

[3.3]- and [4.4](2,7)Pyrenophanes as Excimer Models: Synthesis, Molecular Structure, and Spectroscopic Properties

Heinz A. Staab*, Norbert Riegler, François Diederich, Claus Krieger, and Dieter Schweitzer

Max-Planck-Institut für medizinische Forschung, Abteilung Organische Chemie, and Abteilung Molekulare Physik, Jahnstr. 29, D-6900 Heidelberg

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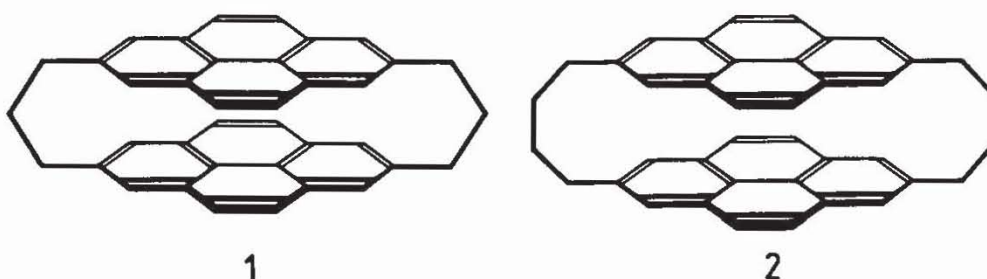
As excimer models the [3.3]- and [4.4]pyrenophanes **1** and **2** were synthesized. As the key precursor for the synthesis of **1** the octahydro-dithia[4.4]pyrenophane **9** was obtained by cyclisation of **4** and **8**, the syntheses of which are described. Disulfone **10**, derived from **9**, on vapour-phase pyrolysis yielded **11** which by dehydrogenation was converted into **1**. In an analogous route **2** was obtained via **16**, **17**, and **18** starting from **4** and **15** (prepared in the reaction sequence **12** → **13** → **14** → **15**). – The molecular structures of **1** and **2**, determined by X-ray structure analyses, are discussed with regard to transannular distances and deviations from planarity of the pyrene units. – Absorption spectra of **1** and **2** are discussed with reference to transannular interactions. The fluorescence emissions of **1** and **2** are found to be 'excimer-like'. Results obtained by ODMR measurements of **1** are reported.

[3.3]- und [4.4](2,7)Pyrenophane als Excimeren-Modelle: Synthese, Molekülstruktur und spektroskopische Eigenschaften

Als Excimeren-Modelle wurden die [3.3]- und [4.4]Pyrenophane **1** und **2** synthetisiert. Als Vorstufe für die Synthese von **1** wurde das Octahydro-dithia[4.4]pyrenophan **9** durch Cyclisierung von **4** und **8** erhalten, deren Synthese beschrieben wird. Das von **9** abgeleitete Disulfon **10** ergab durch Gasphasen-Pyrolyse **11**, das durch Dehydrierung in **1** übergeführt wurde. Auf analogem Wege wurde **2** über **16**, **17** und **18** ausgehend von **4** und **15** (dargestellt in der Reaktionsfolge **12** → **13** → **14** → **15**) erhalten. – Die Molekülstrukturen von **1** und **2** wurden durch Röntgen-Strukturanalyse bestimmt; sie werden im Hinblick auf transannulare Abstände und Abweichungen von der Planarität der Pyren-Einheiten diskutiert. – Die Absorptionsspektren von **1** und **2** werden im Zusammenhang mit der transannularen Wechselwirkung diskutiert. Die Fluoreszenz-Emission von **1** und **2** entspricht dem Excimeren-Charakter dieser Verbindungen. Ergebnisse, die durch ODMR-Messungen an **1** erhalten wurden, werden mitgeteilt.

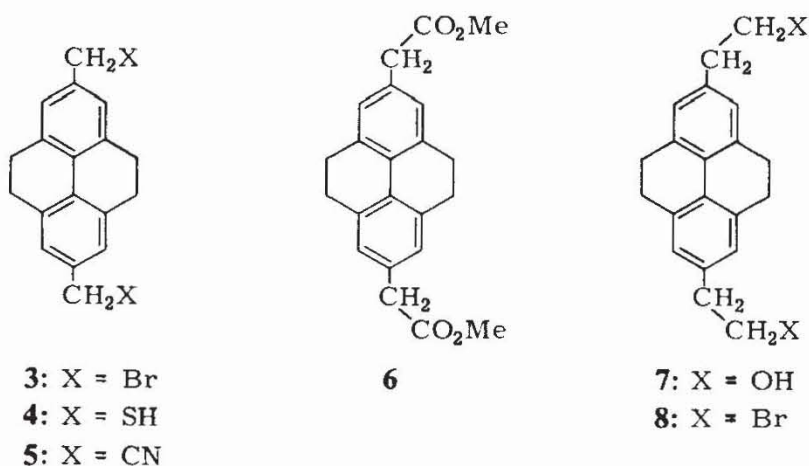
The first and most typical example of an 'excimer' formation has been observed for pyrene¹⁾. On photoexcitation a complex is formed by an excited pyrene molecule with a second pyrene which is in the electronic ground state: $Ar^* + Ar \rightleftharpoons (Ar_2)^*$ (excited dimer = 'excimer'). Whereas absorption spectra are not affected, excimer formation results in a concentration dependent change in the fluorescence emission which, as compared to monomer emission, is strongly red-shifted, broad, and structureless. In spite of the undisputed importance of excimers for the photophysics and photochemistry of aromatic systems, so far only very limited experimental evidence has been

available concerning the sterical structure of excimers, i.e. the mutual orientation and the distance of the components. Recently, compounds with two aromatic units fixed intramolecularly in a well-defined geometry found increasing interest as excimer models²⁾. In this connection [2.2](2,7)pyrenophane has been synthesized³⁾ which in fact shows spectroscopic properties in accordance with an intramolecular excimer analogue⁴⁾. As X-ray structure analysis showed, however, the aromatic π -systems in [2.2](2,7)pyrenophane deviate strongly from planarity due to the high sterical strain present in this [2.2]phane structure^{3d)}. Under this aspect, the higher homologues [3.3](2,7)pyrenophane (**1**) and [4.4](2,7)pyrenophane (**2**) seemed to be of special interest as excimer models since here nearly, or even completely, planar pyrene units were to be expected. We report here on the synthesis of **1** and **2**, on the determination of their molecular structures by X-ray analysis, and on spectroscopic properties as related to the excimer state.



