1,8-Dipyrenylnaphthalenes: Syntheses, Molecular Structure, and Spectroscopic Properties

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Syntheses of the 1,8-dipyrenylnaphthalenes **1 – 3** are reported. The stereoisomers **1** and **2** were separated; their structural assignment is based on ^{1}H NMR, on the optical activity of **2**, and on X-ray structure analyses of **1** and **2**. Kinetic parameters for the isomerisation **2 ⇌ 1** were determined by optical rotation measurements. – Emission spectra of **1 – 3** are discussed in comparison to monopyrenyl compounds **4** and **8**. For **1** and **3** typical 'excimer-like' fluorescence is observed. The difference between **1** and **2** clearly demonstrates the dependence of excimer interactions between the pyrene units on the mutual orientation of the π-systems involved. – On the basis of X-ray analyses the molecular structures of **1 – 3** are discussed with emphasis on π ··· π-interactions between the pyrene units.

**1,8-Dipyrenylnaphthalin: Synthesen, Molekülstruktur und spektroskopische Eigenschaften**

Synthesen der 1,8-Dipyrenylnaphthaline **1 – 3** werden mitgeteilt. Die Stereoisomeren **1** und **2** wurden getrennt; ihre strukturelle Zuordnung basiert auf ^{1}H-NMR, auf der optischen Aktivität von **2** und auf den Röntgenstrukturanalysen von **1** und **2**. Kinetische Parameter für die Isomerisierung **2 ⇌ 1** wurden durch Messung der optischen Rotationen bestimmt. – Emissionsspektren von **1 – 3** werden im Vergleich zu den Monopyrenyl-Verbindungen **4** und **8** diskutiert. Für **1** und **3** wird eine typische „excimeren-artige" Fluoreszenz beobachtet. Der Unterschied zwischen **1** und **2** demonstriert deutlich die Abhängigkeit der Excimeren-Wechselwirkung zwischen den Pyren-Einheiten von der gegenseitigen Orientierung der beteiligten π-Systeme. – Auf der Grundlage von Röntgen-Strukturanalysen werden die Molekülstrukturen von **1 – 3** im Hinblick auf die π ··· π-Wechselwirkung zwischen den Pyren-Einheiten diskutiert.

For reasons discussed in the preceding paper on pyrenophanes[1] excimer models were of interest which contain in an intramolecular system two pyrene units fixed in well-defined sterical arrangements. As a different approach to this problem the syntheses of 1,8-di(1-pyrenyl)naphthalene, of which two stereoisomers **1** and **2** with different overlap of the pyrene units were to be expected, and of 1,8-di(2-pyrenyl)naphthalene **3** were considered.

1,8-Di(1-pyrenyl)naphthalenes (1, 2)

Synthesis, Separation, and Structural Assignment of **1** *and* **2**: The synthesis of **1** and **2** was achieved in analogy to the synthesis of 1,8-diphenylnaphthalene[2]. The Grignard reagent prepared from 1-bromopyrene[3] in tetrahydrofuran was reacted with 1,8-di-

iodonaphthalene[4] in the presence of catalytic amounts of bis(acetylacetonato)nickel-
(II). In addition to the 1,8(di-1-pyrenyl)naphthalenes **1/2** (26.5% yield) 1-(1-pyrenyl)-
naphthalene (**4**) and 8,8'-di(1-pyrenyl)-1,1'-binaphthalene (**5**) were obtained as by-pro-
ducts as well as the known 1,1'-bipyrene[5] (for details see Exp. Part).
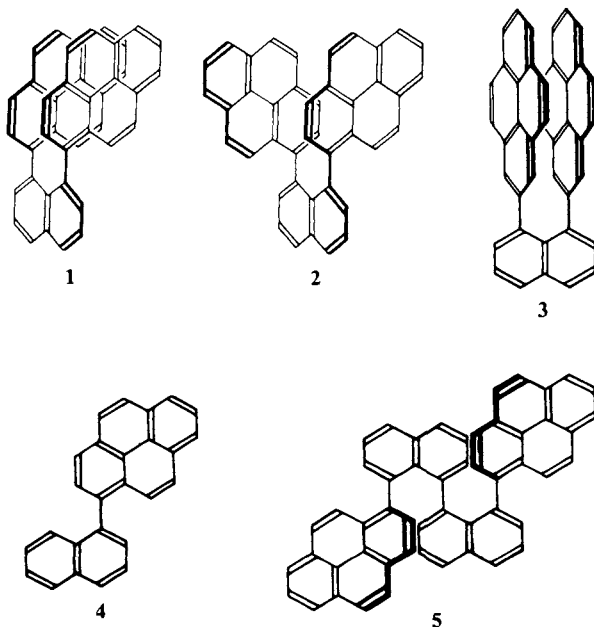
The rotamers **1** and **2** were separated by pressure-chromatography on silica from
tetrachloromethane and crystallized from dichloromethane/toluene. Analytical and
spectroscopie data support the structures suggested [MS: **1**: m/z = 528 (100%, M$^+$),
326 (8), 264 (10, M^{2+}); **2**: m/z = 528 (100%, M$^+$), 326 (9), 264 (14, M^{2+}). – ^{1}H
NMR (360 MHz, [D$_2$]-1,1,2,2-tetrachloroethane): **1**: δ = 6.947 and 7.038 (AB, J =
9.1 Hz, 4H), 7.26 – 7.40 (m, 10H), 7.450 (dd, J = 6.8 and 1 Hz, 2H), 7.588 (t, J =
7.7 Hz, 2H), 7.64 – 7.72 (m, 4H), 8.182 (dd, J = 8.4 and 1 Hz, 2H); **2**: δ = 6.201 and
7.009 (AX, J = 7.7 Hz, 4H), 6.734 and 7.548 (AX, J = 9.6 Hz, 4H), 7.40 – 7.43 (m,
4H), 7.679 (t, 2H, J = 7.7 Hz), 7.841 (d, J = 8.9 Hz, 2H), 7.98 – 8.02 (m, 2H),
8.09 – 8.15 (m, 4H), 8.184 (d, J = 8.4 Hz, 2H)].

The assignment of the structures **1** and **2** to the two separated rotamers was first
based on the ^{1}H NMR data: One of the two isomers shows a signal with a striking high-
field-shift (δ = 6.201, 2H) which can be explained by assigning this signal to the
3-protons of the pyrenyl group of the *trans*-rotamer. These protons are located close to
the center of the neighbouring pyrene unit and, thus, are shielded most effectively by
the anisotropy of the aromatic system.

This structural assignment has been confirmed by X-ray structure analyses of **1** and
2 (see later). It is further established conclusively by the fact that **2**, being a chiral
compound unlike **1**, has been obtained optically active as discussed below.

cis-trans-Isomerisation **1** ⇌ **2**: ^{1}H NMR spectra reveal that in solution an interconversion of **1** and **2** occurs above 60°C. By integration of specific ^{1}H NMR signals the equilibrium reached both from pure **1** and from pure **2** was determined at 80 and 120°C to be approximately 1 : 1.

For establishing kinetic parameters for the interconversion of **1** and **2** use has been made of the crystallographic result that **2** crystallizes in the chiral space group $P2_1$. Thus, a separation of enantiomers was possible by picking out single crystals. For 5 single crystals of **2** (0.8 to 2.1 mg) absolute values of specific rotations $[\alpha]_D^{20°C}$ varied between 1930 and 2050° (in dichloromethane).

By determining the decrease of the optical rotations with time the rate constants for the *trans-cis*-isomerisation were measured in the temperature range 60 – 120°C (in 1,1,2,2,-tetrachloroethane, Table 1). From these measurements an Arrhenius plot was obtained from which the activation energy E_A = 24.8 kcal/mol and the preexponential factor A = 4.07 · 10[12] were derived. These data are in rather good correspondence with results obtained for other 1,8-diarylnaphthalenes[6].

Table 1. Rate Constants k_1 [min[-1]] of Isomerisation **2** ⇌ **1** as Determined by Optical Rotation Measurements (in 1,1,2,2-Tetrachloroethane)

T (K)	$10^4 \cdot k_1$ [min[-1]]	T (K)	$10^4 \cdot k_1$ [min[-1]]
333	2.182	373	120.4
343	6.355	383	291.9
353	18.04	393	652.2
363	46.72		

Synthesis of 1-(1-Pyrenyl)naphthalene (**4**): As reference compound for the spectroscopic comparison with the excimer models **1** and **2** compound **4** with only one pyrenyl group was prepared from 1-naphthylmagnesium bromide and 1-iodopyrene[7] [bis-(acetylacetonato)nickel(II), tetrahydrofuran; 62%]. Analytical and spectroscopic data (see Exp. Part) are in agreement with the structure suggested.

