Formation of *sec*-Alkylpyrenes by Friedel-Crafts and Cathodic Alkylation Methods. Structure and Spectroscopic Properties of Products. Catalytic Hydrogenation of Pyrene and Some Alkylpyrenes

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Friedel-Crafts isopropylation of pyrene in neat isopropyl chloride yielded a series of mono, di, tri, tetra, and pentaisopropylpyrenes. Tetra and pentacyclopentyl- and cyclohexylpyrenes were formed analogously. Cathodic isopropylation by controlled potential electrolysis yielded both fully aromatic and partly hydrogenated isopropylpyrenes. Structures of these compounds, spectroscopic properties and mechanistic aspects of their formation are discussed.
The catalytic hydrogenation (Raney nickel) of pyrene and isopropylpyrenes under very mild conditions has also been studied.

In an early investigation,[1] it was found that Friedel-Crafts alkylation of pyrene with tertiary alkyl halides (*t*-butyl and *t*-amyl) yielded di-*t*-alkylpyrenes exclusively, while secondary alkyl halides (isopropyl, cyclopentyl and cyclohexyl) gave tetra and pentaalkylpyrenes (see Scheme 1, footnotes *d–f*). NMR[2] and X-ray[3] studies later on have shown that the tertiary substituents occupied the unusual 2 and 7 positions, presumably due to steric interference in the four usually occupied positions (1,3,6,8)[4] which, on the other hand, appeared to be occupied in the tetraisopropyl derivative.[2] The appearance of well defined tetra and pentaalkylpyrenes, and of isomerism occurring with the former, called for further structural investigations, the results of which are reported here. In addition, a reexamination of the Friedel-Crafts isopropylation reaction was performed in order to look for additional products and to examine the time-dependence of product distribution.

Cathodic alkylation has proven a useful method for preparing some alkylated aromatic as well as hydroaromatic polycyclic hydrocarbons.[5,6] Thus, the production of the elusive 1-*t*-butylpyrene[6] in high yield showed that this method might be a valuable supplement to the Friedel-Crafts alkylation reaction. Moreover, as a need arose for these types of alkylated derivatives as reference compounds in geochemical work[7] a reductive isopropylation study using controlled potential electrolysis was undertaken.

When 1-isopropenylpyrene was hydrogenated in the presence of Raney nickel as a catalyst in order to make 1-isopropylpyrene, it was found that the aromatic system was also attacked under the very mild conditions used. This behaviour is in contrast with literature statements concerning hydrogenation of aromatic hydrocarbons over Raney nickel.[8–12] A closer investigation of this procedure has therefore been included. As a practical result, some hydropyrenes have become readily available.

Hansen, Berg *et al.*[13] have, in a series of publications (see Ref. 13), studied the ^{13}C NMR spectra of different types of aromatic com-

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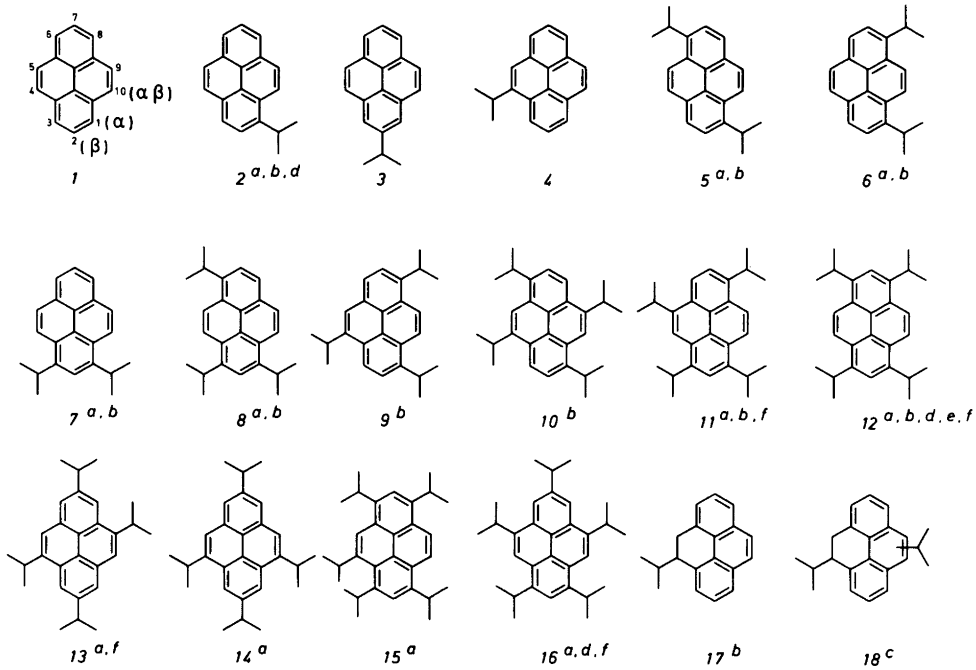


Scheme 1. Products of Friedel-Crafts alkylation and cathodic alkylation of pyrene. *Isopropyl* derivatives: [a]Isolated in Friedel-Crafts experiments (Table 1). [b]Isolated in cathodic alkylation (Table 2). [c]Identified, not isolated, in cathodic alkylation. [d]Isolated in early Friedel-Crafts (Ref. 1). [e]Structural assignment, see Ref. 2. [f]In the early work (Ref. 1) were isolated, without structural assignments, two *cyclohexyl*pyrenes corresponding to *11* and *12* and three *cyclopentyl*pyrenes corresponding to *12, 13* and *16,* assignments of which are included in this work.

pounds, including pyrene derivatives, with emphasis on substituent effects and rotational orientation of the substituent. These subjects are also discussed in the ^{1}H and ^{13}C NMR studies of this work.

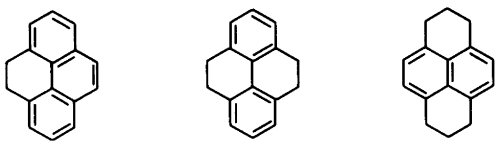
Recent investigations on the carbonization chemistry of partially hydrogenated pyrenes and other polycyclic aromatic hydrocarbons and their alkylated derivatives[14-16] have opened new perspectives to the importance of such compounds for the study of coal structure and industrial processes like coal liquefaction and coke formation in catalytic oil cracking.

Results and discussion

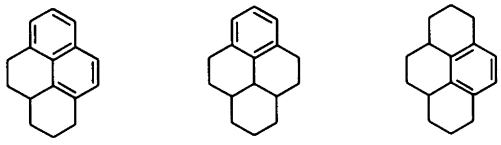
Most of the structures discussed are presented in Schemes 1 and 2. Besides the numbering of pyrene (*1*) the denotations α for positions 1, 3, 6, and 8, β for 2 and 7, and αβ for 4, 5, 9, and 10 are used.[17]

Friedel-Crafts alkylation. The results of an experiment run in neat isopropyl bromide are shown in Table 1. Only two of the products shown (Scheme 1, *12* and *16*) were found in the early investigation[1] which also reported the disappearance of *12* after prolonged reaction time. Because of its marked insolubility, *12* was the most easily isolated and purified among the products. While the structure of *12* was determined previously,[2] that of *16* is included in this work. In similar experiments in the early work, five polycycloalkylpyrenes were isolated, the structures of which have now been established. They include two tetracyclopentylpyrenes with structures analogous to those of *12* and *13,* a pentacyclopentylpyrene analogous to *16,* and two tetracyclohexylpyrenes corresponding to *11* and *12.* The earlier tentative assignment[1] of a structure like *12* to the highest melting tetraalkylpyrene in each case has proven correct.