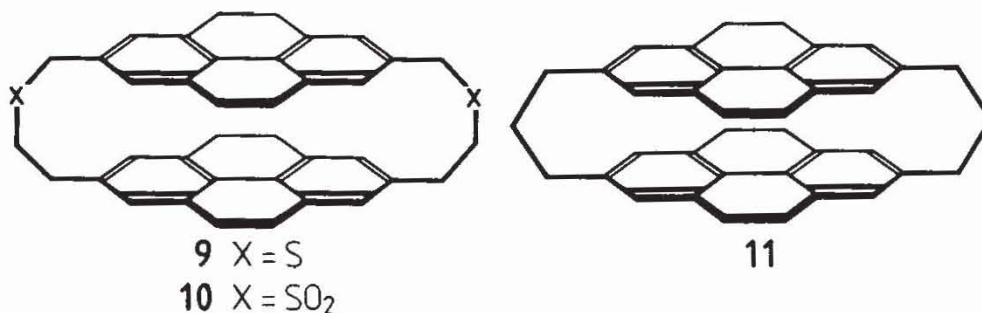
Synthesis of [3.3](2,7)Pyrenophane (**1**)

For the preparation of the pyrene derivatives needed for the cyclisation to **1**, direct functionalisation of pyrene or tetrahydropyrene proved to be inconvenient in yield and procedure considering the long synthetic route to follow. Instead, we made use of the approach *via* correspondingly substituted [2.2]metacyclophanes as suggested by *Misumi et al.*^{3a)} and *Mitchell et al.*^{3b)}. Following these procedures with slight modifications 2,7-bis(bromomethyl)-4,5,9,10-tetrahydropyrene (**3**) was prepared starting from 1,3-bis(bromomethyl)- and 1,3-bis(mercaptomethyl)-5-methylbenzenes. From **3** by the thiourea method 4,5,9,10-tetrahydro-2,7-bis(mercaptomethyl)pyrene (**4**) was obtained as the first cyclisation component for the synthesis of **1**. For the second component the extension of the side chains to C_2 -units was necessary. For this purpose, **3** was converted to the 2,7-bis(cyanomethyl) compound **5** (NaCN, dimethyl sulfoxide,



20°C; 83%) which with hydrogen chloride/methanol yielded dimethyl 4,5,9,10-tetrahydro-2,7-pyrenediacetate (**6**; 95%). Lithium aluminum hydride reduction led to 4,5,9,10-tetrahydro-2,7-bis(2-hydroxyethyl)pyrene (**7**; 82%) which with tetrabromomethane/triphenylphosphane was converted into the 2,7-bis(2-bromoethyl) compound **8** (88%).

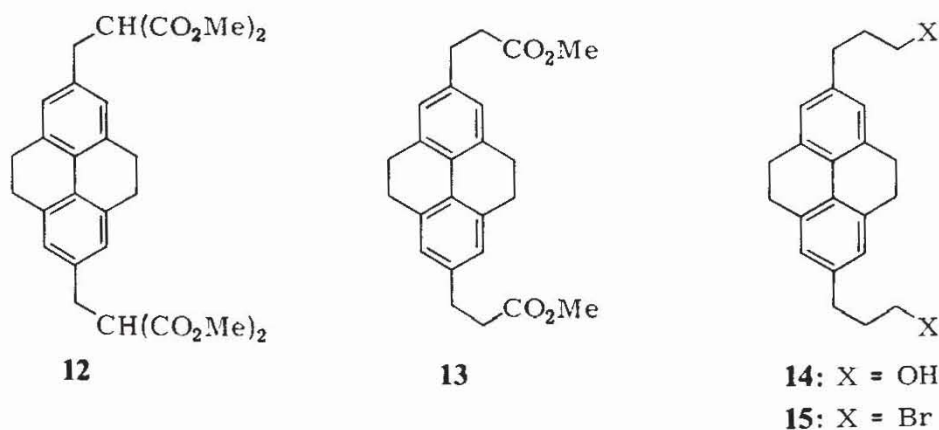
Cyclisation of **4** and **8** [potassium carbonate, boil. ethanol/*tert*-butyl alcohol (1:1), high dilution] yielded 7,8,12,13,21,22,26,27-octahydro-2,17-dithia[4.4](2,7)pyrenophane (**9**; 53%). Oxidation with 3-chloroperoxybenzoic acid/chloroform resulted in the formation of the disulfone **10** (87%). By sulfone pyrolysis⁵⁾ of **10** at 580–600°C/ $2 \cdot 10^{-6}$ Torr 6,7,11,12,19,20,24,25-octahydro[3.3](2,7)pyrenophane (**11**), together with some partially dehydrogenated product, was obtained in 25% yield. Dehydrogenation (Pd/C, 1-methylnaphthalene, 24 h, 245°C) converted **11** into **1** (72%).



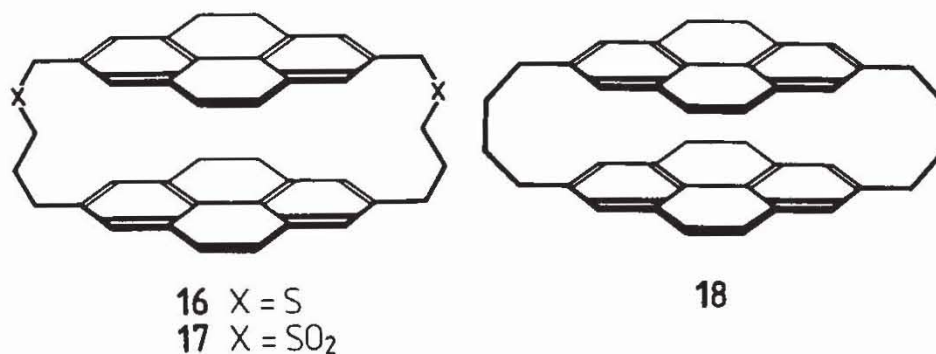
1 crystallized in yellow plates (dec. >355°C). Elemental analysis and spectroscopic properties are in accordance with structure **1** [¹H NMR (CDCl₃, 360 MHz): δ = 2.50–2.61 (m, 4H), 3.15–3.31 (m, 8H), 7.378 (s, 8H), 7.405 (s, 8H). – MS: *m/z* = 484 (100%, M⁺), 242 (44, M²⁺), 230 (41), 215 (13)].

Synthesis of [4.4](2,7)Pyrenophane (**2**)

As in the case of the synthesis of **1**, the preparation of the higher homologue **2** started from 2,7-bis(bromomethyl)-4,5,9,10-tetrahydropyrene (**3**) which by malonic ester synthesis yielded 2,7-bis[2,2-bis(methoxycarbonyl)ethyl]-4,5,9,10-tetrahydropyrene (**12**, 90%). By demethoxycarbonylation⁶⁾ (NaCl/H₂O, dimethyl sulfoxide, 3 h, 160–170°C; 59%), 4,5,9,10-tetrahydro-2,7-bis[2-(methoxycarbonyl)ethyl]pyrene (**13**) was obtained which *via* 4,5,9,10-tetrahydro-2,7-bis(3-hydroxypropyl)pyrene (**14**; by lithium aluminum hydride reduction of **13**; 97%) was converted into the bis(bromopropyl) compound **15** (tetrabromomethane, triphenylphosphane; 73%).