Emission Spectra of **1**, **2**, *and* **4**: Fluorescence spectra of *cis*- and *trans*-1,8-di(1-pyrenyl)naphthalenes (**1** and **2**) are shown in Figure 1 together with the fluorescence of the monopyrenylnaphthalene **4**. Whereas for **4** with regard to wavelength and vibrational structure the normal fluorescence of a pyrene chromophore is observed, we see characteristic changes in the fluorescence spectra of the dipyrenyl systems **1** and **2**. As compared to **4** the *trans*-isomer **2** shows a fluorescence band which is only moderately red-shifted and still has some vibrational structure. In contrast to **2**, however, the *cis*-isomer **1** has a typical 'excimer' emission with strong red-shift (Δv = 5800 cm^{-1}) and complete loss of vibrational structure. This remarkable difference between the stereoisomers **1** and **2** must be due to the fact that in **1** we have an optical face-to-face arrangement of the two pyrene units whereas in **2** only a rather limited overlap of partial regions of the pyrene π-systems is possible. Comparison of the absorption spectra of **1** and **2**, on the other hand, shows only minor differences, namely for **1** a small red-shift and a slight broadening of the absorption band. The strong Stokes shift,

which for **1** leads to a complete spectral separation of absorption and emission, must therefore be due to an 'excimer'-like interaction between the pyrene units in the excited state. The differences in the fluorescence between **1** and **2**, then, prove conclusively that excimer formation is strongly dependent on the mutual orientation of the π-systems involved.
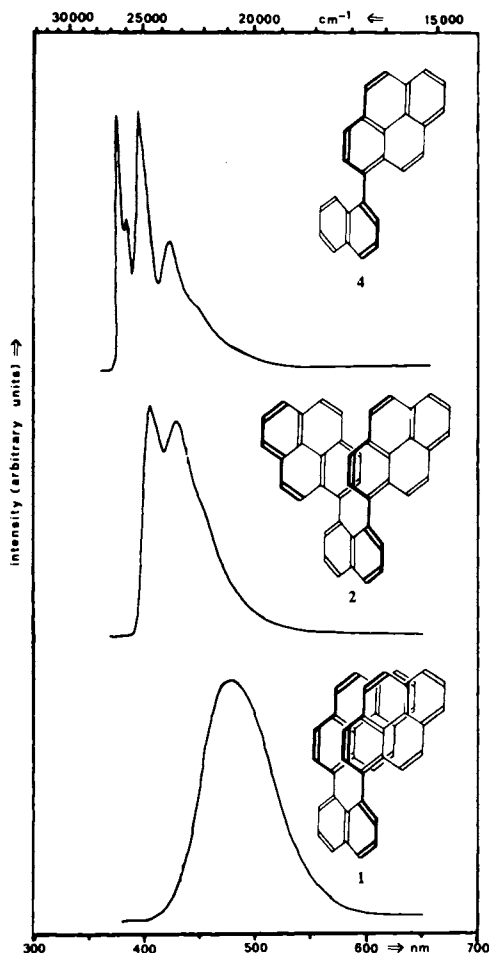
Figure 1. Fluorescence Emission of **1**, **2**, and **4** (in Methylcyclohexane, 1.3 K)

In contrast to the fluorescence, the phosphorescence emission of both **1** and **2** is very similar in spectral position and vibrational structure to the phosphorescence of the reference compound **4**. This means that in the triplet state even of **1** there is only very small interaction of the pyrene units as was also found in the series of pyrenophanes[1].

Synthesis and Emission Spectra of 1,8-Di(2-pyrenyl)naphthalene (3)

Synthesis of **3**: The synthesis of **3** started from 2-bromo-4,5,9,10-tetrahydropyrene (**6**), the preparation of which from [2.2]metacyclophane[8] was considerably improved. The Grignard reagent from **6** was reacted with 1,8-diiodonaphthalene in the presence of bis(acetylacetonato)nickel(II) to give 1,8-bis(4,5,9,10-tetrahydro-2-pyrenyl)naphthalene (**7**) in 22% yield; as by-product of this reaction 4,4′,5,5′,9,9′,10,10′-octahydro-2,2′-bipyrene was isolated. By dehydrogenation of **7** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene **3** was obtained (83%).
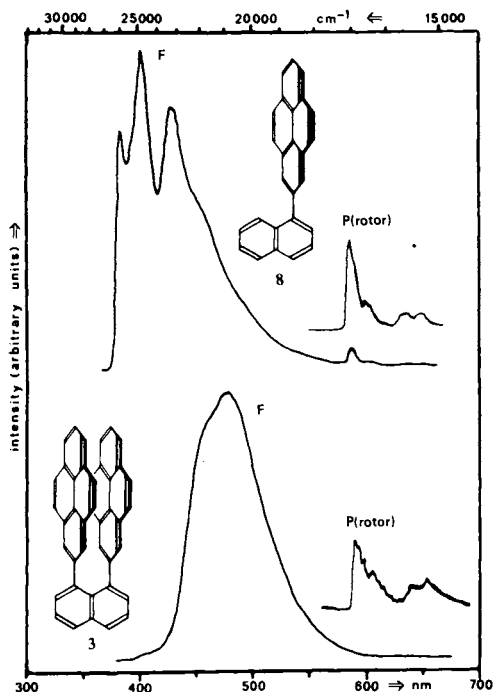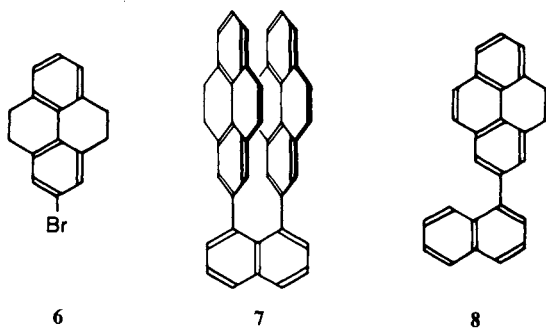

Figure 2. Fluorescence (F) and Phosphorescence (P) of **3** and **8** (in Methylcyclohexane, 1.3 K)

3 forms pale-yellow crystals (m. p. 331 – 333 °C). Elemental analysis and spectroscopic data are in accordance with the assumed structure [MS: *m/z* = 528 (100%, M$^+$), 326 (16), 264 (9, M^{2+}). – ^{1}H NMR (360 MHz, [D$_2$]-1,1,2,2-tetrachloroethane): δ = 7.261 (s, 8H), 7.51 – 7.54 (m, 8H), 7.575 – 7.615 (m, 2H), 7.63 – 7.66 (m, 4H), 8.08 – 8.12 (m, 2H)]. The molecular structure of 3 has been determined by X-ray analysis (see below).

Synthesis of 1-(2-Pyrenyl)naphthalene (8): Derivative 8[9] which was needed as reference compound for spectroscopic comparison with 3 was synthesized in analogy to 4 by reacting 2-iodopyrene[7] with 1-naphthylmagnesium bromide in the presence of bis(acetylacetonato)nickel(II) (tetrahydrofuran, – 10 °C; 54%).

Emission Spectra of 3 and 8: Figure 2 shows the emission spectra (in methylcyclohexane, 1.3 K) of 3 and 8. For 8 a fluorescence band is observed which with regard to wavelength and vibrational structure is very similar to the emission of the analogous 1-pyrenylnaphthalene 4 (Figure 1). For both compounds the emission is likely to be essentially due to the pyrene chromophore; although for 8 conjugative interaction with the naphthalene π-system is sterically less hindered a similar torsion around the Ar – Ar bond in 4 and 8 has to be assumed which is also indicated by the very similar absorption spectra.

In comparison to 8 the dipyrenyl compound 3 shows a strongly red-shifted, broad, and structureless emission band. Obviously the similarity of the emission spectra of 3 and 1 must be attributed to the analogous mutual orientations of the pyrene systems in both compounds.

As in the case of compounds 1, 2, and 4, for 3 and 8 almost identical phosphorescence spectra were observed. This means that the triplet state is not significantly affected by an interaction between the two pyrene units in 3.