Table 1 reveals how the product distribution



19 20 21



22 23 24

Scheme 2. Hydrogenation patterns in catalytic hydrogenation of pyrene, hydropyrenes and some alkyl derivatives. Yields and alkyl groups represented appear in Table 3.

developed during the reaction. In the initial stages the picture was dominated by compounds *5–8, 11* and *12* substituted at the positions of most available electrons,[18,19] the four α positions, in agreement with the general pattern known for pyrene in other electrophilic substitution reactions.[4,19,20] The absence of *2* was most likely due to rapid further alkylation of this compound; *2* could be isolated when a solvent was used in order to decrease reaction rate.[1] However, in the most abundant initial product, *11,* one of the four isopropyl groups occupies an αβ position. According to Dewar[18,19] there is only a small difference between the reactivities predicted for positions 1 and 4, and the αβ position occupied in *11* may well have been a primary substitution site. Bavin and Dewar[18] failed to find 4-nitropyrene in the nitration of pyrene. In the alkylation reaction, however, three isopropyl groups already present might render the 9 position in *8* more reactive than position 8. The 'normal' product, *12,* seemed accordingly to be formed predominantly, if not exclusively, by rearrangement of *11.* Even small amounts of two pentasubstitutes (*15* and *16*) were present among the initial products. Product *15* was probably formed directly from *11,* whereas the formation of *16* must have involved isomerizations.

With prolonged reaction time, thermodynamic control takes over completely, resulting in rearranged tetra and penta substitutes (*13, 14, 16*). This is also supported by the fact that the isolated compound *12,* when subjected to the reaction conditions, yielded *16.* The driving force in these rearrangements may be found in the steric strain accumulated in compounds like *11, 12,* and *15.* The last one, in addition to three isopropyl-hydrogen *peri* interactions, also comprises two isopropyl groups *peri* to each other. The strain due to *peri* interaction involving an isopropyl group can be somewhat released by appropriate rotation of the group about the bond to the aromatic carbon and this may be one reason for the formation of several polyisopropylpyrenes involving such interactions. This possibility does not exist for a *t*-butyl group; thus it is understandable that 2,7-di-*t*-butylpyrene is the sole product in that instance.[1,2] That the latter compound is formed via initial attack at the α positions, followed by a rapid rearrangement, seems doubtful.[2] ^{1}H NMR observations support the suggested role of rotation of the isopropyl group (see below).

Cathodic alkylation. Controlled potential electrolysis (cpe) of pyrene in the presence of isopropyl chloride results in the formation of several isopropylpyrenes and isopropylhydropyrenes (Scheme 1), the number of isopropyl groups ranging from one to six. Compounds that have been isolated are shown in Table 2. They comprise chiefly mono, di, tri and tetraisopropylpyrenes though some partly hydrogenated products were also isolated, especially *17.* The presence of penta and hexaisopropylated compounds appeared from MS (see below). The results of cpe at −1.5 V (Ag/AgI) under strictly anhydrous conditions could be reproduced safely, whereas the results at −1.7 V, or when small amounts of water were present, were rather variable. The products of cathodic *t*-butylation[6] are shown in Table 2 for comparison.

Formation of *2* and *17* through coupling between the aromatic anion radical and the alkyl radical is analogous to the formation of the corresponding *t*-butyl derivatives.[6] The suspected precursor of *2,* a 1-isopropyldihydropyrene, suffered oxidative aromatization during work-up, which obviously did not happen to *17,* a derivative of the stable 4,5-dihydropyrene.

It is conceivable that the higher reactivity of an isopropyl radical compared with that of a *t*-butyl radical may cause radical aromatic substitution to play a role in the occurrence of fully aromatized

products. This suggestion finds support in the high total yield (~30 %) of di and polyisopropylpyrenes (*5–12*) that would otherwise require extensive oxidative aromatization. In the cathodic *t*-butylation of pyrene,[6] the di-*t*-butylpyrenes (1,6- and 1,8-) were formed only in minor amounts, while 1-*t*-butylpyrene, corresponding to *2*, was the major product (52 %) thus indicating a different mechanism. It should also be noted that the extensive tar formation that followed autooxidation in the *t*-butyl case was absent in the present reaction.

Catalytic hydrogenation. The rate of hydrogenation of pyrene under the conditions used (Table 3 and Scheme 2) was rather insensitive to the nature of the solvent, although hydrogenation from the dihydro stage (*19*) to the tetrahydro stage (*20*) proceeded faster in the less polar solvent. In cyclohexane, no *19* remained as it did in ethyl acetate when the reaction was run to complete disappearance of *1*. This is in agreement with the results of an experiment where *19* served as the substrate when the shift from ethyl acetate to cyclohexane accelerated the reaction considerably.

The predominance of 1,2,3,6,7,8-hexahydropyrene (*21*) indicates that the adsorbed pyrene molecule was attacked preferentially at the biphenyl moiety. An alternative path to *21*, however, would be via initial attack at the central naphthalene portion of the molecule with subsequent isomerization as evidenced by the occurrence of considerable amounts of *21* in the hydrogenation of *19*. The importance of isomerizations was seen in an attempt to hydrogenate *20* completely to the decahydropyrene *23*, using a surplus of catalyst, when complete conversion to *24* took place. On the other hand, *21* was entirely unaffected under the same conditions.

The presence of bulky alkyl groups slowed down the hydrogenation reaction. Just one isopropyl group did so irrespective of position; but it did not change considerably the relative amounts of the products. No hydrogenation of *12*, with four isopropyl groups, took place. This could be partly a result of hindered access to the catalyst surface, partly a result of poor solubility.

Table 1. Time-dependence of substitution products in the Friedel-Crafts isopropylation of pyrene in neat isopropyl bromide as solvent and $AlBr_3$ as catalyst. Temperature, *ca.* 60 °C (reflux).

Products[a]	Yield/%[b] after		
	1.25 h	3.5 h	48 h
5,6,7[c]	27	5	
8	6	6	
11	58	36	
12		35	
13			13
14			11
15	3		
16	6	18	76

[a]For structures see Scheme 1.
[b]Mol % of recovered material.
[c]Mixture.

Table 2. Isolated products of cathodic isopropylation of pyrene in dry DMF/TBAI/isopropyl chloride.[a] Corresponding products from cathodic *t*-butylation are shown for comparison.

Products[b]	Yield/%[c]	
	Isopropylation	*t*-Butylation[d]
1	4.4	
2	19.0	52
5,6[e]	20.9	3.3
7	1.3	
8	2.6	
9	2.0	
10	2.3	
11,12[e]	0.4	
17	10.1	14
f	8.3	

[a]170 ml/0.1 M/5 ml (0.06 mol). −1.5 V (Ag/AgI). Room temperature. [b]For structures see Scheme 1. [c]Mol % of recovered material, analysed by GLC and ^{1}H NMR on fractions obtained by column chromatography. [d]Ref. 6. [e]Mixture. [f]A mixture of hydrogenated compounds, see Scheme 1 and experimental part.