Cyclisation of **15** with the bis(mercaptomethyl) compound **4** (potassium carbonate, methanol, high dilution) yielded 8,9,13,14,23,24,28,29-octahydro-2,19-dithia[5.5](2,7)-pyrenophane (**16**; 29%) which was oxidized to the corresponding disulfone **17** (3-chloroperoxybenzoic acid, chloroform; 86%). Gas-phase pyrolysis of **17** at 580–600°C/10⁻⁶ Torr led to the octahydro[4.4](2,7)pyrenophane **18**. Considering the very drastic conditions of this reaction and the fact that a 24-membered macrocyclic system is formed in a two-step reaction the pyrolysis yield of 69% is very remarkable. By dehydrogenation (DDQ, toluene) of **18** [4.4](2,7)pyrenophane (**2**) was obtained in 66% yield.



2 forms yellow crystals of mp 402–404°C (under argon). Elemental analysis and spectroscopic data agree with the structure suggested [¹H NMR ([D₂]-1,1,2,2-tetrachloroethane, 100°C, 360 MHz): δ = 2.16 (br 's', 8H), 2.78 (br 's', 8H), 7.276 (s, 8H), 7.293 (s, 8H). – MS: *m/z* = 512 (100%, M⁺), 256 (12, M²⁺)].

Molecular and Crystal Structures of **1** and **2**⁷⁾

X-Ray Structure Analysis: Crystal and data collection parameters of **1** and **2** are listed in Table 1. Intensity data were collected using a graphite-monochromated Mo-K_α radiation and applying $\Theta/2\Theta$ -scan technique. The structures were solved by conventional direct methods (MULTAN) and were refined by full-matrix least-squares technique using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. Atomic coordinates and thermal parameters for non-hydrogen atoms of **1** and **2** are given in Tables 2 and 3 (for numbering of atoms which for the sake of comparison between **1** and **2** differ from conventional phane rules see Figures 1A and 2A).

Molecular Structure of 1: Figure 1 shows the molecular structure of **1** in a top-view perpendicular to the pyrene planes (A) and in a side-view (B). As expected the pyrene units in **1** are much less bent out of planarity than in the analogous [2.2]pyrenophane^{3d)}. Whereas for the latter compound transannular distances vary from 279 pm for the distance between the bridgehead carbons to 378 pm for the interplanar distance in the center of the molecule, the corresponding distances in **1** are 318 and 348 pm. Thus, in spite of the longer bridges, in **1** there is considerable overlap of the two pyrene π -systems. In contrast to [2.2](2,7)pyrenophane where corresponding carbon atoms are nearly in eclipsed positions, for **1**, however, a lateral displacement of $L = 40$ pm in the long pyrene axis and $M = 106$ pm perpendicular to that axis is found as shown in Figure 1A. As a consequence of this displacement the shortest transannular distance is not between corresponding carbon atoms (see Figure 1B).

Table 1. Crystal and Data Collection Parameters for 1 and 2

Compound	1	2
Formula	C ₃₈ H ₂₈	C ₄₀ H ₃₂
Molecular mass	484.6	512.7
<i>a</i> [pm]	1005.2(2)	1046.8(3)
<i>b</i> [pm]	1013.7(2)	1016.5(2)
<i>c</i> [pm]	1192.6(2)	1255.2(2)
β [°]	91.05(2)	96.29(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	2
<i>D</i> _x [gcm ⁻³]	1.32	1.28
Max. $\sin \Theta / \lambda$ [nm ⁻¹]	6.2	6.7
No. of reflections measured	2404	2329
No. of reflections with $I \geq 1.96 \sigma(I)$	1611	1462
<i>R</i>	0.043	0.060

Table 2. Atomic Coordinates and Thermal Parameters U_{equ} (in pm²) of Non-Hydrogen Atoms of 1 (Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digits)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{equ}
C(1)	0.3603(2)	0.1886(2)	0.4489(1)	465(5)
C(2)	0.2377(2)	0.2498(2)	0.4627(1)	455(5)
C(3)	0.2299(2)	0.3528(2)	0.5391(1)	430(5)
C(3A)	0.3418(2)	0.4015(2)	0.5965(1)	371(4)
C(3B)	0.4672(2)	0.3417(2)	0.5781(1)	358(4)
C(4)	0.3355(2)	0.5138(2)	0.6692(1)	410(4)
C(5)	0.4464(2)	0.5652(2)	0.7172(1)	416(4)
C(5A)	0.5752(2)	0.5093(2)	0.6985(1)	368(4)
C(5B)	0.5840(2)	0.3957(2)	0.6296(1)	355(4)
C(6)	0.6912(2)	0.5677(2)	0.7396(1)	437(5)
C(7)	0.8163(2)	0.5197(2)	0.7131(1)	453(5)
C(8)	0.8243(2)	0.4036(2)	0.6511(1)	463(5)
C(8A)	0.7111(2)	0.3400(2)	0.6082(1)	405(4)
C(9)	0.7153(2)	0.2238(2)	0.5386(1)	464(5)
C(10)	0.6047(2)	0.1738(2)	0.4897(1)	471(5)
C(10A)	0.4761(2)	0.2316(2)	0.5050(1)	405(4)
C(11)	0.9380(2)	0.6011(2)	0.7411(1)	552(5)
C(12)	0.9824(2)	0.6898(2)	0.6449(2)	551(5)
C(13)	0.8835(2)	0.7959(2)	0.6053(2)	593(6)

Table 3. Atomic Coordinates and Thermal Parameters U_{equ} (in pm^2) of Non-Hydrogen Atoms of **2** (Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digits)

Atom	x	y	z	U_{equ}
C(1)	0.2206(3)	0.3636(3)	0.6385(2)	573(9)
C(2)	0.2290(3)	0.4718(3)	0.7062(2)	579(9)
C(3)	0.3464(3)	0.5344(3)	0.7282(2)	566(9)
C(3A)	0.4557(2)	0.4923(3)	0.6836(2)	495(8)
C(3B)	0.4469(2)	0.3819(3)	0.6139(2)	458(8)
C(4)	0.5781(3)	0.5569(3)	0.7056(2)	581(9)
C(5)	0.6824(3)	0.5146(3)	0.6620(2)	571(9)
C(5A)	0.6769(2)	0.4023(3)	0.5916(2)	505(8)
C(5B)	0.5575(2)	0.3368(3)	0.5681(2)	456(8)
C(6)	0.7833(3)	0.3556(3)	0.5460(2)	585(9)
C(7)	0.7776(3)	0.2466(3)	0.4784(2)	573(9)
C(8)	0.6602(3)	0.1843(3)	0.4550(2)	599(9)
C(8A)	0.5492(3)	0.2260(3)	0.4984(2)	505(8)
C(9)	0.4269(3)	0.1625(3)	0.4771(2)	575(9)
C(10A)	0.3271(3)	0.3164(3)	0.5914(2)	498(8)
C(10)	0.3225(3)	0.2044(3)	0.5213(2)	570(9)
C(11)	0.8988(3)	0.1962(3)	0.4353(3)	750(10)
C(12)	0.9742(3)	0.3028(3)	0.3784(3)	780(10)
C(13)	0.9170(3)	0.3333(3)	0.2652(3)	830(10)
C(14)	0.8862(3)	0.4784(3)	0.2423(2)	740(10)