Molecular Structures of 1 – 3[10]

X-Ray Structure Analysis: Crystal and data collection parameters for 1 – 3 are listed in Table 2. Intensity data were collected by using a graphite-monochromated Mo-K_α radiation and applying Θ/2Θ-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 are given in Tables 3 – 5 (for the numbering of atoms cf. Figures 3 – 5).

Molecular Structure of 1: In Figure 3A a view is shown in the direction onto the naphthalene plane which, however, is inclined against the drawing plane by about 20° by rotation around the C(4A) – C(8A) axis (since otherwise only the lateral edges of the pyrenes were to be seen). Figure 3B represents a side-view of the molecule in the naphthalene plane perpendicular to C(4A) – C(8A).

In the projection on the naphthalene plane the *peri*-bonds C(1) – C(1') and C(8) – C(1'') are spread for 13°. Furthermore, these bonds deviate from the naphthalene plane for 7 and 9° in an opposite up-and-down version as, to a minor extent, C(1) and C(8) do (Figure 3B). Due to these deformations the bond angles C(1') – C(1) – C(8A), C(1) – C(8A) – C(8), and C(8A) – C(8) – C(1'') are increased to 123.2, 125.4, and 124.4°, respectively. The result is a widening of distances from 255 pm for C(1)···C(8)

Table 2. Crystal and Data Collection Parameters for **1 – 3**

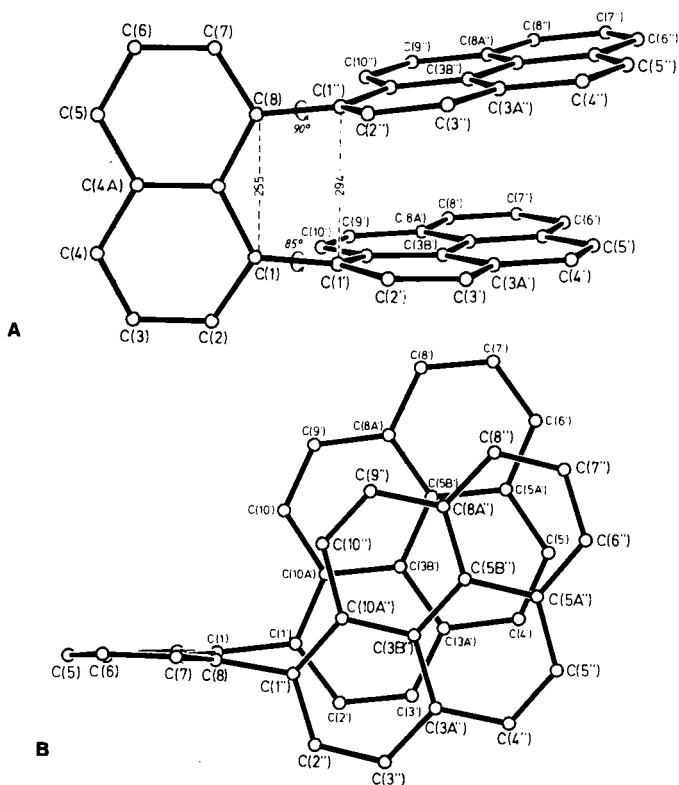| Compound	**1**	**2**	**3**
Formula	$C_{42}H_{24}$	$C_{42}H_{24}$	$C_{42}H_{24}$
Molecular mass	528.6	528.6	528.6
a [pm]	2030.1(3)	858.1(1)	1144.8(2)
b [pm]	1141.4(1)	1097.1(1)	1079.0(2)
c [pm]	1157.2(1)	1465.5(2)	2154.4(4)
β [°]	98.89(1)	92.50(2)	93.50(3)
Space group	$P2_1/c$	$P2_1$	$P2_1/n$
Z	4	2	4
D_x [gcm^{-3}]	1.32	1.27	1.32
Max. sin Θ/λ [nm^{-1}]	6.78	6.78	6.64
No. of reflections measured	7009	3490	6705
No. of reflections with $I \geqslant 1.96 \, \sigma(I)$	3837	1824	2309
R	0.040	0.038	0.043

Figure 3. Molecular Structure of **1** in a View onto the Naphthalene Plane (A) and in a View Parallel to the Naphthalene Plane (B) (for Details see Text)

Table 3. Atomic Coordinates and Thermal Parameters $U_{equ.}$ (in pm²) for 1 (Numbers in Parentheses are Estimated Standard Deviations in Units of the Last Quoted Digit)

Atom	x	y	z	Uequ.
C(1)	0.68518(7)	-0.0380(1)	0.7748(1)	499(5)
C(2)	0.56929(8)	0.0194(2)	0.6819(2)	692(6)
C(3)	0.49915(8)	0.0172(2)	0.6605(2)	782(6)
C(4)	0.46535(8)	0.0400(2)	0.7333(2)	685(6)
C(4A)	0.49089(7)	-0.1004(2)	0.8314(1)	544(5)
C(5)	0.46190(8)	-0.1560(2)	0.9095(2)	688(6)
C(6)	0.49246(9)	-0.2121(2)	1.0053(2)	795(6)
C(7)	0.56235(8)	-0.2195(2)	1.0245(2)	694(6)
C(8)	0.60099(7)	-0.1704(1)	0.9511(1)	506(5)
C(8A)	0.57021(7)	-0.1030(1)	0.8527(1)	466(4)
C(1')	0.67921(7)	-0.0220(1)	0.7947(1)	442(4)
C(2')	0.72078(8)	-0.1040(1)	0.7542(1)	500(5)
C(3')	0.78921(7)	-0.0961(1)	0.7800(1)	468(4)
C(3A')	0.81947(7)	0.0045(1)	0.8476(1)	413(4)
C(3B')	0.77858(7)	0.0845(1)	0.8841(1)	393(4)
C(4')	0.88982(7)	0.0024(1)	0.8822(1)	482(5)
C(5')	0.91797(7)	0.0911(1)	0.9490(1)	513(5)
C(5A')	0.87846(7)	0.1827(1)	0.9871(1)	463(4)
C(5B')	0.80855(7)	0.1789(1)	0.9534(1)	422(4)
C(6')	0.90647(8)	0.2750(2)	1.0572(1)	605(5)
C(7')	0.86668(9)	0.3606(2)	1.0932(2)	687(6)
C(8')	0.79953(9)	0.3580(1)	1.0618(1)	634(6)
C(8A')	0.76825(8)	0.2679(1)	0.9914(1)	494(5)
C(9')	0.69781(8)	0.2607(1)	0.9564(1)	571(5)
C(10')	0.66922(7)	0.1701(1)	0.8928(1)	536(5)
C(10A')	0.70799(7)	0.0767(1)	0.8556(1)	425(4)
C(1")	0.67356(7)	-0.2014(1)	0.9749(1)	449(4)
C(2")	0.69403(8)	-0.3031(1)	0.9251(1)	529(5)
C(3")	0.75968(8)	-0.3388(1)	0.9457(1)	540(5)
C(3A")	0.80741(7)	-0.2739(1)	1.0166(1)	459(4)
C(3B")	0.78726(7)	-0.1720(1)	1.0723(1)	400(4)
C(4")	0.87657(8)	-0.3059(1)	1.0375(1)	609(5)
C(5")	0.92133(8)	-0.2426(2)	1.1088(2)	662(5)
C(5A")	0.90258(7)	-0.1405(1)	1.1668(1)	553(5)
C(5B")	0.83514(7)	-0.1052(1)	1.1471(1)	450(4)
C(6")	0.94060(8)	-0.0731(2)	1.2411(2)	734(6)
C(7")	0.92847(9)	0.0257(2)	1.2936(2)	833(7)
C(8")	0.86323(9)	0.0613(2)	1.2750(1)	690(6)
C(8A")	0.81520(8)	-0.0031(1)	1.2019(1)	506(5)
C(9")	0.74665(8)	0.0292(1)	1.1810(1)	544(5)
C(10")	0.70120(7)	-0.0338(1)	1.1102(1)	493(5)
C(10A")	0.71963(7)	-0.1368(1)	1.0519(1)	400(4)

Table 4. Atomic Coordinates and Thermal Parameters $U_{equ.}$ (in pm²) for 2 (Numbers in Parentheses are Estimated Standard Deviations in Units of the Last Quoted Digit)