Spectrosopic results and discussion

^{1}H NMR spectra. For data, see *Survey of products.* The simple spin systems in pyrene and its derivatives make the assignments of substituted structures relatively straightforward, even in cases where a mixture of two compounds is considered. The assignments are based on the well docu-

Table 3. Catalytic hydrogenation over Raney Nickel of pyrene derivatives at room temperature and low hydrogen pressure (2.5 atm.). Yields of hydrogenated products.

Substrate[a]	Solvent[b]	Reaction time/h	Conversion /%[c]	Yield of hydro derivatives/%[d]					
				4,5-Di-	Tetra-[e]	Hexa-[f]	Hexa-[g] /%	Deca-[h]	Deca-[i]
1	E	0.5	53	23	2	28			
	E	3	100	30	9	61			
	C	0.5	50	24	4	22			
	C	3	100		32	68			
19	E	48	68		29	39			
	C	1	12		7	5			
	C	3	86		69	17			
20	E	24	9			9			
	C	24	56			30		9	17
21	C	24	0						
2[j]	E	2	54	23		31			
	E	5	89	32		57			
	E	10	100	26	14	60			
3	E	22.5	100	18	31	51			
4	E	20.5	100	25	14	61			
12	C	24	0						
DtB-1[k]	E	47	54	4		34	16		
	C	24	100	26	2	48	24		
DtB-*19*[k]	C	24	97		51		15[l]		31
	C	69	100		36			12	52
DtB-*20*[k]	C	118	19					19	

[a]For structures, see Schemes 1 and 2. [b]C, cyclohexane; E, ethyl acetate. [c]Mol % of substrate (sum of percentages of hydro derivatives). [d]Mol % of recovered material; the balance is unconverted substrate. Analyzed by ^{1}H NMR and GLC. Recovery was nearly quantitative. [e]4,5,9,10-Tetra- (cf. 20). [f]1,2,3,6,7,8-Hexa- (cf. 21). [g]1,2,3,3a,4,5-Hexa- (cf. 22). [h]1,2,3,3a,4,5,9,10,10a,10b-Deca- (cf. 23). [i]1,2,3,3a,4,5,5a,6,7,8-Deca- (cf. 24). [j]The substrate proper was 1-isopropenylpyrene that was at first hydrogenated to *2*. [k]DtB denotes 2,7-di-*t*-butyl. [l]Total yield of hexa-[f], hexa-[g] and deca-[h].

mented characteristic ranges of chemical shift values and coupling constants in pyrene as well as substituent effects on these quantities.[2,21,22] The effect on ^3J(H-αβ, H-αβ) of α substituents, for instance, owing to their magnitude and additivity, may indicate the number and relative positions of isopropyl groups, and the observation of a coupling constant of 1.5 Hz (typically a coupling over four bonds) between two α protons allows *13*, with a centre of symmetry, to be distinguished from *14*, which has an axis of symmetry.

The chemical shifts of the methyl protons (doublets) are indicators of the numbers of different isopropyl groups and of the symmetry of the molecule, while the chemical shifts of the methine protons of these groups are highly indicative of the groups being in α-, β- or αβ- positions, or if substitution occurs at an aromatic or hydrogenated ring position.

The high field chemical shift of the methine proton in *3*, as compared to the corresponding values in *2* and *4*, suggests that this proton, in *3*, spends less time in the plane of the aromatic system than is the case in *2* or *4*, and thus suffers less deshielding due to the aromatic ring current. The methine proton chemical shifts are therefore

Table 4. ^{13}C chemical shifts and substituent effects of isopropylpyrenes.[a]

	2	*3*	*4*	*6*	*7*	*8*
C-1	142.6(17.8)	123.1(–1.7)	124.2(–0.6)	142.4(17.6) (17.7)	142.4(17.6) (18.0)	141.9(17.1) (17.6)
C-2	122.5(–3.2)	146.7(21.0)	125.4(–0.3)	122.4(–3.3) (–3.4)	119.3(–6.4) (–6.5)	119.2(–6.5) (–6.6)
C-3	125.0(0.2)	123.1(–1.7)	120.8(–4.0)	124.6(–0.2) (–0.2)	142.4(17.6) (18.0)	142.1(17.3) (17.9)
C-4	127.4(0.2)	127.2(0.0)	143.5(16.3)	127.2(0.0) (–0.1)	122.7(–4.5) (–4.4)	121.8(–5.4) (–5.2)
C-5	127.0(–0.2)	127.2(0.0)	122.3(–4.9)	127.2(0.0) (–0.1)	126.2(–1.0) (–1.1)	121.6(–5.6) (–5.6)
C-6	124.4(–0.4)	124.7(–0.1)	124.7(–0.1)	124.6(–0.2) (–0.2)	124.3(–0.5) (–0.6)	141.9(17.1) (17.4)
C-7	125.6(–0.1)	125.3(–0.4)	125.7(0.0)	122.4(–3.3) (–3.4)	125.4(–0.3) (–0.3)	122.4(–3.3) (–3.5)
C-8	124.6(–0.2)	124.7(–0.1)	124.6(–0.2)	142.4(17.6) (17.7)	124.3(–0.5) (–0.6)	124.5(–0.3) (–0.4)
C-9	126.4(–0.8)	127.1(0.0)	127.0(–0.2)	121.8(–5.4) (–5.4)	126.2(–1.0) (–1.1)	126.4(–0.8) (–1.0)
C-10	122.7(–4.5)	127.2(0.0)	127.5(0.3)	121.8(–5.4) (–5.4)	122.7(–4.5) (–4.4)	122.2(–5.0) (–4.6)
C-3a	129.3(–1.7)	131.2(0.2)	130.1(–0.9)	129.1(–1.9) (–1.9)	126.1(–4.9) (–4.9)	–[b] (–4.5)
C-5a	130.7(–0.3)	130.8(–0.2)	131.6(0.6)	129.1(–2.0) (–2.0)	131.1(0.1) (0.1)	127.9(–3.2) (–3.1)
C-8a	131.4(0.4)	130.8(–0.2)	130.8(–0.2)	128.1(–2.9) (–2.9)	131.1(0.1) (0.1)	129.4(–1.6) (–1.6)
C-10a	127.8(–3.2)	131.2(0.2)	131.1(0.1)	128.1(–2.9) (–2.9)	126.1(–4.9) (–4.9)	126.0(–5.0)[b] (–5.2)
C-10b	–[b]	124.4(–0.2)	125.1(0.5)	–[b]	125.6(1.0)	
C-10c	–[b]	123.2(–1.4)	123.5(–1.1)	–[b]	125.4(0.8	
CH′	28.9(C-1′)	34.6(C-2′)	28.8(C-4′)	29.0(C-1′)	29.1(C-1′)	29.2[c] 29.1[c] 29.0[c]
CH_3′	23.9(C-1″)	24.5(C-2″)	23.3(C-4″)	23.9(C-1″)	24.0(C-1″)	24.0[c] 24.0[c] 23.9[c]

