**, identified by R_F and IR.

[2.2](3,11)Dibenzo[a,j]anthracenophane-1,17-diene (**18**): A solution of 130 mg (0.21 mmol) of **15** and 232 mg (1.0 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 50 ml of benzene was refluxed under nitrogen for 24 h. Evaporation of the solvent in vacuo, chromatography over a short alumina column from chloroform and recrystallisation from dimethyl sulfoxide yielded after intensive drying (48 h at 120°C/10^{-3} torr) 85 mg (66%) of pure **18**, yellow needles, mp > 520°C (sublimation). – ^{1}H NMR and MS: see above.

$C_{48}H_{28}$ (604.8) Calcd. C 95.33 H 4.67 Found C 95.55 H 4.96
Molecular Mass: Calcd. 604.2191, Found 604.2197 (M^+, MS)

Attempted Catalytic Cyclodehydrogenations of **13** *and* **14**: All experiments were carried out in a quartz tube (length 40 cm, diameter 1 cm) sealed at one end and provided with a cooling finger and a vacuum exit at the other end. The quartz tube was hold in horizontal position and equipped with five mobile ring-ovens which could each be heated independently up to 650°C. **13** and **14** were sublimed at 10^{-3} torr through these catalyst zones at 500–600°C. The sublimate obtained was analyzed by mass spectrometry. Catalysts used were palladium, platinum, rhodium on activated carbon, asbestos, pumice or alumina as well as active copper powder prepared by heating copper oxide in a stream of hydrogen. Example: 30 mg (0.05 mmol) of **14** was sublimated at 500°C through three zones of palladium (10%) on activated charcoal, copper powder, and palladium (30%) on asbestos, each heated to 500°C. The mass spectrum of the yellow sublimate (5 mg) showed the following peaks: m/z = 608 (100%, M^+ of **14**), 606 (63), 604 (52), 602 (15), 600 (21).

Scholl Reaction of **13**: 50 mg (0.08 mmol) of **13** were intimately mixed by magnetic stirring with 300 mg (5.1 mmol) of sodium chloride in a 5 ml flask. After addition of 1.5 g (11 mmol) of aluminum trichloride the flask was closed with a drying tube (silica gel) and immersed into an oil-bath preheated to 140°C. The mixture was stirred at this temperature for 15 min, then carefully hydrolysed with water; the formed green solid was collected by filtration, washed with water, dried and subjected to a sublimation at 500°C/10^{-3} torr. The sublimate was extracted by refluxing 15 h with 20 ml of 1,2,4-trichlorobenzene and filtered after cooling. After washing with acetone and drying: 8 mg (17%) of a green-yellow product, identified by IR and MS as almost pure **1** (see below). Further purification did not succeed.

Attempted Photochemical Cyclodehydrogenation of **14**: 20 mg (0.033 mmol) of **14** in 300 ml benzene was irradiated under nitrogen in the presence of 18 mg (0.07 mmol) of iodine and 19 mg (2.25 mmol) of sodium hydrogencarbonate with a 500 W mercury high-pressure lamp for 24 h. The solid obtained after evaporation and washing with water and acetone was shown by IR to be nearly pure **14**. Essentially the same result was obtained by irradiating in the presence of benzophenone.

1,2,4,5,10,11,13,14-Octahydrokekulene (**19**): 50 mg (0.08 mmol) of **15** in 70 ml of benzene was irradiated in the presence of a catalytic amount of iodine for 10 min with a 300 W Osram-Ultra-Vitalux lamp. After 2–3 min the precipitation of the product started; after 10 min TLC (silica, CCl_4, R_F for **15**: 0.55) showed complete conversion of **15**. The insoluble solid residue, obtained by evaporation of the mixture in vacuo, was suspended in methanol, filtered, washed with methanol and recrystallized from nitrobenzene. The obtained pale-yellow needles were washed extensively with methanol and dried 72 h at 150°C/10^{-3} torr: 35 mg (70%) **19**, mp > 620°C (dec., under nitrogen). – ^{1}H NMR and MS: see General Part.