Table 4. C...C Bond Lengths of **1** and **2** (in pm; Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digit)

		<u>1</u>	<u>2</u>			<u>1</u>	<u>2</u>
C(1) - C(2)		139.3(2)	138.6(3)	C(5A) - C(6)		138.9(2)	139.0(3)
C(1) - C(10A)		140.1(2)	140.3(3)	C(5B) - C(8A)		142.4(2)	142.3(3)
C(2) - C(3)		138.9(2)	138.5(3)	C(6) - C(7)		138.9(2)	139.2(3)
C(2) - C(13')		152.2(2)	-	C(7) - C(8)		139.3(2)	138.5(3)
C(2) - C(14')		-	151.6(3)	C(7) - C(11)		150.9(2)	152.2(3)
C(3) - C(3A)		139.6(2)	139.4(3)	C(8) - C(8A)		139.6(2)	140.1(3)
C(3A) - C(3B)		142.0(2)	142.0(3)	C(8A) - C(9)		144.2(2)	143.2(3)
C(3A) - C(4)		143.4(2)	143.9(3)	C(9) - C(10)		134.5(2)	134.8(3)
C(3B) - C(5B)		142.4(2)	142.4(3)	C(10) - C(10A)		143.5(2)	143.6(3)
C(3B) - C(10A)		142.0(2)	142.1(3)	C(11) - C(12)		153.0(2)	155.9(3)
C(4) - C(5)		134.8(2)	134.4(3)	C(12) - C(13)		153.4(2)	151.2(3)
C(5) - C(5A)		143.5(2)	144.1(3)	C(13) - C(14)		-	153.0(3)
C(5A) - C(5B)		141.8(2)	141.8(3)				

Table 5. Bond Angles of 1 and 2 (in °; Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digit)

			1	2				1	2
C(2) - C(1) - C(10A)	122.3(1)	122.0(2)	C(3B) - C(5B) - C(8A)	120.4(1)	120.4(2)				
C(1) - C(2) - C(3)	118.2(1)	118.8(2)	C(5A) - C(5B) - C(8A)	119.4(1)	119.5(2)				
C(1) - C(2) - C(13')	120.2(1)	-	C(5A) - C(6) - C(7)	121.8(1)	122.6(2)				
C(1) - C(2) - C(14')	-	121.7(3)	C(6) - C(7) - C(8)	118.5(1)	118.1(2)				
C(3) - C(2) - C(13')	121.6(1)	-	C(6) - C(7) - C(11)	119.4(1)	120.1(3)				
C(3) - C(2) - C(14')	-	119.5(3)	C(8) - C(7) - C(11)	121.7(1)	121.7(3)				
C(2) - C(3) - C(3A)	122.2(1)	121.9(2)	C(7) - C(8) - C(8A)	122.0(1)	122.2(2)				
C(3) - C(3A) - C(3B)	118.9(1)	119.3(2)	C(5B) - C(8A) - C(8)	118.6(1)	118.7(2)				
C(3) - C(3A) - C(4)	122.2(1)	122.4(2)	C(5B) - C(8A) - C(9)	117.5(1)	117.7(2)				
C(3B) - C(3A) - C(4)	118.8(1)	118.3(2)	C(8) - C(8A) - C(9)	123.8(1)	123.6(2)				
C(3A) - C(3B) - C(5B)	119.8(1)	120.2(2)	C(8A) - C(9) - C(10)	121.6(1)	121.9(2)				
C(3A) - C(3B) - C(10A)	119.7(1)	119.3(2)	C(9) - C(10) - C(10A)	122.1(1)	121.9(2)				
C(5B) - C(3B) - C(10A)	120.4(1)	120.5(2)	C(1) - C(10A) - C(3B)	118.5(1)	118.7(2)				
C(3A) - C(4) - C(5)	121.2(1)	121.5(2)	C(1) - C(10A) - C(10)	123.7(1)	123.7(2)				
C(4) - C(5) - C(5A)	121.5(1)	121.6(2)	C(3B) - C(10A) - C(10)	117.8(1)	117.6(2)				
C(5) - C(5A) - C(5B)	118.5(1)	118.3(2)	C(7) - C(11) - C(12)	113.7(1)	114.4(2)				
C(5) - C(5A) - C(6)	122.1(1)	122.9(2)	C(11) - C(12) - C(13)	116.5(1)	113.9(3)				
C(5B) - C(5A) - C(6)	119.3(1)	118.8(2)	C(2') - C(13) - C(12)	117.3(1)	-				
C(3B) - C(5B) - C(5A)	120.2(1)	120.1(2)	C(2') - C(14) - C(13)	-	113.7(2)				