	10	*11*	*12*	*13*	*15*	*16*
C-1	141.4(16.6) (17.0)	141.8(17.0) (17.7)	141.5(16.7) (17.5)	122.4(–2.4) (–2.5)	140.3(15.5) (16.9)	141.6(16.8) (17.6)
C-2	122.1(3.6) (3.1)	119.1(–6.6) (–6.6)	118.9(–6.8) (–6.8)	145.7(20.0) (20.3)	118.9(–6.8) (–7.1)	118.8(–6.9) (–6.8)
C-3	119.8(–5.0) (–4.1)	141.6(16.8) (17.5)	141.5(16.7) (17.5)	118.6(–6.2) (–6.0)	143.2(18.4) (13.5)	141.6(16.8) (17.6)
C-4	142.5(15.2) (17.0)	116.9(–10.3) (–9.6)	121.5(–5.7) (–5.5)	143.0(15.8) (16.0)	142.7(15.5) (10.8)	118.3(–8.9) (–9.6)

Table 4. (continued)

	10	*11*	*12*	*13*	*15*	*16*
C-5	117.0(–10.2)	141.1(13.9)	121.5(–5.7)	122.4(–4.8)	120.9(–6.3)	141.0(13.8)
	(–9.5)	(15.3)	(–5.2)	(–4.9)	(–10.4)	(15.4)
C-6	141.4(16.6)	120.3(–4.5)	141.5(16.7)	122.4(–2.4)	140.9(16.1)	117.5(–7.3)
	(17.0)	(–4.3)	(17.5)	(–2.5)	(17.4)	(–6.8)
C-7	122.1(3.6)	122.2(–3.5)	118.9(–6.8)	145.7(20.0)	120.1(–5.6)	145.1(19.4)
	(3.1)	(–3.8)	(–6.8)	(20.3)	(–6.7)	(20.1)
C-8	119.8(–5.0)	141.4(16.6)	141.5(16.7)	118.6(–6.2)	140.8(16.0)	117.5(–7.3)
	(–4.1)	(16.7)	(17.5)	(–6.0)	(17.3)	(–6.8)
C-9	142.5(15.3)	121.6(–5.6)	121.5(–5.7)	143.0(15.8)	121.4(–5.8)	141.0(13.8)
	(17.0)	(–5.9)	(–5.5)	(16.0)	(–5.7)	(15.4)
C-10	117.0(–10.2)	121.9(–5.3)	121.5(–5.7)	122.4(–4.8)	121.5(–5.7)	118.3(–8.9)
	(–9.5)	(–5.0)	(–5.5)	(–4.9)	(–5.8)	(–9.6)
C-3a	128.5(–2.5)	126.4(–4.6)	126.1(–4.9)	129.7(–1.3)	125.7(–5.3)	125.4(–5.6)
	(–2.4)	(–4.6)	(–4.8)	(–1.2)	(–5.7)	(–4.7)
C-5a	127.7(–3.3)	128.3(–2.7)	126.1(–4.9)	131.5(0.5)	127.1(–3.9)	130.6(–0.4)
	(–2.9)	(–2.5)	(–4.8)	(0.6)	(–4.2)	(–0.6)
C-8a	128.5(–2.5)	128.3(–2.7)	126.1(–4.9)	129.7(–1.3)	126.1(–4.9)	130.6(–0.4)
	(–2.4)	(–3.1)	(–4.8)	(–1.2)	(–5.0)	(–0.6)
C-10a	127.7(–3.3)	126.2(–4.8)	126.1(–4.9)	131.5(0.5)	126.1(–4.9)	125.4(–5.6)
	(–2.9)	(–4.7)	(–4.8)	(0.6)	(–4.8)	(–4.7)
C-10b	–[b]	–[b]	126.4(1.8)	122.7(–1.9)	127.8(3.2)	–[b]
C-10c	–[b]	–[b]	126.4(1.8)	122.7(–1.9)	125.1(0.5)[b]	–[b]
CH′	28.9(C-1′)	29.2[c]	29.1(C-1′)	34.9(C-2′)	32.1(C-3′)[d]	29.1(C-1′)
	28.9(C-4′)	29.0[c]		28.7(C-4′)	32.0(C-4′)[d]	29.1(C-5′)
		28.9[c]		34.9(C-7′)	29.3[c]	35.1(C-7′)
		28.8[c]			29.1[c]	
					28.9[c]	
CH_3′	23.8(C-1″)	24.0[c]	24.0(C-1″)	24.6(C-2″)	25.6(C-3″)[e]	24.0(C-1″)
	23.5(C-4″)	23.9[c]		23.5(C-4″)	25.5(C-4″)[e]	23.4(C-5″)
		23.9[c]		24.6(C-7″)	24.0[c]	24.7(C-7″)
		23.4[c]			23.9[c]	
					23.9[c]	

[a]In ppm. Substituent effects (in parentheses): The top value is observed, the bottom value calculated from the effects observed for the monoisopropylpyrenes on the assumption of additivity. A negative value means shift to high field. Pyrene resonances used: C-1, 124.8; C-2, 125.7; C-4, 127.2; C-3a, 131.0; C-10b, 124.6 (measured in this work).[b]Not unambiguously identified. [c]Not assigned. [d]Possibly to be interchanged. [e]Possibly to be interchanged. [f]The isopropyl carbon in question is shown behind the chemical shift value. C-1′ and C-1″ mean, respectively, the methine carbon and the methyl carbon of an isopropyl group at C-1 in pyrene, and correspondingly for other isopropyl groups.

clues to the preferred rotamer distribution of the isopropyl groups in the polyisopropylpyrenes.

The difference between proton shifts in $CDCl_3$ and in CS_2 was nearly constant because both solvents interact uniformly with the aromatic protons. C_6D_6 created a more varied picture as seen from the following selected values for the difference ΔH-i (in ppm) = δ (in C_6D_6) – δ (in CS_2): *1*

(ΔH-1 = ΔH-2 = ΔH-4 = −0.07), *3* (ΔH-1 = −0.03, ΔH-6 = ΔH-7 = −0.07, ΔH-5 = 0.06, ΔCH = −1.3, ΔCH_3 = −0.1), *12* (ΔH-2 = 0.23, ΔH-4 = 0.13, ΔCH = 0.01, ΔCH_3 = 0.02), *15* (ΔH-2 = 0.27, ΔH-5 = 0.32, ΔH-7 = 0.26, ΔH-9 = 0.14), *16* (ΔH-2 = 0.23, Δ-4 = 0.27, ΔH-6 = 0.21, ΔCH-1 = 0.04, ΔCH-5 = 0.09, ΔCH-7 = −0.04, ΔCH_3-1 = 0.03, ΔCH_3-5 = 0.03, ΔCH_3-7 = 0.01).

The protons in *1* and the unperturbed aromatic protons in *3* resonated at lower frequency in C_6D_6 than in CS_2, but the solvent-induced shifts were small because of a similar effect at the TMS protons. The aromatic protons of *12, 15* and *16* resonated at higher frequency in C_6D_6 than in CS_2 because the substituents prevent the approach of the solvent molecules to the ring protons.

The effect at the methine protons depends on the rotamer distribution. The methine proton of *3* and that of the isopropyl group at C-7 of *16* resonate at higher frequency in CS_2 than in C_6D_6, whereas in *12* and for the α and αβ isopropyl groups in *16,* the effect was in the opposite direction. For the methyl groups, which were exposed to solvent to the same extent as TMS, the effect was in all cases small. These findings indicate again that the methine proton of the β isopropyl groups, on the average, spent much of its time outside the aromatic ring plane exposed to the solvent.