Atom	x	y	z	Uequ.
C(1)	0.0399(3)	0.170	0.3445(2)	549(9)
C(2)	-0.0912(3)	0.1952(3)	0.3929(2)	763(10)
C(3)	-0.1757(3)	0.1047(4)	0.4348(2)	1011(10)
C(4)	-0.1319(3)	-0.0116(4)	0.4294(2)	878(10)
C(4A)	-0.0001(3)	-0.0447(3)	0.3801(2)	649(10)
C(5)	0.0439(4)	-0.1679(3)	0.3761(2)	891(10)
C(6)	0.1670(5)	-0.2030(3)	0.3385(2)	998(10)
C(7)	0.2574(4)	-0.1156(3)	0.2857(2)	784(10)
C(8)	0.2204(3)	0.0052(3)	0.2869(2)	512(9)
C(8A)	0.0884(3)	0.0458(3)	0.3358(2)	518(9)
C(1')	0.1179(3)	0.2775(3)	0.3032(2)	512(9)
C(2')	0.0462(3)	0.3352(3)	0.2280(2)	661(10)
C(3')	0.1136(3)	0.4321(3)	0.1857(2)	718(10)
C(3A')	0.2583(3)	0.4774(3)	0.2173(2)	607(10)
C(3B')	0.3287(3)	0.4246(3)	0.2976(2)	493(8)
C(4')	0.3394(4)	0.5710(3)	0.1709(2)	781(10)
C(5')	0.4804(4)	0.6096(3)	0.2022(2)	830(10)
C(5A')	0.5538(3)	0.5623(3)	0.2841(2)	679(10)
C(5B')	0.4755(3)	0.4698(2)	0.3323(2)	552(9)
C(6')	0.7005(4)	0.6010(3)	0.3197(2)	880(10)
C(7')	0.7658(4)	0.5535(3)	0.3979(2)	894(10)
C(8')	0.6890(3)	0.4664(3)	0.4467(2)	722(10)
C(8A')	0.5450(3)	0.4218(3)	0.4138(2)	555(9)
C(9')	0.4659(3)	0.3259(3)	0.4581(2)	561(9)
C(10')	0.3317(3)	0.2786(3)	0.4235(2)	503(9)
C(10A')	0.2577(3)	0.3264(3)	0.3412(2)	465(8)
C(1")	0.3214(3)	0.0864(3)	0.2333(2)	449(8)
C(2")	0.4717(3)	0.1144(3)	0.2671(2)	515(9)
C(3")	0.5681(3)	0.1888(3)	0.2203(2)	590(10)
C(3A")	0.5204(3)	0.2412(3)	0.1375(2)	555(9)
C(3B")	0.3696(3)	0.2118(3)	0.1000(2)	459(8)
C(4")	0.6159(3)	0.3244(3)	0.0885(2)	773(10)
C(5")	0.5650(3)	0.3745(3)	0.0112(2)	846(10)
C(5A")	0.4137(3)	0.3494(3)	-0.0298(2)	663(10)
C(5B")	0.3162(3)	0.2652(3)	0.0160(2)	550(9)
C(6")	0.3543(4)	0.4033(3)	-0.1089(2)	838(10)
C(7")	0.2114(4)	0.3758(3)	-0.1461(2)	871(10)
C(8")	0.1155(4)	0.2925(3)	-0.1041(2)	802(10)
C(8A")	0.1676(3)	0.2371(3)	-0.0217(2)	599(10)
C(9")	0.0740(3)	0.1526(3)	0.0242(2)	660(10)
C(10")	0.1221(3)	0.1024(3)	0.1053(2)	595(9)
C(10A")	0.2717(3)	0.1321(2)	0.1473(2)	458(8)

Table 5. Atomic Coordinates and Thermal Parameters $U_{equ.}$ (in pm^2) for **3** (Numbers in Parentheses are Estimated Standard Deviations in Units of the Last Quoted Digit)

Atom	x	y	z	Uequ.
C(1)	-0.1572(3)	0.4964(4)	0.0698(2)	523(10)
C(2)	-0.2125(4)	0.5501(4)	0.0189(2)	689(20)
C(3)	-0.2376(4)	0.4886(5)	-0.0379(2)	793(20)
C(4)	-0.2068(4)	0.3655(4)	-0.0410(2)	760(20)
C(4A)	-0.1473(3)	0.3047(4)	0.0090(2)	607(10)
C(5)	-0.1183(4)	0.1762(4)	0.0030(2)	706(20)
C(6)	-0.0648(4)	0.1155(4)	0.0504(2)	754(20)
C(7)	-0.0311(3)	0.1766(4)	0.1061(2)	647(10)
C(8)	-0.0532(3)	0.3020(3)	0.1146(2)	486(9)
C(8A)	-0.1170(3)	0.3680(4)	0.0666(2)	522(10)
C(1')	-0.1927(3)	0.5348(4)	0.1831(2)	496(9)
C(2')	-0.1458(3)	0.5710(4)	0.1275(2)	504(9)
C(3')	-0.0836(3)	0.6837(4)	0.1276(2)	547(10)
C(3A')	-0.0640(3)	0.7535(4)	0.1807(2)	501(10)
C(3B')	-0.1062(3)	0.7106(3)	0.2372(2)	444(8)
C(4')	0.0051(3)	0.8651(4)	0.1814(2)	639(10)
C(5')	0.0293(3)	0.9266(4)	0.2346(2)	683(20)
C(5A')	-0.0107(3)	0.8855(4)	0.2929(2)	576(10)
C(5B')	-0.0799(3)	0.7756(3)	0.2929(2)	478(9)
C(6')	0.0137(4)	0.9467(4)	0.3484(2)	760(20)
C(7')	-0.0245(4)	0.9045(4)	0.4050(2)	796(20)
C(8')	-0.0920(3)	0.7965(4)	0.4045(2)	703(20)
C(8A')	-0.1195(3)	0.7316(4)	0.3499(2)	571(9)
C(9')	-0.1868(3)	0.6171(4)	0.3481(2)	639(10)
C(10')	-0.2153(3)	0.5579(4)	0.2952(2)	548(9)
C(10A')	-0.1740(3)	0.6006(3)	0.2371(2)	436(8)
C(1")	-0.0347(3)	0.2984(4)	0.2307(2)	532(10)
C(2")	-0.0057(3)	0.3523(4)	0.1748(2)	479(9)
C(3")	0.0730(3)	0.4518(4)	0.1782(2)	503(10)
C(3A")	0.1159(3)	0.4994(4)	0.2340(2)	488(9)
C(3B")	0.0831(3)	0.4452(3)	0.2905(2)	480(9)
C(4")	0.1905(3)	0.6083(4)	0.2385(2)	589(9)
C(5")	0.2244(3)	0.6568(4)	0.2937(2)	683(20)
C(5A")	0.1938(3)	0.6030(4)	0.3511(2)	605(10)
C(5B")	0.1218(3)	0.4964(4)	0.3483(2)	549(9)
C(6")	0.2295(4)	0.6532(4)	0.4081(2)	763(20)
C(7")	0.1985(4)	0.5989(4)	0.4621(2)	891(20)
C(8")	0.1284(4)	0.4927(5)	0.4611(2)	829(20)
C(8A")	0.0895(3)	0.4415(4)	0.4046(2)	647(10)
C(9")	0.0142(4)	0.3334(4)	0.4006(2)	744(20)
C(10")	-0.0263(4)	0.2900(4)	0.3455(2)	680(10)
C(10A")	0.0066(3)	0.3416(4)	0.2876(2)	509(9)

to 294 pm for C(1')···C(1''). The pyrene systems show a deviation from planarity for C(1') and C(1'') [angles of planes C(10A')/C(1')/C(2') and C(10A'')/C(1'')/C(2'') with the mean planes through all other carbon atoms of the pyrene units: 7.5 and 3.9°, respectively]. The remaining carbon atoms of both pyrene systems are nearly coplanar (maximal deviation from best plane 6 and 2 pm). The pyrenyl groups are rotated against the naphthalene plane for 85 and 90°. This different torsion together with the spreading of C(1) − C(1') and C(8) − C(1'') bonds leads to a relatively strong lateral displacement from an ecliptic arrangement of the two pyrene units the overlap of which nevertheless is considerable. With regard to the 'excimer-like' state of **1** it should be mentioned that the overlap between the two pyrene systems may easily be increased by mere changes of torsional angles. The interplanar distance for the central parts of the pyrenyl groups is about 340 pm. Some short distances between carbon atoms of the two pyrene units are listed in Table 6.