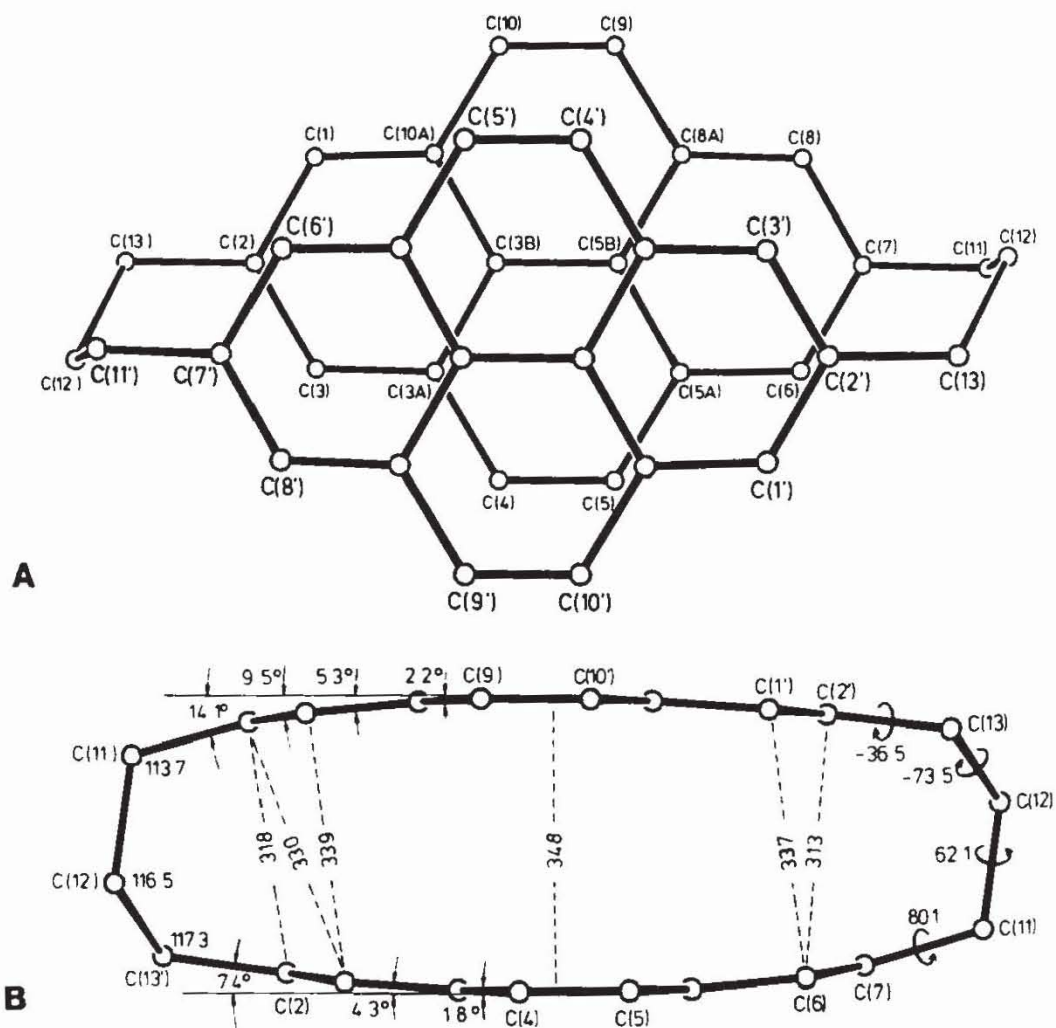


Figure 1. Molecular Structure of 1 in a Top-View (A) and in a Side-View (B)

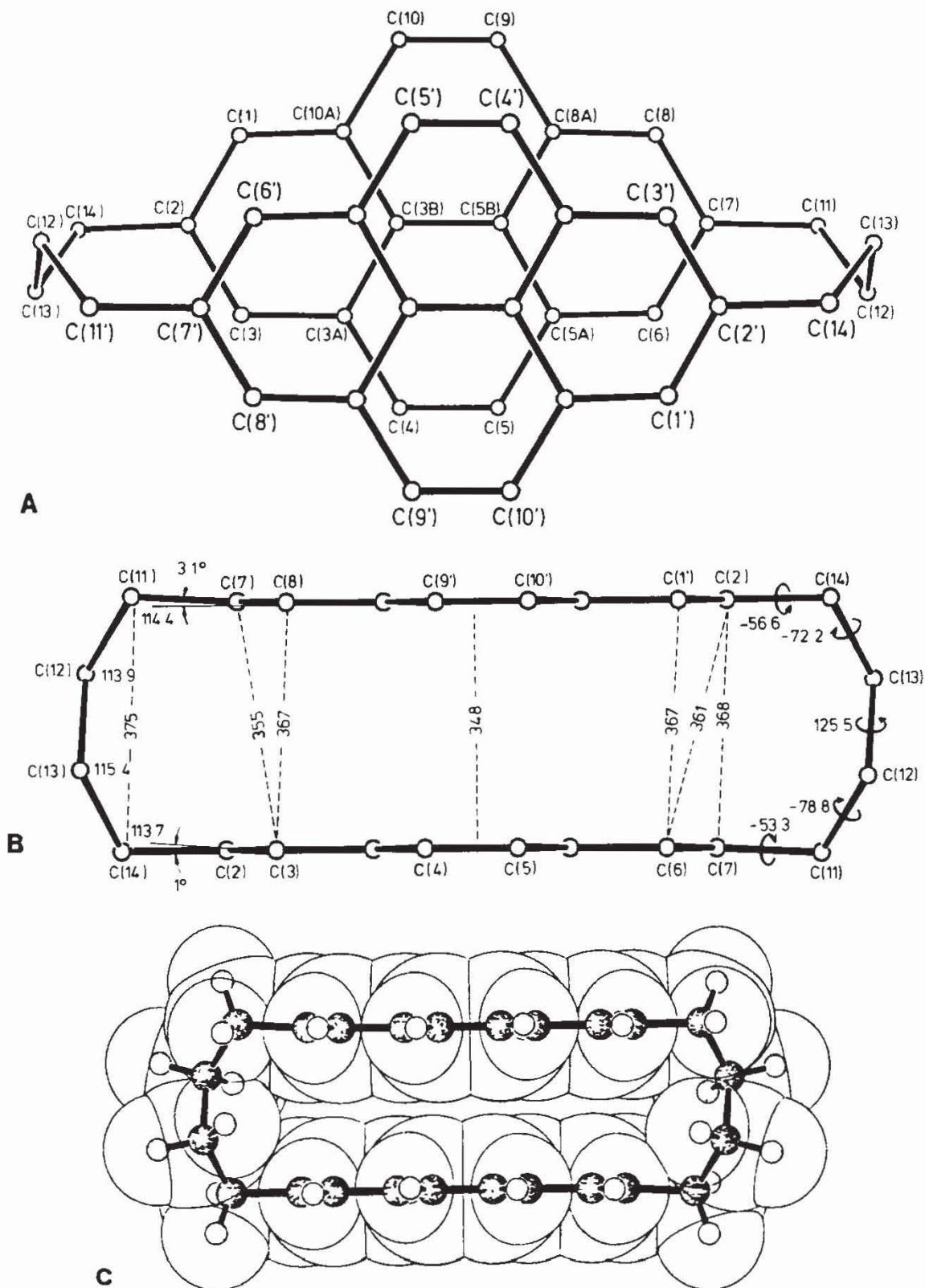


Figure 2. Molecular Structure of 2 in a Top-View (A), in a Side-View (B), and in a Side-View with van der Waals Radii (C)

The phane bridges [C(11)–C(12)–C(13)/C(11')–C(12')–C(13')] in 1 show a 'chair'-like arrangement with staggered C–H Bonds of neighbouring methylene groups (see torsional angles in Figure 1B). C···C-bond lengths of 1 are listed together with those of 2 in Table 4. In spite of the considerably different deformation cor-

responding pyrene bond lengths in [2.2](2,7)pyrenophane, **1** and **2** are very similar to each other and to those of 2,7-dimethylpyrene^{3d)}. Bond angles of **1** and **2** are listed in Table 5.

Molecular Structure of 2: Figure 2 shows the molecular structure of **2** in a top-view along the projection upon the pyrene planes (A) and in a side-view (B). In contrast to [2.2](2,7)pyrenophane^{3d)} and to the [3.3]-analogue **1**, the two pyrene units of the [4.4]pyrenophane **2** are of almost ideal planarity; the mean deviation of the carbon atoms from the best plane through all carbon atoms of a pyrene unit amounts to only 0.5 pm. With 348 pm the transannular distance between the pyrene planes is well in the range of normal intermolecular distances of aromatic hydrocarbons (e.g., interplanar distance of 2,7-dimethylpyrene: 345 pm^{3d)}). Accordingly, **2** is a strain-free molecule with regard to transannular $\pi \cdots \pi$ -interactions as is demonstrated in Figure 2C where the van der Waals radii are plotted into the framework of experimentally determined atomic positions of **2**.