^{13}C NMR spectra. The assignment of the simple isopropylpyrenes is based on a comparison within a series of compounds with substituents in similar positions. The internal consistency is further checked by a comparison of predicted with observed substituent effects as given in Table 4. Additivity is an assumption for these assignments and is fully confirmed e.g. in *12* that is well suited because of symmetry.

The isopropyl group interacts only weakly with the pyrene nucleus, as seen from the UV spectra, and is mainly felt at the carbons of the substituted ring and the one *peri* to the substituent position. The low range effects are very similar to those observed in fluoropyrenes.[23] The effects observed for the substituted ring vary considerably for α, β and αβ substitution. This variation depends on bond orders of pyrene and also on the averaged conformation of the isopropyl group. The effects observed for the *o* carbons as well as the chemical shifts of the methyl and methine carbons support the suggestion that the isopropyl group in α- or αβ-position, on the average, points the methine proton towards the *peri* position. The additivity is less pronounced for a number of substituted carbons, and also on the whole, for *10, 11, 15* and *16.* For *15,* it is clearly a consequence of the strong steric interaction between the isopropyl groups in positions 3 and 4, which forces these groups to take up an orientation different from that in the monoisopropylpyrenes. for *10, 11* and *16,* it may be a result of a buttressing effect comprising an αβ-proton and two isopropyl groups, one in the other αβ-position *ortho* to the proton, the other *peri* to the proton; *10, 11* and *16* all have this disposition in common. Such a buttressing effect is evidenced by the increased value of ^3J(H-αβ, H-αβ) in *12,* which may be seen as the effect of an α isopropyl group pushing the *peri* proton towards its adjacent proton in *12.* No appreciable deviation from additivity is observed for *13,* in which the isopropyl group in the 4 position no doubt pushes the 3 proton; but the 2-isopropyl group apparently interacts less because of its different rotamer distribution.

UV spectra. The three strong main bands in the UV spectrum of pyrene are designated β' (241.3 nm), β (273.3 nm), and *p* (para) (325.4 nm) according to Clar.[20] These bands show different behaviour towards substitution (see Experimental). The shift of the β-band is small and practically independent of the position of the substituent. The β'-band is most strongly displaced by substitution in the β-positions* (2 and 7), while the *p*-band is affected strongly by substitution in α-positions but not in β-positions. The displacements show reasonably good additivity for di- and tri- substituted pyrene compounds and may be helpful in structural assignments of unknowns.

The *p*-band is due primarily to a transition from the HOMO to the LUMO, while the β'-band is primarily a transition from the next higher occupied to the next lower unoccupied MO. Using the equation given by Longuet-Higgins and Sowden[24] and taking configurational interaction into account, the substituent effects can thereby be predicted reasonably well. It can thus

*There is no connection between the band designations by Clar[20] and those for the different positions by Martin.[17]

be expected that the trends observed for isopropyl groups will also be valid for other alkyl-substituted pyrenes. A comparison of different alkyl substituents shows that their contributions vary as follows: cyclopentyl > cyclohexyl > isopropyl > *t* butyl in analogy with the corresponding benzenes.[25] The observed displacements reflect primarily the hyperconjugative interaction with the substituent.[24] Hence, the effects depend on the conformation of the isopropyl group. A strong deviation from additivity was noticed for *15* in the case of the β band. The strong interaction between the two isopropyl groups in positions 3 and 4 may explain this.

IR spectra have proven a very powerful means of identifying the substitution patterns of pyrene derivatives as shown in a recent paper.[26] From the IR spectra (900–600 cm^{-1}) of a great number of mono-, di-, tri- and tetra-substituted pyrenes of known structures, a set of rules has been formulated that connects substitution pattern with the IR spectrum. These results allow information about other tetra- and penta-substituted pyrenes to be drawn from the IR spectra. As a simple example, the structure *16* assigned to a pentaisopropylpyrene and analogously to a pentacyclopentylpyrene is supported by their IR spectra which, in the range cited above, only display bands due to isolated hydrogen atoms.

Mass Spectra. All the mono and polyisopropylpyrenes exhibit intense molecular peaks (base peak in most cases) and M-15 peaks (loss of CH_3; base peak for *8*). The M-15 peak is in all cases confirmed by a corresponding metastable peak. The monoisopropylpyrenes all exhibit a peak at M-29, which may be interpreted as corresponding to $M - 2CH_3 + H$, representing a condensed tropylium ion structure, and the occurrence of a peak corresponding to a further loss of C_2H_2 supports this conclusion. Most other peaks are weak, for instance, peaks corresponding to loss of an isopropyl group. An isopropyl group is split off much easier from an alicyclic than from an aromatic position, as seen from the intense peaks at *m/z* 203 (M-43, *m** 167.5) and 202 (pyrene) in the mass spectrum of *17*.

In the spectra of the polycyclohexyl and polycyclopentylpyrenes, the molecular peak is the base peak in all instances and very much stronger than most of the other peaks. The fragmentation patterns are dominated by the elimination of one or more cycloalkyl group or of a $(CH_2)_x$ group, in the latter case, leaving a fragment ion that may stabilize itself as a condensed tropylium ion structure.

Experimental

Materials. Pyrene (*1*) and 1,2,3,6,7,8-hexahydropyrene (*21*) were commercial products (Rütgerswerke). They were purified by column chromatography and recrystallization. Additional *21*, produced in this work, was also used. The following starting compounds (for catalytic hydrogenation) were prepared as previously described: 4,5-dihydropyrene (*19*),[27] 4,5,9,10-tetrahydropyrene (*20*),[27] 1-isopropenylpyrene[28] (precursor of *2*), 2-isopropylpyrene (*3*) (this work), 4-isopropylpyrene (*4*) (this work), 1,3,6,8-tetraisopropylpyrene (*12*),[1,2] 2,7-di-*t*-butylpyrene (D*t*B-*1*),[1,2] 2,7-di-*t*-butyl-4,5-dihydropyrene (D*t*B-*19*),[27,29] and 2,7-di-*t*-butyl-4,5,9,10-tetrahydropyrene (D*t*B-*20*).[27,29]

Spectroscopy. The different types of spectra were recorded on the following instruments. MS: Micromass MM 7070 (IP 70 eV). ^1H NMR: Varian A-60 or Varian CFT-20. ^{13}C NMR: ^{13}C spectra were recorded in $CDCl_3$ using TMS as internal reference on a Bruker HX 270 instrument. Spectral width was 17857 Hz and 64 K memory was used giving a digital resolution of 0.008 ppm/point. Temperature was 303 K. Concentrations ranged from 130 to 6 mg per 3 ml. UV: Bausch and Lomb, Spectronic 505. IR: Beckman IR-18A or Perkin-Elmer Infracord.

Friedel-Crafts isopropylation of pyrene. To a solution of pyrene (10.1 g, 0.05 mol) in isopropyl bromide (250 ml, freshly distilled) were added 3.3 g (0.12 mol) of crushed freshly distilled $AlBr_3$. The solution was stirred and heated to reflux. After 1.25 h and 3.5 h, a quarter of the initial volume was removed and worked up. The remaining half was worked up after 48 h. Separation followed by combined use of column chromatography (silica gel with 10 % caffeine[30] admixed; solvent, light petroleum) and preparative TLC (same adsorbent and eluent). Yields are shown in Table 1.