Table 6. Some Short Distances between Carbon Atoms of Different Pyrene Units in **1** (in pm)

C(1′)	⋯C(1′′)	294	C(3A′)⋯C(3B′′)		337
C(2′)	⋯C(1′′)	307	C(3′) ⋯C(3A′′)		338
C(2′)	⋯C(2′′)	311	C(10′) ⋯ C(10′′)		341
C(10A′)⋯C(10′′)		323	C(3′) ⋯C(3′′)		347
C(1′)	⋯C(10A′′)	324	C(2′) ⋯C(10A′′)		347
C(10A′)⋯C(10A′′)		331	C(2′) ⋯C(3′′)		349

Table 7. C ⋯ C Bond Lengths of **1** and **2** (in pm; Numbers in Parentheses are Estimated Standard Deviations in Units of the Last Quoted Digit)

	1	**2**		**1**	**2**
C(1) − C(2)	137.8(1)	138.4(4)	C(6′) − C(7′)	137.3(1)	135.8(5)
C(1) − C(8A)	143.7(1)	143.1(4)	C(7′) − C(8′)	137.5(1)	137.9(4)
C(1) − C(1′)	149.6(1)	149.7(4)	C(8′) − C(8A′)	139.4(1)	139.6(4)
C(2) − C(3)	140.7(1)	138.8(6)	C(8A′)− C(9′)	142.7(1)	142.4(4)
C(3) − C(4)	133.6(1)	133.3(6)	C(9′) − C(10′)	134.8(1)	134.2(4)
C(4) − C(4A)	141.1(1)	141.7(5)	C(10′)− C(10A′)	143.1(1)	143.7(3)
C(4A) − C(5)	141.2(1)	140.5(4)	C(1′′) − C(2′′)	138.8(1)	139.5(3)
C(4A) − C(8A)	143.1(1)	142.4(3)	C(1′′) − C(10A′′)	139.8(1)	140.5(3)
C(5) − C(6)	134.5(1)	133.1(5)	C(2′′) − C(3′′)	137.9(1)	136.9(4)
C(6) − C(7)	140.4(1)	141.3(5)	C(3′′) − C(3A′′)	138.4(1)	138.7(4)
C(7) − C(8)	136.3(1)	136.3(4)	C(3A′′)− C(3B′′)	142.0(1)	142.1(3)
C(8) − C(8A)	143.4(1)	143.7(3)	C(3A′′)− C(4′′)	143.5(1)	144.0(4)
C(8) − C(1′′)	149.9(1)	149.0(3)	C(3B′′)− C(5B′′)	142.0(1)	142.0(3)
C(1′) − C(2′)	138.9(1)	139.1(4)	C(3B′′)− C(10A′′)	141.5(1)	141.5(3)
C(1′) − C(10A′)	140.8(1)	140.7(3)	C(4′′) − C(5′′)	134.1(1)	133.6(5)
C(2′) − C(3′)	137.8(1)	137.1(4)	C(5′′) − C(5A′′)	142.6(1)	142.9(4)
C(3′) − C(3A′)	139.1(1)	139.8(4)	C(5A′′)− C(5B′′)	141.2(1)	142.7(4)
C(3A′)− C(3B′)	141.6(1)	142.2(4)	C(5A′′)− C(6′′)	139.9(1)	138.9(4)
C(3A′)− C(4′)	142.4(1)	142.9(4)	C(5D′′)− C(8A′′)	141.5(1)	140.2(3)
C(3B′)− C(5B′)	142.3(1)	142.7(3)	C(6′′) − C(7′′)	137.2(2)	135.4(5)
C(3B′)− C(10A′)	142.3(1)	140.5(3)	C(7′′) − C(8′′)	137.8(2)	139.2(5)
C(4′) − C(5′)	134.7(1)	134.3(4)	C(8′′) − C(8A′′)	139.7(1)	140.7(4)
C(5′) − C(5A′)	142.9(1)	142.8(4)	C(8A′′)− C(9′′)	142.4(1)	141.6(4)
C(5A′)− C(5B′)	141.3(1)	142.1(4)	C(9′′) − C(10′′)	134.4(1)	135.7(4)
C(5A′)− C(6′)	139.6(1)	140.7(4)	C(10′′)− C(10A′′)	143.4(1)	143.7(3)
C(5B′)− C(8A′)	141.6(1)	141.4(4)			

Bond lengths of **1** are listed in Table 7 together with those of the isomer **2**. Bond angles of **1** and **2** are given in Table 8. With the exception of the deformations mentioned the bond lengths and angles are in the normal range.

Table 8. Bond Angles of **1** and **2** (in °; Numbers in Parentheses are Estimated Standard Deviations in Units of the Last Quoted Digit)

	1	2		1	2		1	2
C(2) - C(1) - C(8A)	119.8(1)	118.8(3)	C(3A')- C(3B')- C(5B')	119.4(1)	119.3(3)	C(2'') - C(3'') - C(3A'')	120.9(1)	121.6(3)
C(2) - C(1) - C(1')	117.5(1)	115.8(3)	C(3A')- C(3B')- C(10A')	120.1(1)	120.8(3)	C(3'') - C(3A'')- C(3B'')	118.9(1)	118.3(3)
C(8A) - C(1) - C(1')	123.3(1)	125.3(2)	C(5B')- C(3B')- C(10A')	120.4(1)	119.9(3)	C(3'') - C(3A'')- C(4'')	122.7(1)	123.1(3)
C(1) - C(2) - C(3)	122.8(1)	122.4(4)	C(3A')- C(4') - C(5')	121.4(1)	120.9(4)	C(3B'')- C(3A'')- C(4'')	118.4(1)	118.6(3)
C(2) - C(3) - C(4)	120.2(1)	120.3(4)	C(4') - C(5') - C(5A')	121.3(1)	122.8(4)	C(3A'')- C(3B'')- C(5B'')	119.9(1)	119.7(3)
C(3) - C(4) - C(4A)	121.8(1)	120.6(4)	C(5') - C(5A')- C(5B')	118.7(1)	118.4(3)	C(3A'')- C(3B'')- C(10A'')	119.8(1)	120.8(3)
C(4) - C(4A) - C(5)	119.8(1)	119.3(4)	C(5') - C(5A')- C(6')	122.3(1)	123.8(4)	C(5B'')- C(3B'')- C(10A'')	120.3(1)	120.2(3)
C(4) - C(4A) - C(8A)	119.9(1)	120.5(4)	C(5B')- C(5A')- C(6')	119.1(1)	117.8(4)	C(3A'')- C(4'') - C(5'')	121.3(1)	121.3(4)
C(5) - C(4A) - C(8A)	120.3(1)	120.2(3)	C(3B')- C(5B')- C(5A')	120.2(1)	120.8(3)	C(4'') - C(5'') - C(5A'')	121.7(1)	122.4(4)
C(4A) - C(5) - C(6)	121.2(1)	121.3(4)	C(3B')- C(5B')- C(8A')	120.1(1)	120.3(3)	C(5'') - C(5A'')- C(5B'')	118.7(1)	118.4(3)
C(5) - C(6) - C(7)	119.1(1)	120.0(4)	C(5A')- C(5B')- C(8A')	119.7(1)	119.6(3)	C(5'') - C(5A'')- C(6'')	122.5(1)	124.0(4)
C(6) - C(7) - C(8)	122.7(1)	121.4(4)	C(5A')- C(6') - C(7')	120.5(1)	121.7(4)	C(5B'')- C(5A'')- C(6'')	118.7(1)	117.7(4)
C(7) - C(8) - C(8A)	119.5(1)	119.8(3)	C(6') - C(7') - C(8')	121.3(1)	121.8(4)	C(3B'')- C(5B'')- C(5A'')	120.8(1)	119.6(3)
C(7) - C(8) - C(1'')	115.6(1)	115.7(3)	C(7') - C(8') - C(8A')	120.3(1)	120.0(4)	C(3B'')- C(5B'')- C(8A'')	119.9(1)	120.3(3)
C(8A) - C(8) - C(1'')	124.6(1)	124.5(2)	C(5B')- C(8A')- C(8')	119.:(1)	119.8(3)	C(5A'')- C(5B'')- C(8A'')	120.8(1)	120.1(3)
C(1) - C(8A) - C(4A)	117.8(1)	117.4(3)	C(5B')- C(8A')- C(9')	118.2(1)	118.8(3)	C(5A'')- C(6'') - C(7'')	120.5(1)	122.5(4)
C(1) - C(8A) - C(8)	125.3(1)	125.3(2)	C(8') - C(8A')- C(9')	122.7(1)	122.3(3)	C(6'') - C(7'') - C(8'')	121.4(1)	120.7(4)
C(4A) - C(8A) - C(8)	116.9(1)	117.3(3)	C(8A')- C(9') - C(10')	121.8(1)	122.1(3)	C(7'') - C(8'') - C(8A'')	120.4(1)	119.4(4)
C(1) - C(1') - C(2')	121.8(1)	119.3(3)	C(9') - C(10')- C(10A')	121.7(1)	121.1(3)	C(5B'')- C(8A'')- C(8'')	118.9(1)	119.6(3)
C(1) - C(1') - C(10A')	120.3(1)	122.8(3)	C(1') - C(10A')-C(3B')	119.4(1)	119.4(3)	C(5B'')- C(8A'')- C(9'')	118.5(1)	118.8(3)
C(2') - C(1') - C(10A')	118.8(1)	118.7(3)	C(1') - C(10A')-C(10')	122.0(1)	122.1(3)	C(8'') - C(8A'')- C(9'')	122.6(1)	121.7(3)
C(1') - C(2') - C(3')	121.8(1)	122.8(3)	C(3B')- C(10A')-C(10')	117.7(1)	118.5(3)	C(8A'')- C(9'') - C(10'')	121.7(1)	121.6(3)
C(2') - C(3') - C(3A')	120.9(1)	120.8(3)	C(8) - C(1'') - C(2'')	118.0(1)	119.6(3)	C(9'') - C(10'')- C(10A'')	121.4(1)	121.8(3)
C(3') - C(3A')- C(3B')	118.5(1)	117.9(3)	C(8) - C(1'') - C(10A'')	122.3(1)	121.7(2)	C(1'') - C(10A'')-C(3B'')	119.5(1)	119.8(2)
C(3') - C(3A')- C(4')	122.4(1)	122.8(3)	C(1'') - C(10A'')-C(10'')	118.7(3)		C(1'') - C(10A'')-C(10'')	122.3(1)	122.3(3)
C(3B')- C(3A')- C(4')	119.8(1)	119.2(3)	C(1'') - C(2'') - C(3'')	119.5(1)	121.3(1)	C(3B'')- C(10A'')-C(10'')	118.1(1)	117.9(3)