$C_{48}H_{32}$ (608.8) Calcd. C 94.70 H 5.30 Found C 94.54 H 5.59

The photoconversion **15** → **19** was also achieved with similar yield by 10 min irradiation with a 125 W mercury high-pressure lamp under otherwise identical conditions as mentioned above.

Cyclo[d.e.d.e.d.e.d.e.d.e.d.e]dodecakisbenzene (Kekulene) (**1**): To 50 mg (0.08 mmol) of **19**, dissolved at 100°C in 180 ml of 1,2,4-trichlorobenzene (freshly purified by two distillations), 300 mg (1.32 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added. The reaction mixture was heated for 3 d under nitrogen to 100°C. From the cooled suspension the precipitate was collected by filtration, washed several times with ethyl acetate, chloroform and ether, and dried 3 d at 150°C/10^{-3} torr: 45 mg (91%) of **1** was obtained, which for further purification was sublimated at 500°C/10^{-3} torr during 24 h. Recrystallization of 10 mg of **1** from 350 ml of boiling 1-methylnaphthalene (bp 245°C) gave greenish-yellow microcrystals of **1** in quantitative yield, mp > 620°C (slow dec., under nitrogen). – ^{1}H NMR and MS: see General Part.

$C_{48}H_{24}$ (600.7) Calcd. C 95.97 H 4.03 Found C 95.99 H 3.83

[D_3]-1,3,5-Trichlorobenzene: 7.0 g (38 mmol) of 1,3,5-trichlorobenzene, recrystallized from ethanol and sublimated twice, was stirred under nitrogen with 60 g of D_2SO_4 and 5 ml of D_2O for 24 h at 105°C. After cooling the reaction mixture was poured into ice, the colourless precipitate was isolated by filtration, washed with water, dried and sublimated at 40°C/10^{-3} torr: ^{1}H NMR indicated 80% deuteration. After two more deuteration cycles 4.8 g (68%) of [D_3]-1,3,5-trichlorobenzene with deuteration grade of about 98% was obtained. This product was recrystallized from [D_1]ethanol and sublimated twice before it was used as NMR solvent for **1**.

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[1] The advice of Beilstein-Institut, Frankfurt am Main, for the development of this nomenclature is acknowledged. An alternative naming of cycloarenes as "coronaphenes" suggested by *W. Jenny* et al., l.c.[9,10], has not been adopted since it is less systematic and does not take into account the necessity to specify the annellation sequence.

[2] *R. McWeeny*, Proc. Phys. Soc., London, Sect. A **64**, 261, 921 (1951); cf. also *L. Pauling*, J. Chem. Phys. **4**, 673 (1936).

[3] *E. Clar*, Polycyclic Hydrocarbons, Vols. I and II, Academic Press, New York 1964; The Aromatic Sextet, J. Wiley, London 1972.

[4] *Preliminary Commun.: F. Diederich* and *H. A. Staab*, Angew. Chem. **90**, 383 (1978); Angew. Chem., Int. Ed. Engl. **17**, 372 (1978).

[5] *H. A. Staab*, Plenary Lecture at the Annual Meeting of Gesellschaft Deutscher Chemiker (Kekulé Centennial), Bonn, 14.09.1965.