Cathodic isopropylation of pyrene was performed using the alkylation procedure previously de-

scribed.[6] Experimental conditions and yields of products are given in Table 2. Separation was effected as above; monitoring the products by MS and GLC (SE 30) followed. The product mixture from 1 g of pyrene (0.005 mol) was separated into 28 fractions, some of which were further divided by TLC and HPLC. The total yield of the isolated fractions was 1.16 g.

According to the mass spectral data obtained from a large number of fractions, the following isopropyl derivatives were detected. They are presented as follows: (order of appearance in the eluate) number of isopropyl groups – degree of hydrogenation (molecular weight):
(1) Hexa-hexa (460); (2) penta-hexa (418); (5) hexa-tetra (458); (3) penta-tetra (416); (4) tetra-tetra (374); (6) tri-tetra (332); (8) di-tetra (290); (7) penta-di (414); (10) tetra-di (372); (12) tri-di (330); (14) di-di (288); (15) mono-di (246); (9) hexa-nil (454); (11) penta-nil (412); (13) tetra-nil (370); (16) tri-nil (328); (17) di-nil (286); (18) mono-nil (244). The six last-mentioned all possess the fully aromatic pyrene nucleus. It is seen that the elution order, with only one exception (No. 5), is determined by the sum of hydrogens and alkyl substituents. In cases with equal sums, there is no clear picture.

The above series represents the minimum number of products since some may be mixtures of isomers. A number of compounds were fully characterized by GLC and NMR, showing that three diisopropylpyrenes (*5, 6, 7*), at least two triisopropylpyrenes (*8, 9*) and three tetraisopropylpyrenes (*10, 11, 12*) had been formed (Table 2 and Scheme 1). Spectroscopic evidence indicated that, besides the isolated compound *17,* a number of other hydrogenated products such as *18* occurred.

Catalytic hydrogenation. The aromatic hydrocarbon (0.01 mol) was dissolved in 200 ml of solvent (ethyl acetate or cyclohexane) and a measured amount of a slurry of Raney nickel (~3–3.5 g of metal) and ethanol added. The reaction was carried out at ambient temperature in a Parr low pressure hydrogenation apparatus at a hydrogen pressure of 2–3 atm. After the time scheduled (Table 3) filtration and evaporation gave a crude product that was analysed by ^{1}H NMR (Table 3). When cyclohexane was used, 5–10 g of molecular sieves (4 Å) were added to the solvent along with the catalyst and let stand for two days with occasional shaking. By this procedure, agglomeration of the catalyst was avoided. The substrate was then added without removing the molecular sieves.

The Raney nickel was a commercial ready-for-use product (Fluka *puriss.*) covered with water. For our purpose, the water was replaced by ethanol by repeated washings. The ethanol-covered material was stored in the refrigerator, and the activity frequently controlled by a standard procedure (hydrogenation of 100 mg of pyrene for 1 h following the procedure described). The activity began to decrease after storage for 3–6 months.

In an experiment scaled up to 10 g of pyrene (cyclohexane, 3 h) 3 g of 4,5,9,10-tetrahydropyrene (*20*) was easily separated by chromatography (silica gel, 10 % caffeine). Compound *20* has not been readily available before.

Survey of products. Data found in Tables 1–4 are not repeated here. Melting points are given only where a reasonably pure product was obtained; a number of compounds were only obtained in mixtures (see Tables). Chemical shift data from analysis of ^{1}H NMR spectra are presented here. For IR data see Ref. 26. Friedel-Crafts reaction is abbreviated as F-C and cathodic alkylation as C-A.

UV data. For each compound are cited: λ_{max} (log ε) $\Delta_{obs}/\Delta_{calc}$ for the β'-band, the β-band and the *para*-band in that order; Δ denotes the substituent effect; Δ_{calc} values (from *5* and onwards) are calculated on the assumption of additivity from the observed values for the monoisopropylpyrenes (*2, 3* and *4*); λ_{max} and Δ are in nm.

1, 241.3 (4.9) –, 273.3 (4.7) –, 335.4 (4.7) –. *2,* 243.3 (4.8) 2.0, 275.9 (4.7) 2.6, 342.8 (4.6) 7.4. *3,* 245.7 (4.9) 4.4, 275.8 (4.6) 2.5, 337.1 (4.6) 1.7. *4,* 243.1 (4.8) 1.8, 275.8 (4.6) 2.5, 338.8 (4.5) 3.4. *5,* 245.1 (4.8) 3.9/4.1, 278.4 (4.7) 5.1/5.2, 348.7 (4.6) 13.3/14.8. *6,* 244.8 (4.8) 3.5/4.1, 278.3 (4.7) 5.0/5.2, 348.0 (4.6) 12.6/14.8. *7,* 245.4 (4.8) 4.1/4.1, 279.0 (4.7) 5.7/5.2, 349.9 (4.6) 14.5/14.8. *8,* 246.9 (4.7) 5.6/6.1, 281.5 (4.7) 8.2/7.8, 355.3 (4.6) 19.9/22.2. *12,* 248.4 (4.8) 7.1/8.2, 284.3 (4.8) 10.0/10.4, 360.8 (4.6) 25.4/29.6. *13,* 251.8 (5.0) 10.5/12.5, 282.1 (4.7) 8.9/10.1, 345.0 (4.6) 9.6/10.1. *15,* 252.1 (4.7) 10.8/10.0, 289.9 (4.7) 16.6/13.0, 367.6 (4.6) 32.2/32.9. *16,* 252.1 (4.9)

10.8/12.1, 287.7 (4.8) 14.4 (12.8), 358.5 (4.7) 23.1/23.2.

Pyrene (1). ^{1}H NMR (CS_2):[22] δ 7.92 (H-1), 7.80 (H-4), 7.76 (H-2).

2-(1-Pyrenyl)-propan-2-ol (dimethyl-1-pyrenyl carbinol). 1-Acetylpyrene[4] and methylmagnesium iodide in benzene/ether (1:1), reflux 1 h, hydrolysis with ice and ammonium chloride gave the carbinol in several portions; yield 85 %. The first portion had m.p. 103–104 °C, the following melted at 120–121 °C. Mixed m.p. of the two was 119–120 °C (sharp). When the first portion was recrystallized from benzene/ether (1:1), seeded with the high melting crystals, the m.p. changed to 120–121 °C. Anal. $C_{19}H_{16}O$: C, H.

2-(1-Pyrenyl)-propene (1-isopropenylpyrene). Shaking the above carbinol in ether with concentrated hydrochloric acid yielded the olefinic compound as light yellow crystals (yield 91 %); m.p. (ethanol) 61 °C (lit.[28] 60–61 °C). Purification on alumina raised the m.p. to 63–64 °C. Dry HCl in ether converted the carbinol into the chloride (m.p. 75 °C; found: Cl 12.3; calc. for $C_{19}H_{15}Cl$: Cl 12.8), which, when treated with sodium ethoxide in ethanol, besides the 1-isopropenylpyrene gave a dimerized product, 4-methyl-2,4-di(1-pyrenyl)-1-pentene, $C_{16}H_9C(CH_3)_2CH_2C(=CH_2)C_{16}H_9$; m.p. (acetic acid) 176–178 °C. Found: C 93.6, H 5.86; calc. for $C_{38}H_{38}$: C 94.16, H 5.84. This structure was supported by IR and the ^{1}H NMR spectrum. α-Methylstyrene and α-methyl-*p*-methylstyrene[31] dimerize analogously.