Molecular Structure of **2**: In Figure 4 views of **2** normal and parallel to the naphthalene plane are shown (A, B). In contrast to **1** the spreading of the *peri*-bonds C(1) – C(1') and C(8) – C(1'') occurs mainly as an in-plane bending of about 16°. The out-of-plane deviations of these bonds as well as of C(1) and C(8) are negligible. The bond angles C(1') – C(1) – C(8A), C(1) – C(8A) – C(8) and C(8A) – C(8) – C(1'') are widened to 125.2, 125.3, and 124.5°, respectively. The pyrenyl groups show a deviation from planarity for C(1') and C(1'') [angles of planes C(10A')/C(1')/C(2') and C(10A'')/ C(1'')/C(2'') with the mean planes through all other pyrenyl carbon atoms: 8.1 and 5.7°]. The pyrene planes are twisted against the naphthalene plane for 75° both; the inclination of the two pyrene planes against each other is 6.8°. There are short interplanar distances only between the ring of carbon atoms 1′,2′,3′,3A′,3B′, and 10A′ and the corresponding ring of the neighbouring pyrene (Table 9). The overlap for the other regions of the pyrene units is very small, and in contrast to **1** it cannot be

increased considerably by changes of torsional angles. Bond lengths and bond angles of **2** are listed in Tables 7 and 8.
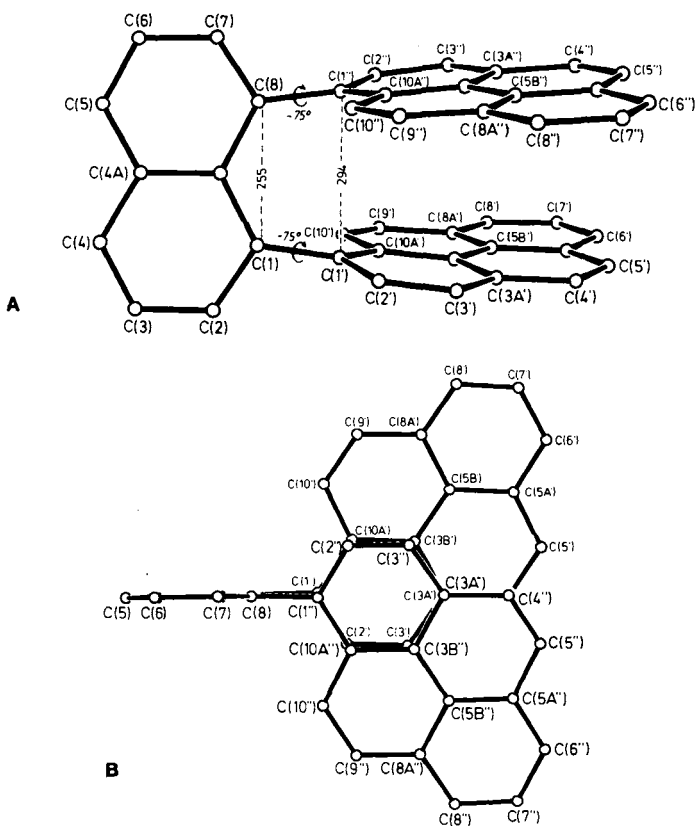

Figure 4. Molecular Structure of **2** in a View Normal to the Naphthalene Plane (A) and in a View Parallel to the Naphthalene Plane (B)

Table 9. Some Short Distances in **2** between Carbon Atoms of Different Pyrene Units (in pm)

C(1')	···C(1'')	294	C(2')	···C(10A'')	321
C(1')	···C(10A'')	313	C(1')	···C(10'')	348
C(10A')	···C(1'')	314	C(10')	···C(1'')	350
C(10A')	···C(2'')	319	C(3B')	···C(3'')	352
C(10')	···C(2'')	320	C(3')	···C(3B'')	354
C(2')	···C(10'')	321	C(3A')	···C(3B'')	354

Molecular Structure of **3**: In Figure 5A a view is given onto the naphthalene plane which by rotation around the C(4A) − C(8A) axis forms an angle with the drawing plane of 40°. In Figure 5B the structure is shown in a view parallel to the naphthalene plane. The in-plane and out-of-plane deformations of the naphthalene *peri*-bonds
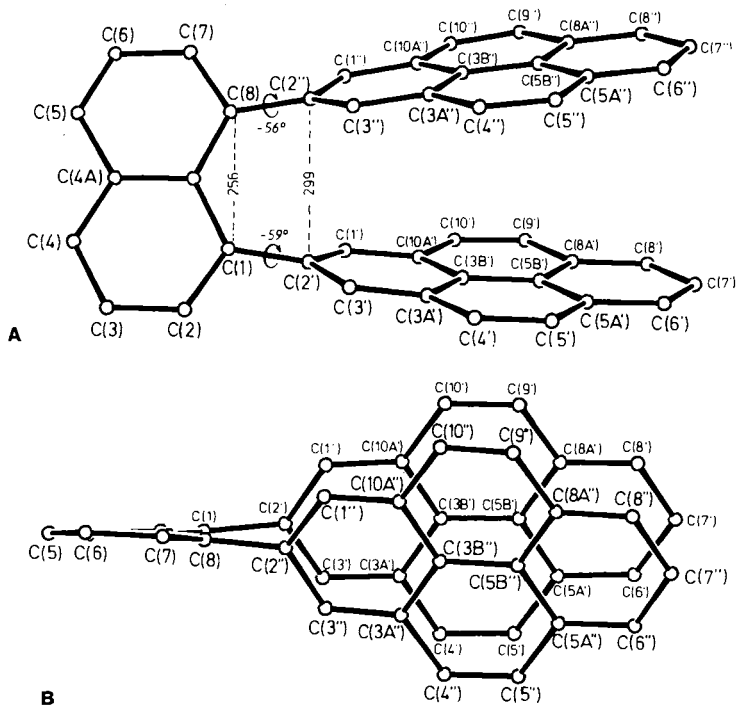
Figure 5. Molecular Structure of **3** in a View onto the Naphthalene Plane (A) and in a View Parallel to the Naphthalene Plane (B)

Table 10. Some Short Distances between Carbon Atoms of Different Pyrene Units in **3** (in pm)

C(1')···C(2'')	292	C(1') ···C(1'')	326
C(2')···C(3'')	296	C(3B') ···C(3A'')	342
C(2')···C(2'')	299	C(10') ···C(10A'')	346
C(1')···C(3'')	318	C(3A') ···C(4'')	347
C(3')···C(3'')	323	C(10A')···C(3A'')	350