[6] *H. A. Staab* and *F. Binnig*, Tetrahedron Lett. **1964**, 319; Chem. Ber. **100**, 293, 889 (1967); *H. Bräunling, F. Binnig*, and *H. A. Staab*, ibid. **100**, 880 (1967).
[7] *H. A. Staab, H. Bräunling*, and *K. Schneider*, Chem. Ber. **101**, 879 (1968).
[8] *F. Vögtle* and *H. A. Staab*, Chem. Ber. **101**, 2709 (1968).
[9] *K. Burry* and *W. Jenny*, Helv. Chim. Acta **50**, 1978, 2542 (1967); *W. Jenny* and *R. Paioni*, Chimia **22**, 248 (1968); **23**, 41 (1969); Helv. Chim. Acta **53**, 141 (1970); *P. Baumgartner, R. Paioni*, and *W. Jenny*, ibid. **54**, 266 (1971).
[10] *W. Jenny, P. Baumgartner*, and *R. Paioni*, Proceedings of ISNA, Sendai/Japan, August 1970.
[11] *W. Jenny* and *R. Peter*, Angew. Chem. **77**, 1027 (1965); Angew. Chem., Int. Ed. Engl. **4**, 979 (1965).
[12] Cp. *R. Peter* and *W. Jenny*, Helv. Chim. Acta **49**, 2123 (1966); see also *H. A. Staab, F. Diederich*, and *V. Čaplar*, Liebigs Ann. Chem., in press.
[13] *C. F. Wilcox jr., P. M. Lahti, J. R. Rocca, M. B. Halpern*, and *J. Meinwald*, Tetrahedron Lett. **1978**, 1893.
[14] *F. Diederich, K. Schneider*, and *H. A. Staab*, Chem. Ber., in press.
[15] *H. A. Staab* and *M. W. Haenel*, Chem. Ber. **106**, 2190 (1973).
[16] *V. Boekelheide, I. D. Reingold*, and *M. Tuttle*, J. Chem. Soc., Chem. Commun. **1973**, 406; *J. Bruhin* and *W. Jenny*, Tetrahedron Lett. **1973**, 1215.
[17] *F. Vögtle*, Angew. Chem. **81**, 258 (1969); Angew. Chem., Int. Ed. Engl. **8**, 274 (1969); *M. W. Haenel* and *H. A. Staab*, Tetrahedron Lett. **1970**, 3585; Chem. Ber. **106**, 2190 (1973); see also *A. Ruland* and *H. A. Staab*, ibid. **111**, 2997 (1978).
[18] *P. Wahl*, Dissertation, Univ. Heidelberg 1981.
[19] *P. J. Jessup* and *J. A. Reiss*, Aust. J. Chem. **30**, 851 (1977).
[20] *T. Liljefors* and *O. Wennerström*, Tetrahedron **33**, 2999 (1977).
[21] *H. Budzikiewicz* and *S. E. Drewes*, Liebigs Ann. Chem. **716**, 222 (1968).
[22] *W. Baker, F. Glockling*, and *J. F. McOmie*, J. Chem. Soc. **1951**, 1118.
[23] *T. Sato* and *T. Takemura*, J. Chem. Soc., Perkin Trans. 2 **1976**, 1195; there further references to earlier work.
[24] *W. H. Laarhoven, Th. J. H. M. Cuppen*, and *R. J. F. Nivard*, Tetrahedron **26**, 1069, 4865 (1970).
[25] *H. Vogler*, private communication.
[26] Cf., for example, *A. H. A. Tinnemanns, W. H. Laarhoven, S. Sharafi-Ozeri*, and *K. A. Muszkat*, Rec. Trav. Chim. Pays-Bas **94**, 239 (1975); *K. A. Muszkat, S. Sharafi-Ozeri, G. Seger*, and *T. A. Pakkanen*, J. Chem. Soc., Perkin Trans. 2 **1975**, 1515.
[27] The only polycyclic aromatic hydrocarbon the insolubility of which comes close to that of **1**, to our knowledge, is hexabenzo[*bc,ef,hi,kl,no,qr*]coronene: *E. Clar, C. T. Ironside*, and *M. Zander*, J. Chem. Soc. **1959**, 142.
[28] *H. A. Staab, F. Diederich, C. Krieger*, and *D. Schweitzer*, Chem. Ber. **116**, 3504 (1983), following. See also the preliminary communication: *C. Krieger, F. Diederich, D. Schweitzer*, and *H. A. Staab*, Angew. Chem. **91**, 733 (1979); Angew. Chem., Int. Ed. Engl. **18**, 699 (1979).
[29] We thank Dr. *W. Otting*, Heidelberg, for recording the mass spectra of **1**.
[30] The great effort Professor *J. Dabrowski* and *D. Griebel* of our Department made in overcoming the unusual technical difficulties in the ^{1}H NMR measurements of **1** is gratefully acknowledged.
[31] *H. Zimmermann*, Mol. Cryst. Liq. Cryst. Lett. **49**, 1 (1978); we thank *H. Zimmermann* for providing us with a sample of this compound.
[32] *P. Ruggli, A. Zimmermann*, and *R. Thouvay*, Helv. Chim. Acta **14**, 1250 (1931).

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