As in **1** the pyrene units are not in an ecliptic arrangement to each other (Figure 2A). The lateral displacement is considerable perpendicular to the long pyrene axis ($M = 111$ pm) whereas the parallel shift along this axis is rather small ($L = 17$ pm). Consequently, shortest transannular distances are not between corresponding carbon atoms (see Figure 2B). The C₄-bridges of **2** form a zigzag conformation with staggered orientations of vicinal hydrogen atoms (for torsional angles see Figure 2B).

Bond lengths and angles of **2** are listed together with those of **1** in Tables 4 and 5. In general, they are in the normal range as expected. The only exception is the short bond length of the central bond C(12)–C(13) of the bridges. Similar results have been obtained from X-ray analyses of other [4.4]phanes⁸⁾.

Spectroscopic Properties of **1** and **2**

In the absorption spectrum of [2.2](2,7)pyrenophane, as compared to 2,7-dimethylpyrene, the absorption at longest wavelength appears strongly red-shifted as a broad, structureless band in the range of 380 to 430 nm^{3c)}. This red-shift and broadening, which is the result of transannular interactions ('phane effect'), is reduced in the absorption of the [3.3]pyrenophane **1** [$\lambda_{\text{max}} = 382$ nm (sh, $\lg \epsilon \approx 3.1$), 368 (3.34), 328 (4.75), 314 (4.40), 271 (4.70), 259 (4.46), 237 (5.14); in dioxane]. For the [4.4]pyrenophane **2** the long-wavelength start of the absorption shows a further hypsochromic shift to about 410 nm, and the vibration structure is still more pronounced [$\lambda_{\text{max}} = 380$ nm ($\lg \epsilon = 2.98$), 365 (sh, ≈ 3.4), 342 (4.13), 327 (4.74), 314 (4.36), 302 (sh, ≈ 4.0), 273 (4.72), 261 (4.55), 239 (5.22); in dioxane]. Thus, the absorption spectra reflect the decreasing transannular interactions in the series of [2.2]-, [3.3]-, and [4.4]pyrenophanes.

Fluorescence spectra of **1** and **2** in solution at room temperature as well as in glasses at very low temperature do not show the fluorescence of the pyrene chromophors but strongly red-shifted, broad, and structureless 'excimer-like' emissions, as is shown in Figure 3 for **2** (in 2-methyltetrahydrofuran glass, 1.3 K). In Table 6 emission spectra of **1** and **2** are compared with those of [2.2](2,7)pyrenophane and 2,7-dimethylpyrene⁴⁾. The latter compound under the conditions mentioned shows the typical strongly

vibration-structured fluorescence of a monomeric pyrene. With reference to this 2,7-dimethylpyrene fluorescence the excimer-like emissions of the pyrenophanes are red-shifted for 4500 to 8250 cm^{-1} . The red-shift decreases from [2.2](2,7)pyrenophane to the [3.3]-analogue **1** and further to the [4.4]phane **2**. If these red-shifts are, however, corrected by considering the differences in the long-wavelength beginning of the absorptions nearly the same red-shift is found for all three pyrenophanes which is comparable to the red-shift of the excimer from pyrene itself ($\Delta\nu = 5050 \text{ cm}^{-1}$; 2-methyltetrahydrofuran, 298 K).

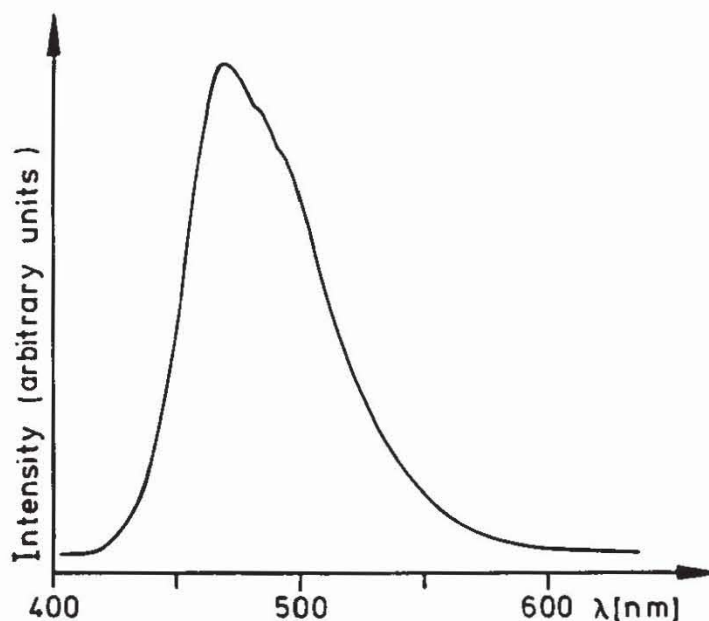


Figure 3. Fluorescence Emission of **2** in 2-Methyltetrahydrofuran at 1.3 K (Excitation at 361 nm, Kr Laser)

Table 6. Emission Spectra at 1.3 K (MTHF: 2-Methyltetrahydrofuran)

Compound	Matrix	Fluorescence [cm^{-1}]		Phosphorescence ν_{max} [cm^{-1}]
		ν_{max}	$\Delta\nu$	
2,7-Dimethylpyrene ⁴⁾	MTHF	25850	(reference)	16935
[2.2](2,7)Pyrenophane ⁴⁾	MTHF	18000	7850	16690
	Crystals	17600	8250	16785
[3.3](2,7)Pyrenophane (1)	MTHF	19400	6450	16890
	Crystals	19600	6250	
[4.4](2,7)Pyrenophane (2)	MTHF	21300	4550	16800
	Crystals	20800	5050	16100

Whereas for **2** from X-ray structure determination and absorption spectra it must be concluded that ground-state interactions between the two pyrene π -systems are rather small, the pyrene units in **2** obviously are in a sterical arrangement which allows an intramolecular 'excimer state' to be reached upon excitation. In contrast to excimers known so far excimer emission from pyrenophanes is an intramolecular property and, therefore, independent of concentration. With these molecules a new principle of a complete spectral separation of absorption and emission has been realised⁹⁾.

As compared to the monomeric 2,7-dimethylpyrene the phosphorescence of the pyrenophanes is not significantly shifted (Table 6). This indicates that in the excited triplet state transannular interactions between the pyrene π -systems must be small. Accordingly, triplet zero field splitting parameters D and E , measured by the ODMR technique⁴⁾, are very similar for pyrenophanes and for pyrene monomers [1: $|D| = 0.0842 \text{ cm}^{-1}$, $|E| = 0.0165 \text{ cm}^{-1}$; 2,7-dimethylpyrene: $|D| = 0.0855 \text{ cm}^{-1}$, $|E| = 0.0169 \text{ cm}^{-1}$; in 2-methyltetrahydrofuran, 1.3 K]. From these results it can be concluded that for the triplet states of pyrenophanes at a given time the triplet electrons are confined to a single pyrene unit; electron separation by transannular transfer to the neighbouring pyrene π -system should result in a reduction of $|D|$ as has been observed for donor-acceptor cyclophanes¹⁰⁾.