C(1) – C(1') and C(8) – C(1'') are similar as in **1** (16 and 10°, respectively). The angles C(2') – C(1) – C(8A), C(1) – C(8A) – C(8), and C(8A) – C(8) – C(2'') are widened to 123.6, 126.2, and 126.3°, respectively. Of the pyrene units C(2') and C(2'') deviate from planarity [angles of planes C(1')/C(2')/C(3') and C(1'')/C(2'')/C(3'') with the mean plane through all other pyrene carbon atoms: 6.8 and 5.1°, respectively]; for the remaining carbon atoms the maximal deviations from planarity are 6 pm only. As the most interesting feature in the structure of **3** it is found that the pyrene planes are not nearly orthogonal to the naphthalene plane but form torsional angles of only 56 and 59°, respectively. This twisting of the pyrene planes results in a substantial reduction of overlap as compared to an ecliptic arrangement of corresponding pyrene carbon atoms. On the other hand, as for **1** by an increase of torsional angles only a more extended

Table 11. C···C Bond Lengths of **3** (in pm; Numbers in Parentheses are Estimated Standard Deviations in Units of the Last Quoted Digit)

Bond	Length	Bond	Length	Bond	Length
C(1) – C(2)	136.2(3)	C(6') – C(7')	139.7(4)		
C(1) – C(8A)	145.3(3)	C(7') – C(8')	139.8(4)		
C(1) – C(2')	140.8(3)	C(8') – C(8A')	138.8(3)		
C(2) – C(3)	140.7(4)	C(8A') – C(9')	140.7(4)		
C(3) – C(4)	137.7(4)	C(9') – C(10')	137.7(4)		
C(4) – C(4A)	140.2(4)	C(10') – C(10A')	133.8(3)		
C(4A) – C(5)	143.4(3)				
C(4A) – C(8A)	143.9(3)				
C(5) – C(6)	133.8(4)				
C(6) – C(7)	140.2(4)				
C(7) – C(8)	139.1(3)				
C(8) – C(8A)	142.1(3)				
C(8) – C(2')	147.9(3)				
C(1') – C(2')	139.7(3)				
C(1') – C(10A')	136.8(3)				
C(2') – C(3')	141.0(3)				
C(3') – C(3A')	137.7(3)				
C(3A') – C(3B')	141.4(3)				
C(3A') – C(4')	144.1(3)				
C(3B') – C(5B')	140.6(3)				
C(3B') – C(10A')	141.8(3)				
C(4') – C(5')	133.7(3)				
C(5') – C(5A')	143.3(3)				
C(5A') – C(5B')	142.6(3)				
C(5A') – C(6')	138.0(4)				
C(5B') – C(8A')	141.8(3)				

Table 12. Bond Angles of **3** (in °; Numbers in Parentheses are Estimated Standard Deviations in Units of the Last Quoted Digit)

Angle	°	Angle	°	Angle	°
C(2) – C(1) – C(8A)	119.7(3)	C(3A') – C(3B') – C(5B')	120.3(3)	C(2') – C(3') – C(3A')	121.9(3)
C(2) – C(1) – C(2')	117.3(3)	C(3A') – C(3B') – C(10A')	119.1(3)	C(3') – C(3A') – C(3B')	119.8(3)
C(8A) – C(1) – C(2')	122.9(2)	C(5B') – C(3B') – C(10A')	120.6(3)	C(3') – C(3A') – C(4')	122.6(3)
C(1) – C(2) – C(3)	124.1(3)	C(3A') – C(4') – C(5')	120.6(3)	C(3B') – C(3A') – C(4')	117.5(3)
C(2) – C(3) – C(4)	117.2(3)	C(4') – C(5') – C(5A')	122.4(3)	C(3A') – C(3B') – C(5B')	120.6(3)
C(3) – C(4) – C(4A)	121.9(3)	C(5') – C(5A') – C(5B')	117.9(3)	C(3A') – C(3B') – C(10A')	118.9(3)
C(4) – C(4A) – C(5)	119.2(3)	C(5') – C(5A') – C(6')	123.6(3)	C(5B') – C(3B') – C(10A')	120.4(3)
C(4) – C(4A) – C(8A)	121.4(3)	C(5B') – C(5A') – C(6')	118.7(3)	C(3A') – C(4') – C(5')	120.9(3)
C(5) – C(4A) – C(8A)	119.5(3)	C(3B') – C(5B') – C(5A')	128.3(3)	C(4') – C(5') – C(5A')	122.8(3)
C(4A) – C(5) – C(6)	120.3(3)	C(3B') – C(5B') – C(8A')	119.1(3)	C(5') – C(5A') – C(5B')	117.5(3)
C(5) – C(6) – C(7)	121.8(3)	C(5A') – C(5B') – C(8A')	117.9(3)	C(5') – C(5A') – C(6')	122.8(3)
C(6) – C(7) – C(8)	121.8(3)	C(6') – C(7') – C(8')	121.6(3)	C(5B') – C(5A') – C(6')	119.7(3)
C(7) – C(8) – C(8A)	118.7(3)	C(7') – C(8') – C(8A')	119.8(3)	C(3B') – C(5B') – C(5A')	128.5(3)
C(7) – C(8) – C(2')	114.4(3)	C(5B') – C(8A') – C(8')	117.2(3)	C(3B') – C(5B') – C(8A')	120.5(3)
C(8A) – C(8) – C(2')	126.9(2)	C(5B') – C(8A') – C(9')	122.9(3)	C(5A') – C(5B') – C(8A')	118.9(3)
C(1) – C(8A) – C(4A)	115.5(3)	C(8') – C(8A') – C(9')	122.2(3)	C(5A') – C(6') – C(7')	120.9(4)
C(1) – C(8A) – C(8)	126.1(3)	C(8A') – C(9') – C(10')	121.8(3)	C(6') – C(7') – C(8')	121.8(4)
C(4A) – C(8A) – C(8)	118.4(3)	C(9') – C(10') – C(10A')	119.8(3)	C(7') – C(8') – C(8A')	119.8(3)
C(2') – C(1') – C(10A')	122.3(3)	C(1') – C(10A') – C(3B')	121.8(3)	C(5B') – C(8A') – C(8')	117.9(3)
C(1') – C(2') – C(1)	122.3(3)	C(1') – C(10A') – C(10')	122.9(3)	C(5B') – C(8A') – C(9')	122.2(3)
C(1') – C(2') – C(3')	119.2(3)	C(3B') – C(10A') – C(10')	121.9(2)	C(8') – C(8A') – C(9')	120.7(3)
C(3') – C(2') – C(3')	121.8(3)	C(8) – C(2') – C(1')	120.6(2)	C(9') – C(10') – C(10A')	122.8(3)
C(3') – C(34') – C(3B')	118.7(3)	C(8) – C(2') – C(3')	121.9(2)	C(1') – C(10A') – C(3B')	119.8(3)
		C(1') – C(2') – C(4')	117.4(3)	C(1') – C(10A') – C(10')	123.5(3)
				C(3B') – C(10A') – C(10')	117.5(3)

overlap of the pyrene units can easily be reached. Some short distances between carbon atoms of different pyrene units are listed in Table 10. Bond lengths of **3** are quoted in Table 11, bond angles in Table 12.

Conclusion: With regard to pyrene-pyrene interactions in **1, 2,** and **3** the X-ray structure analyses are in an excellent accordance with the emission spectra discussed above. Thus, the dependence of the formation of an 'excimer-like' state on the mutual overlap of the pyrene units in **1 – 3** is strongly supported.