1-Isopropylpyrene (2). *a.* By F-C in 1,1,2,2-tetrachloroethane[1]; m.p. 80 °C. By repetition of this reaction with only 0.5 equivalent of isopropyl bromide, a nearly quantitative yield of an oily product was separated, which, according to ^{1}H NMR, GLC and MS, was for the major part monoisopropylpyrene. From this, a small amount of crystalline *2* (m.p. 73–74 °C), was obtained by chromatography. *b.* By catalytic hydrogenation of 1-isopropenylpyrene (*wet* Raney nickel; Fluka, water-covered) in ethyl acetate, H_2 pressure 2 atm., room temperature, 7 h). Separation by "dry column" chromatography[32] on alumina with cyclohexane as eluant. Yield 68 %, m.p. 77–78 °C; mixed m.p. with product in *a* without depression. *c.* By C-A of pyrene (Table 2). MS: *m/z* 244 (M). ^{1}H NM (CS_2/$CDCl_3$): δ 8.11/8.16 (H-10), 7.89/7.94 (H-6,8), 7.89/7.91 (H-3), 7.83/7.88 (H-9), 7.76/7.80 (H-2), 7.75/7.79 (H-4,5), 7.74/7.78 (H-7), 3.87/3.98 (CH), 1.41/1.43 (CH_3). H-2 and H-3 may be interchanged.

2-Acetyl-4,5,9,10-tetrahydropyrene. The crude product was prepared according to Bolton.[33] Chromatography on alumina (light petroleum with increasing amounts of benzene) yielded 2.23 g (62 %) of the ketone, m.p. 111–112 °C. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene converted the ketone to 2-acetylpyrene, m.p. 140 °C (lit.[33] 141–142 °C).

2-(4,5,9,10-Tetrahydropyren-2-yl)-propan-2-ol. 2-Acetyl-4,5,9,10-tetrahydropyrene and methylmagnesium iodide gave the carbinol, m.p. 96–98 °C, yield 65 %. IR and NMR supported the structure.

2-Isopropylpyrene (3). The above carbinol was treated in ether with conc. hydrochloric acid, and the crude olefin that formed was aromatized with DDQ. The olefinic double bond was then hydrogenated catalytically with Raney nickel. M.p. 81.8–82.2 °C. MS: *m/z* 244 (M). ^{1}H NMR (CS_2): δ 7.92 (H-6,8), 7.86 (H-1,3), 7.83 (H-4,5,9,10), 7.77 (H-7), 3.21 (CH), 1.42 (CH_3).

2-(1,2,3,6,7,8-Hexahydropyren-4-yl)-propan-2-ol. 4-Acetyl-1,2,3,6,7,8-hexahydropyrene[4] and methylmagnesium iodide were reacted according to Moyle and Ritchie.[34] In working up, however, the crude product was not treated with Girard's reagent but chromatographed on alumina using petroleum ether with increasing amounts of benzene (20–50 %) as eluant. The compounds eluted were, in order of appearance, 4-isopropenyl- and 4-acetyl-1,2,3,6,7,8-hexahydropyrene in small amounts, and the title carbinol (yield 50 %), m.p. 50.5–51 °C. Moyle and Ritchie[34] did not isolate the carbinol but converted it directly into *4* (see below) by heating it with 10 % palladium/charcoal.

4-Acetylpyrene. 4-Acetyl-1,2,3,6,7,8-hexahydropyrene was treated with chloranil in xylene under reflux to give 4-acetylpyrene in low yield (22 %), m.p. 131–132 °C. Found: C 88.06, H 4.88; calc. for $C_{18}H_{12}O$: C 88.50, H 4.95.

2-(1,2,3,6,7,8-Hexahydropyren-4-yl)-propene (4-isopropenylhexahydropyrene). The above carbinol was treated with conc. hydrochloric acid in ether to give the title olefin, yield 71 %, m.p. (petroleum ether) 71–72 °C. IR and ^{1}H NMR supported the structure. When the carbinol was treated in dry benzene with dry hydrogen bromide (anhydrous sodium sulfate present) the olefin and its dimer were formed in equal amounts (total yield 62 %). The dimer (m.p. 225–227 °C) was, according to IR, ^{1}H NMR and elemental

analysis a cyclopentene derivative. Anal. $C_{38}H_{40}$: C, H. With DDQ in boiling benzene, the corresponding compound fully aromatized in the two pyrene nuclei, was obtained, m.p. 267–268 °C.

4-Isopropyl-1,2,3,6,7,8-hexahydropyrene. The above olefin was hydrogenated over Raney nickel in ethyl acetate during 0.5 h (H_2 pressure 2 atm., room temperature) to give the title compound. Chromatography on alumina (dry column) gave 62 % yield, m.p. 81.5–82.2 °C.

4-Isopropylpyrene (4). 4-Isopropyl-1,2,3,6,7,8-hexahydropyrene was aromatized with DDQ in boiling benzene for 6 h. Yield 85 % of a 3:1 mixture of *4* and 4-isopropenylpyrene, which was converted into *4* by hydrogenation over Raney nickel. M.p. 66.5–67 °C (lit.[34] 69–70 °C). MS: *m/z* 244 (M). ^{1}H NMR (CS_2): δ 3.83 (CH), 1.53 (CH_3); the aromatic part of the spectrum was too complex to be analyzed at low field.

1,6-Diisopropylpyrene (5). *a.* By scrutinizing the isopropylpyrene fraction from the F-C mentioned above under the heading 1-isopropylpyrene (*2*), a small amount of *5* could be isolated. *b.* F-C in neat isopropyl bromide as performed in this work, see Table 1. *c.* By C-A, see Table 2. M.p. 226–229 °C. MS: *m/z* 286 (M). ^{1}H NMR ($CDCl_3$): δ 8.21 (H-5,10), 8.03 (H-3,8), 7.95 (H-4,9), 7.87 (H-2,7), 3.99 (CH), 1.46 (CH_3).

1,8-Diisopropylpyrene (6). *a.* By F-C in neat isopropyl bromide (Table 1). *b.* By C-A of pyrene (Table 2). ^{1}H NMR ($CDCl_3$): δ 8.32 (H-9,10), 8.03 (H-3,6), 7.88 (H-2,7), 7.86 (H-4,5), 4.02 (CH), 1.48 (CH_3).

1,3-Diisopropylpyrene (7). *a.* By F-C in neat isopropyl bromide (Table 1). *b.* By C-A of pyrene (Table 2). ^{1}H NMR (CS_2/$CDCl_3$): δ 8.17/8.26 (H-4,10), 7.93/– (H-6,8), 7.85/7.92 (H-2), 7.85/7.94 (H-5,9), 7.78/– (H-7), 3.97/4.03 (CH), 1.48/1.50 (CH_3).

1,3,6-Triisopropylpyrene (8). *a.* By F-C in neat isopropyl bromide (Table 1). *b.* By C-A of pyrene (Table 2). M.p. 157–159 °C. MS: *m/z* 328 (M). ^{1}H NMR ($CDCl_3$): δ 8.35 (H-4,5), 8.26 (H-10), 8.08 (?) (H-8), 7.96 (H-2), 7.96 (H-9), 7.92 (H-7), ca. 4.09 (CH), ca. 1.55 (CH_3).