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Experimental Part

4,5,9,10-Tetrahydro-2,7-pyrenedimethanethiol (4): 10.0 g (25.5 mmol) of 2,7-bis(bromomethyl)-4,5,9,10-tetrahydropyrene (3), prepared according to lit.^{3a,b)}, and 5.0 g (65 mmol) of thiourea in 50 ml of ethanol were heated for 3 h under reflux. After cooling and addition of ether the isothiuronium salt was filtered off, added to 6 g of sodium hydroxide in 100 ml of water and boiled under nitrogen for 3 h. Acidification with diluted hydrochloric acid yielded a colourless precipitate which was recrystallized from tetrachloromethane: 5.14 g (68%), colourless platelets, m.p. 189–191 °C (lit.^{3a)} 190–192 °C).

4,5,9,10-Tetrahydro-2,7-pyrenediacetonitrile (5): To a suspension of 10.0 g (204 mmol) of sodium cyanide in 300 ml of dimethyl sulfoxide at 20 °C 18.8 g (47.7 mmol) of 3 was added under stirring. After 30 min the reaction mixture was added to 1.5 l of ice water, the precipitate was filtered off, washed with water, dried, and chromatographed from dichloromethane on silica: 11.3 g (83%); after recrystallisation from isopropyl alcohol/toluene (4:1) and sublimation at 160–170 °C/10⁻³ Torr m.p. 234–235 °C (dec.).

$\text{C}_{20}\text{H}_{16}\text{N}_2$ (284.3) Calcd. C 84.48 H 5.67 N 9.85 Found C 84.29 H 5.65 N 9.88

Dimethyl 4,5,9,10-Tetrahydro-2,7-pyrenediacetate (6): A solution of 9.3 g (33 mmol) of 5 in 150 ml of methanol saturated with hydrogen chloride was heated under further passing through of hydrogen chloride for 3 h under reflux. The reaction mixture was given on 1.5 l of ice water and the precipitate filtered off: 10.95 g (95%), m.p. 146–148 °C (from methanol).

$\text{C}_{22}\text{H}_{22}\text{O}_4$ (350.4) Calcd. C 75.41 H 6.33 Found C 75.52 H 6.36

4,5,9,10-Tetrahydro-2,7-pyrenediethanol (7): To a boiling solution of 7.0 g (185 mmol) of lithium aluminum hydride in 100 ml of tetrahydrofuran within 30 min 35.0 g (100 mmol) of 6 in 400 ml of tetrahydrofuran was dropped under vigorous stirring. The mixture was heated under reflux for 4 h. To the solution cooled with ice 20 ml of water were added dropwise. The precipitate was filtered off and extracted with dichloromethane in a Soxhlet extractor. From filtrate and extract the solvents were distilled off, and the residue was crystallized from ethanol/toluene: 24.0 g (82%), m.p. 219–221 °C.

$\text{C}_{20}\text{H}_{22}\text{O}_2$ (294.4) Calcd. C 81.60 H 7.53 Found C 81.33 H 7.62

2,7-Bis(2-bromoethyl)-4,5,9,10-tetrahydropyrene (8): To a suspension of 14.7 g (50 mmol) of 7 in 41.5 g (125 mmol) of tetrabromomethane and 250 ml of dichloromethane within 10 min 39.2 g

(150 mmol) of triphenylphosphane was added at 0°C under stirring. After 1 h at room temperature dichloromethane was distilled off, and 500 ml of methanol was added. The precipitate was filtered off and recrystallized from ethanol/toluene: 18.4 g (88%), m.p. 220–222°C (dec.).

$C_{20}H_{20}Br_2$ (420.2) Calcd. C 57.17 H 4.80 Br 38.03 Found C 57.40 H 4.78 Br 37.98

7,8,12,13,21,22,26,27-Octahydro-2,17-dithia[4.4](2,7)pyrenophane (9): A solution of 2.54 g (8.5 mmol) of 4 and 3.58 g (8.5 mmol) of 8 in 500 ml of toluene was dropped within 12 h under nitrogen to a boiling mixture of 5 g of potassium carbonate, 1 l of ethanol (95%), and 1 l of *tert*-butyl alcohol. The solvents were distilled off; the residue was chromatographed from dichloromethane on a short silica column and crystallized from benzonitrile: 2.5 g (53%), m.p. 300–302°C (dec., under nitrogen). – 1H -NMR ($CDCl_3$, 80 MHz): δ = 2.56 (s, 16H), 2.4–3.1 (AA'BB', 8H), 3.44 (s, 4H), 6.60 (s, 4H), 6.67 (s, 4H). – MS: m/z = 556 (37%, M^+), 277 (19), 245 (10), 233 (100), 232 (50); M^+ calcd. 556.2242, exp. 556.2258.

$C_{38}H_{36}S_2$ (556.8) Calcd. C 81.97 H 6.52 S 11.51 Found C 81.78 H 6.76 S 11.78

7,8,12,13,21,22,26,27-Octahydro-2,17-dithia[4.4](2,7)pyrenophane-2,2,17,17-tetraoxide (10): To a suspension of 4.23 g (7.6 mmol) of 9 in 350 ml of chloroform 8.1 g (42 mmol) of 3-chloroperoxybenzoic acid (90%) was added. After addition of 200 ml of chloroform, extraction with 10% sodium hydroxide solution, washing with water, and drying the solvent was distilled off. The residue was dissolved in boiling benzonitrile and the disulfone precipitated by addition of ethanol: 4.1 g (87%), m.p. 344–348°C (dec., under nitrogen).

$C_{38}H_{36}O_4S_2$ (620.8) Calcd. C 73.52 H 5.84 S 10.33 Found C 73.46 H 5.85 S 10.38

6,7,11,12,19,20,24,25-Octahydro[3.3](2,7)pyrenophane (11): 514 mg (0.828 mmol) of 10 was pyrolyzed in a pyrolysis apparatus⁵⁾ in samples of about 100 mg each at 580–600°C/ $2 \cdot 10^{-6}$ Torr (sublimation zone 300°C; duration 5–8 h). The product was chromatographed from tetrachloromethane on silica at 40–50°C and recrystallized from toluene: 104 mg (25%). According to mass spectrum and 1H NMR the product contains some partially dehydrogenated material; it is used for the following reaction without further purification.

[3.3](2,7)Pyrenophane (1): 51 mg (0.104 mmol) of 11 and 5 ml of 1-methylnaphthalene were heated in the presence of 20 mg of palladium (10%)/activated charcoal 24 h under reflux. After addition of toluene to the reaction mixture the catalyst was filtered off at 100°C. The solvents were distilled off *in vacuo*, and the residue was crystallized from toluene: 36 mg (72%) of 1, yellow plates, dec. >355°C (under nitrogen). – 1H NMR, MS: see above.