Experimental Part

cis- and trans-1,8-Di(1-pyrenyl)naphthalenes (**1, 2**): 630 mg (26 mmol) of magnesium and 50 mg of iodine in 5 ml of ether were stirred under argon in an ultrasonic bath for 5 min. After evaporation of the ether about one tenth of a solution of 5.1 g (18.2 mmol) of 1-bromopyrene[3] in 50 ml of tetrahydrofuran was added, and the reaction was started by addition of 0.25 g of dibromoethane and immersion of the reaction flask into an ultrasonic bath of 60°C. Under these conditions the remaining solution of 1-bromopyrene was dropped in within 20 – 30 min, and the reaction mixture was stirred for further 10 – 20 min. The solution of the Grignard reagent then was added dropwise through a glass-wool filter to a solution of 1.14 g (3.0 mmol) of 1,8-diiodonaphthalene[4] and 40 mg of bis(acetylacetonato)nickel(II) in 20 ml of tetrahydrofuran. After warming up to room temperature within 2 – 3 h, further stirring at room temperature for 2 h and hydrolysis with conc. ammonium chloride solution, tetrahydrofuran was evaporated *in vacuo.* To the residue 50 ml of ethanol was added, and the solution was poured into 200 ml of water. The precipitate was filtered off, dried *in vacuo* and extracted with 300 ml of dichloromethane. The insoluble material was filtered off (150 mg, predominantly 1,1'-bipyrene). The soluble products were chromatographed from toluene at basic aluminium oxide (activity grade I – II); in the order of decreasing R_F-values the following compounds were isolated:

1-(1-Pyrenyl)naphthalene (**4**): 90 mg, m. p. 164 – 166°C (from acetone), identified with an authentic sample (see below).

1,1'-Bipyrene: 320 mg, m. p. 323 – 326°C (from xylene; lit.[5] m. p. 327 – 328°C).

1,8-Di(1-pyrenyl)naphthalenes (**1/2**): 420 mg (26.5%) (for separation of **1** and **2** see below).

8,8'-Di(1-pyrenyl)-1,1'-binaphthalene (**5**): 30 mg; m. p. 375°C (dec.). – ^{1}H NMR (360 MHz, [D$_2$]-1,1,2,2-tetrachloroethane): δ = 5.26 ('dd', 2H), 6.37 ('dd', 2H), 6.48 ('dd', 2H), 6.76 (d, J = 9.1 Hz, 2H), 7.31 (dd, J = 7.0 and 1.3 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.43 (dd, J = 8.1 and 1.3 Hz, 2H), 7.47 – 7.49 (m, 4H), 7.53 (d, J = 9.3 Hz, 2H), 7.84 (d, J = 9.0 Hz, 2H), 7.92 – 8.01 (m, 4H), 8.03 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 6.8 Hz, 2H). – MS: *m/z* = 654 (100%, M$^+$), 327 (8%).

$$C_{52}H_{30} \text{ (654.8)}\quad \text{Calcd. C 95.38 H 4.62   Found C 95.51 H 4.63}$$

Separation of cis-trans-Isomers **1** *and* **2**: The **1/2**-fraction from the above-mentioned chromatography was adsorbed on silica (particle size < 0.063 mm) from dichloromethane. By pressure-chromatography (3 – 5 bar) from tetrachloromethane 260 mg (16%) of **1** with R_F = 0.2 and 150 mg (9.5%) of **2** with R_F = 0.1 were obtained. Crystallization of **1** and **2** was achieved by dissolving the respective compound in dichloromethane at room temperature, adding toluene, and slowly evaporating dichloromethane at room temperature.

1: pale-yellow crystals, m. p. 267 – 269 °C (with partial conversion to 2); for spectroscopic data see above.

2: colourless crystals, m. p. 262 – 266 °C (with partial conversion to 1); for spectroscopic data see above.

$C_{42}H_{24}$ (528.6)   Calcd. C 95.42 H 4.58   1: Found C 95.69 H 4.43
2: Found C 95.61 H 4.62

1-(1-Pyrenyl)naphthalene (**4**): To a solution of 1.0 g (3.05 mmol) of 1-iodopyrene[7] and 40 mg of bis(acetylacetonato)nickel(II) in 30 ml of tetrahydrofuran, cooled to – 15 °C, the Grignard solution prepared from 2.5 g (12.1 mmol) of 1-bromonaphthalene in 40 ml of tetrahydrofuran was dropped in within 1 h. The reaction mixture was stirred at – 10 °C for 1 h and then hydrolysed with diluted hydrochloric acid. Tetrahydrofuran was evaporated, the residue was extracted with dichloromethane; the extract was washed with water, dried over sodium sulfate, and chromatographed on silica from tetrachloromethane. Following the fraction of naphthalene 500 mg of 1,1'-binaphthalene (m. p. 152 – 153 °C, lit.[11] 155 °C) and 620 mg (62%) of **4** were obtained: colourless crystals, m. p. 164 – 166 °C (from acetone). – MS: m/z = 328 (100%, M$^+$), 326 (60), 324 (10), 164 (14, M^{2+}) a. o.

$C_{26}H_{16}$ (328.4)   Calcd. C 95.09 H 4.91   Found C 95.24 H 4.78

2-Bromo-4,5,9,10-tetrahydropyrene (**6**): The synthesis of **6** from [2.2]metacyclophane (yield 15%)[8] has been modified as follows: To a solution of 10.4 g (50 mmol) of [2.2]metacyclophane and 200 mg of iodine in 150 ml of tetrachloromethane under ice-cooling a solution of 16 g (100 mmol) of bromine in 100 ml of tetrachloromethane was added within 1 h. The solvent was evaporated, the residue dissolved in dichloromethane and filtered through basic aluminum oxide (activity grade I): 12.8 g (90%), m. p. 94 – 96 °C (lit.[8] 97.5 – 100 °C); the product is sufficiently pure for the following reaction.

1,8-Bis(4,5,9,10-tetrahydro-2-pyrenyl)naphthalene (**7**): A Grignard solution prepared from 5.2 g (18.2 mmol) of **6** as described for the 1/2-synthesis was added dropwise within 1.5 h to a solution of 1.14 g (3.0 mmol) of 1,8-diiodonaphthalene and 50 mg of bis(acetylacetonato)nickel-(II) in 40 ml of tetrahydrofuran cooled to – 15 to – 10 °C. The reaction mixture was stirred for 1 h at – 10 °C, warmed up to room temperature within 1 h and hydrolysed with diluted hydrochloric acid. The solution was evaporated to about 20 ml, mixed with 100 ml of water and extracted three times with 50 ml of dichloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was filtered through basic aluminum oxide from toluene and then chromatographed on silica (< 0.063 mm) from tetrachloromethane (3 – 5 bar). Following a tetrahydropyrene fraction 260 mg of compound A (see below) and 350 mg (22%) of **7** were obtained. **7** forms colourless crystals, m. p. 281 – 283 °C (from toluene). – ^{1}H NMR (360 MHz, CD$_2$Cl$_2$): δ = 2.4 – 2.75 (m, 16H), 6.727 (s, 4H), 6.840 ('d', 4H), 6.957 (m, 2H), 7.48 – 7.58 (m, 4H), 7.935 ('dd', $J \approx$ 8.0 and 1.3 Hz, 2H).

$C_{42}H_{32}$ (536.7)   Calcd. C 93.99 H 6.01   Found C 94.17 H 6.24

Compound A, colourless crystals of m. p. 317 – 321 °C (from toluene), was identified as 4,4',5,5',9,9',10,10'-octahydro-2,2'-bipyrene: ^{1}H NMR (80 MHz, [D$_2$]-1,1,2,2-tetrachloroethane): δ = 2.94 (s, 16H), 7.10 (s, 6H), 7.35 (s, 4H). – MS: m/z = 410 (100%, M$^+$), 408 (4), 205 (10, M^{2+}).

$C_{32}H_{26}$ (410.6)   Calcd. C 93.62 H 6.38   Found C 93.87 H 6.34

1,8-Di(2-pyrenyl)naphthalene (**3**): 100 mg (0.186 mmol) of **7** and 200 mg (0.881 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 20 ml of toluene were heated under reflux for 1.5 h. The cooled reaction mixture was diluted with dichloromethane and filtered through a short column of

aluminum oxide. Evaporation of the solvents yielded 82 mg (83%) of **3**, pale-yellow crystals, m. p. 331 – 333 °C; for spectroscopic data see above.

$$C_{42}H_{24} \ (528.6) \quad \text{Calcd. C 95.42 H 4.58} \quad \text{Found C 95.55 H 4.34}$$

1-(2-Pyrenyl)naphthalene (**8**): Preparation from 1.0 g (3.05 mmol) of 2-iodopyrene[7] and the Grignard solution prepared from 2.5 g (12.1 mmol) of 1-bromonaphthalene following exactly the procedure mentioned for **4**: yield 540 mg (54%), colourless crystals (from isopropyl alcohol), m. p. 123 – 124.5 °C (lit.[9] 112 – 113 °C). – MS: m/z = 328 (100%), 326 (50), 324 (8), 164 (14, M^{2+}), a. o.

$$C_{26}H_{16} \ (328.4) \quad \text{Calcd. C 95.09 H 4.91} \quad \text{Found C 95.21 H 4.86}$$

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