1,4,8-Triisopropylpyrene (9). By C-A of pyrene (Table 2). ^{1}H NMR ($CDCl_3$): δ 8.30 (H-9,10), 8.30 (H-3), 8.00 (H-6), 7.90 (H-2), 7.84 (H-7), 7.77 (H-5), ca. 3.90 (CH), 1.50 (CH_3), 1.42 (CH_3).

1,4,6,9-Tetraisopropylpyrene (10). By C-A of pyrene (Table 2). ^{1}H NMR (CS_2): δ 8.23 (H-3,8), 8.13 (H-5,10), 7.87 (H-2,7), 4.02 (CH-4,9), 3.87 (CH-1,6), 1.55 (CH_3-4,9), 1.51 (CH_3-1,6).

1,3,5,8-Tetraisopropylpyrene (11). *a.* By F-C (Table 1). *b.* By C-A of pyrene (Table 2). MS: *m/z* 370 (M). ^{1}H NMR (CS_2): δ 8.28 (H-6), 8.26 (H-9,10), 8.15 (H-4), 7.87 (H-7), 7.86 (H-2), ca. 3.95 (CH), 1.55 (CH_3-1,3), 1.51 (CH_3-8), 1.48 (CH_3-5).

1,3,6,8-Tetraisopropylpyrene (12). *a.* By F-C (Table 1); m.p. 302 °C (lit.[1] 311–312 °C, corr.). MS: *m/z* 370 (M). *b.* By C-A of pyrene. ^{1}H NMR (CS_2/$CDCl_3$[2]): δ 8.18/8.33 (H-4,5,9,10), 7.81/7.97 (H-2,7), 3.99/4.09 (CH), 1.51/153 (CH_3).

2,4,7,9-Tetraisopropylpyrene (13). By F-C (Table 1). ^{1}H NMR (CS_2): δ 8.11 (H-3,8), 7.89 (H-1,6), 7.83 (H-5,10), 3.88 (CH-4,9), 3.29 (CH-2,7), 1.55 (CH_3-4,9), 1.47 (CH_3-2,7).

2,4,7,10-Tetraisopropylpyrene (14). By F-C (Table 1). ^{1}H NMR (CS_2): δ 8.19 (H-1,3), 7.83 (H-5,9), 7.83 (H-6,8), 3.88 (CH-4,10), 3,29 (CH-2,7), 1.55 (CH_3-4,10), 1.50 (CH_3-2,7).

1,3,4,6,8-Pentaisopropylpyrene (15). By F-C (Table 1). Anal. $C_{31}H_{40}$: C, H. ^{1}H NMR (CS_2): δ 8.14 (H-9), 8.14 (H-10), 8.10 (H-5), 7.82 (H-7), 7.75 (H-2), ca. 3.93 (CH), 1.506 (CH_3-4), 1.500 (CH_3-3), 1.495 (CH_3-1), 1.463 (CH_3-6), 1.446 (CH_3-8). H-2 and H-7 may be interchanged.

1,3,5,7,9-Pentaisopropylpyrene (16). By F-C (Table 1). M.p. 185.5–186.5 °C (lit.[1] 189–190 °C, corr.). MS: *m/z* 412 (M). ^{1}H NMR (CS_2/$CDCl_3$): δ 8.19/8.42 (H-6,8), 8.16/8.40 (H-4,10), 7.82/8.05 (H-2), 4.08/– (CH-1,3), 3.94/– (CH-5,9), 3.39/– (CH-7), 1.58/– (CH_3-5,7), 1.53/– (CH_3-1,3), 1.52/– (CH_3-7).

1,3,5,8-Tetracyclohexylpyrene (cf. 11) (tetracyclohexylpyrene II in Ref. 1). M.p. 239–240 °C (corr.). MS: *m/z* 530 (M). ^{13}C NMR ($CDCl_3$): δ 139.80 (C-1), 139.70 (C-3), 139.46 (C-8), 139.16 (C-5), 127.39 (C-5a), 127.15 (C-8a), 125.60 (C-10b or C-10c), 125.21 (C-3a), 124.56 (C-10a), 123.76 (C-10c or C-10b), 121.39 (C-7). 121.08 (C-9), 120.48 (C-10), 119.29 (C-6), 118.95 (C-2), 116.36 (C-4), 39.17 (CH), 38.94 (CH), 38.74 (CH), 33.52 (–), 33.17 (–), 32.89 (–), 26.87 (–), 26.37 (–), 25.65 (–), 25.52 (–).

1,3,6,8-Tetracyclohexylpyrene[1] (cf. 12) (tetracyclohexylpyrene I in Ref. 1). M.p. 369–370 °C (corr.). MS: *m/z* 530 (M).

1,3,6,8-Tetracyclopentylpyrene[1] (cf. 12) (tetracyclopentylpyrene I in Ref. 1). M.p 295 °C (corr.). MS: *m/z* 474 (M). ^{13}C NMR ($CDCl_3$): δ 138.91 (C-1,3,6,8), 127.00 (C-3a,5a,8a,10a),

121.88 (C-4,5,9,10), 120.13 (C-2,7), 41.72 (C-1′,3′,6′,8′), 34.77 (C-1″,3″,6″,8″), 25.62 (C-1‴,3‴,6‴,8‴).

2,4,7,9-Tetracyclopentylpyrene[1] *(cf. 13)* (tetracyclopentylpyrene II in Ref. 1). M.p. 203–204 °C (corr.). MS: *m/z* 474 (M). ^{13}C NMR ($CDCl_3$): δ 143.21 (C-2,7), 140.47 (C-4,9), 131.24 (C-5a,10a), 130.44 (C-3a,8a), 122.99 (C-5,10), 122.64 (C-10b or 10c), 122.46 (C-1,6), 119.92 (C-3,8), 46.68 (C-2′,7′), 41.31 (C-4′,9′), 35.27 (C-2″,7″), 33.17 (C-4″,9″), 25.67 (C-2‴,7‴), 25.37 (C-4‴,9‴).

1,3,5,7,9-Pentacyclopentylpyrene[1] (cf. 16) (pentacyclopentylpyrene in Ref. 1). M.p. 246 °C (corr.). ^{13}C NMR ($CDCl_3$): δ 142.56 (C-7), 138.77 (C-1,3), 138.33 (C-5,9), 131.22 (C-5a,8a), 126.21 (C-3a,10a), 120.09 (C-2), 119.65 (C-4,10), 118.22 (C-6,8), 46.95 (C-7′), 41.93 (C-1′,3′), 41.78 (C-5′,9′). 35.37 (C-7″), 34.33 (C-1″,3″). 33.25 (C-5″,9″), 25.69 (–), 25.29 (–).

4-Isopropyl-4,5-dihydropyrene (17). By C-A of pyrene (Table 2). According to MS and NMR, the product contained small amounts of di and probably triisopropyl-4,5-dihydropyrene. MS: *m/z* 246 (M). ^1H NMR ($CDCl_3$): δ 7.85–7.35 and 7.74 (m+s, 8H), 3.60–3.25 (m, 2H: ring-CH_2), 3.10–2.80 (m, 1H: ring-CH), 2.10 (centre of h (J = 6.7 Hz), 1H: isopr.-CH), 1.05, 0.97 and 0.81, 0.73 (6H, two d (J = 6.7 Hz) due to C-4 being asymmetric).

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