$C_{38}H_{28}$ (484.6) Calcd. C 94.18 H 5.82 Found C 94.19 H 6.01

Tetramethyl 2,2'-(4,5,9,10-Tetrahydro-2,7-pyrenediylbis(methylene))bispropanedioate (12): To a solution of 5.1 g (220 mmol) of sodium in 200 ml of methanol 30 g (225 mmol) of dimethyl malonate was added at 20°C under stirring. After 30 min 39.2 g (100 mmol) of 3 was added, and the suspension formed was heated under reflux for 5 h with stirring. After cooling the precipitate was filtered off, washed with methanol, and dried: 45 g (90%); crystallized from methyl acetate: colourless crystals, m.p. 151–152°C.

$C_{28}H_{30}O_8$ (494.5) Calcd. C 68.00 H 6.12 Found C 67.91 H 6.09

Dimethyl 4,5,9,10-Tetrahydro-2,7-pyrenedipropionate (13): 45 g (90 mmol) of 12 and 12 g (205 mmol) of sodium chloride were heated under stirring in 50 ml of dimethyl sulfoxide and 5 ml of water for 3 h to 160–170°C. After cooling to room temperature 500 ml of dichloromethane and 500 ml of water were added. The separated aqueous phase was acidified with diluted hydrochloric acid and three times extracted with dichloromethane. The united dichloromethane solutions were washed with water, dried with sodium sulfate, and evaporated *in vacuo*. The residue was

chromatographed from toluene/ethyl acetate (4:1) on silica and crystallized from acetone: 20 g (59%), colourless platelets, m.p. 186–187°C (from methyl acetate).

$C_{24}H_{26}O_4$ (378.5) Calcd. C 76.16 H 6.93 Found C 76.18 H 6.83

4,5,9,10-Tetrahydro-2,7-pyrenedipropanol (14): To a solution of 2.6 g (70 mmol) of lithium aluminum hydride in 50 ml of boiling tetrahydrofuran a solution of 18.9 g (50 mmol) of **13** in 250 ml of tetrahydrofuran was dropped under stirring within 1 h. After 4 h heating under reflux to the reaction mixture, cooled in ice water, 6 ml of water was added dropwise. The precipitate was filtered off and extracted in a Soxhlet extractor with dichloromethane. From the united filtrate and extract the solvents were distilled off: 15.7 g (97%) of **14** which was used for the following reaction without further purification. Crystallized from acetonitrile **14** forms colourless platelets, m.p. 223–225°C.

$C_{22}H_{26}O_2$ (322.4) Calcd. C 81.95 H 8.13 Found C 81.95 H 8.21

2,7-Bis(3-bromopropyl)-4,5,9,10-tetrahydropyrene (15): To a suspension of 16.1 g (50 mmol) of **14** in 41.5 g (125 mmol) of tetrabromomethane and 250 ml of dichloromethane 39.2 g (150 mmol) of triphenylphosphane was added slowly under ice-cooling. After 30 min the solvent was distilled off; 500 ml of methanol was added to the residue, and the precipitate was filtered off and washed with methanol. Chromatography from dichloromethane on silica yielded 18 g (73%), colourless crystals, m.p. 167–169°C (from *n*-hexane).

$C_{22}H_{24}Br_2$ (448.2) Calcd. C 58.95 H 5.40 Br 35.65 Found C 59.19 H 5.24 Br 35.69

8,9,13,14,23,24,28,29-Octahydro-2,19-dithia[5.5](2,7)pyrenophane (16): The solution of 11.2 g (25 mmol) of **15** and 8.2 g (25 mmol) of **4** in 1250 ml of toluene was dropped at constant rate (magnetic valve) within 30 h to a stirred, boiling solution of 14 g (120 mmol) of potassium carbonate in 5 l of methanol. The solvent was distilled off *in vacuo* and the residue was chromatographed on silica from toluene at 80–90°C: 4.3 g (29%). After crystallization from toluene: colourless crystals, m.p. 298–304°C (under argon). – 1H NMR ($CDCl_3$, 80 MHz): δ = 1.65–2.1 (m, 4H), 2.1–2.4 (m, 4H), 2.4–2.75 (m, 4H), 2.55 (s, 16H), 3.59 (s, 4H), 6.63 (s, 4H), 6.74 (s, 4H). – MS: m/z = 584 (34%, M^+), 351 (12), 233 (100).

$C_{40}H_{40}S_2$ (584.9) Calcd. C 82.14 H 6.89 S 10.96 Found C 82.25 H 6.81 S 10.73

8,9,13,14,23,24,28,29-Octahydro-2,19-dithia[5.5](2,7)pyrenophane-2,2,19,19-tetraoxide (17): To a solution of 1.17 g (2.0 mmol) of **16** in 50 ml of chloroform 2.3 g (12 mmol) of 3-chloroperoxybenzoic acid was added, and the solution was stirred for 2 h at room temperature. After extraction with 10% sodium hydroxide solution, washing with water, and drying over sodium sulfate the solvent was distilled off. To the residue 50 ml of ether was added; the precipitate was filtered off and dried: 1.11 g (86%) of the disulfone **17** which was pyrolyzed without further purification. For analysis the material was crystallized from chloroform/ethyl acetate: colourless crystals, m.p. 382–384°C (dec., under argon).

$C_{40}H_{40}O_4S_2$ (648.9) Calcd. C 74.04 H 6.21 S 9.88 Found C 73.91 H 6.30 S 9.63

7,8,12,13,21,22,26,27-Octahydro[4.4](2,7)pyrenophane (18): 1.08 g (1.66 mmol) of **17**, in samples of 200–250 mg each, was pyrolyzed in a pyrolysis apparatus⁵⁾ at 580–600°C/ 10^{-6} Torr (sublimation zone 280–300°C; duration 5–8 h). The pyrolysates were chromatographed from tetrachloromethane on silica at 40°C: 588 mg (69%), after crystallization from toluene/*n*-hexane (1:1) colourless crystals, m.p. 364–368°C (under argon). – 1H NMR ($CDCl_3$, 360 MHz): δ = 1.66 ('s', 8H), 2.35 ('s', 8H), 2.47–2.67 (AA'BB', 16H), 6.53 (s, 8H). – MS: m/z = 520 (100%, M^+), 518 (7), 259 (7), 245 (6), 232 (28), 219 (8), 217 (10), 215 (8), 203 (7), 202 (10).

$C_{40}H_{40}$ (520.7) Calcd. C 92.26 H 7.74 Found C 92.48 H 7.95

[4.4](2,7)Pyrenophane (2): To 52 mg (0.10 mmol) of **18** in 10 ml of boiling toluene a solution of 100 mg (0.44 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 10 ml of toluene was added under stirring. After further heating until the solution was decolourized (approx. 2 h) the solvent was distilled off *in vacuo*, the residue was suspended in boiling ethanol, filtered off, and chromatographed at 80–90 °C from toluene on silica: 34 mg (66%), yellow crystals (from toluene), m.p. 402–404 °C (under argon). – ¹H NMR, MS: see above.

C₄₀H₃₂ (512.7) Calcd. C 93.71 H 6.29 Found C 93.72 H 6.56

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