Infrared Spectra of Pyrene Derivatives. Relation to the Substitution Pattern

POUL ERIK HANSEN * and ARNE BERG

Department of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

The IR spectra of 137 pyrene derivatives counting twentyone different types of substitution patterns have been investigated and a set of empirical rules based on band positions and intensities have been formulated which allow most types of pyrene derivatives to be structurally assigned. The investigation of 1-, 1,3-, 1,6-, 1,8- and 1,3,6,8-substituted pyrenes has made a reassignment of the 680 cm^{-1} band to an A_u species possible.

Wiberley and Gonzales [1] investigated the IR spectra of a number of condensed aromatic ring systems in the frequency range $900-700$ cm^{-1} with the aim of correlating the positions of the bands with the substitution pattern in terms of numbers of adjacent hydrogen atoms, in analogy to the well-known rules for benzene derivatives.[2−4] A fairly good correlation was found for the acene and the phene series. However, no conclusive results were reached for pyrene, which is a *peri*-condensed hydrocarbon.

Having access to a broad variety of substituted pyrenes we undertook an examination of their IR spectra by inspection of the frequency range $900-600$ cm^{-1} in a search for empirical rules connecting substitution pattern and band positions. Band intensities have been roughly considered.

The following substitution patterns have been included (compare formula *1*). The number of derivatives of each kind is given in parentheses: 1- (47), 2- (22), 4- (16), 1,2- (2), 1,3- (2), 1,6- (6), 1,7- (5), 1,8- (5), 2,7- (5), 4,9- (2), 4,10- (2), 1,2,7- (3), 1,3,6- (1), 1,3,7- (2), 4,5,9- (3), 1,2,6,7- (1), 1,3,5,8- (2), 1,3,6,8- (7), 2,4,7,9- (1), 1,3,4,6,8- (1), 1,3,5,7,9- (2).

---

* Present address: Institute for Life Sciences and Chemistry, RUC, P.O. Box 260, DK-4000 Roskilde, Denmark.

A broad series of substituents is represented, and in polysubstitutes the substituents may be alike or different. The designations α, β and $\alpha\beta$ [5] have been used for the three sets of identical positions in pyrene.

1
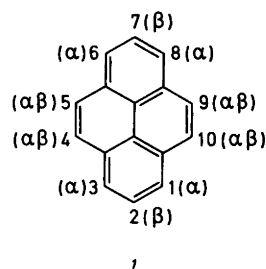
RESULTS

Band frequencies in the six absorption regions within which the great majority of the compounds absorb are tabulated in Table 1 with indications of band intensities. Explanatory details are found in the table. The short notations for the six band regions (see Table 1) will be used in the following.

As most of the compounds included (108) fall in the categories: 1-, 2-, 4-, 1,6-, 1,8-, 2,7- and 1,3,6,8-, the features of spectra of such derivatives and of that of pyrene will be briefly described.

A number of representative IR spectra (frequency range $900-600$ cm^{-1}) are shown in Fig. 1 (a−g).

Pyrene, Fig. 1a. The frequency range concerned is dominated by three intense bands: 841, 750 and 711 cm^{-1}. The last-mentioned band is found in the majority of pyrene derivatives. However, when the number of substituents gets large it may vanish.

1-Derivatives, Fig. 1b. The three pyrene bands remain as strong absorptions. Two new bands of

variable intensity have appeared. One, in the region 680, also appears in 1,6-substitutes (see below). It is generally of weak to medium intensity. The other one is in the 820 region.

2-Derivatives, Fig. 1c. Three strong bands of almost equal intensity in the regions 870, 840 and 820 constitute a conspicuous feature in the spectra of these compounds. The first band is connected with the existence of isolated hydrogens (H-1 and H-3). The 750 band is of medium intensity or weak and the 710 band is strong, while the 680 band is lacking.

4-Derivatives, Fig. 1d. The 870 region band also shows up in these spectra (isolated hydrogens, H-5) as a fairly strong band. The band in the 840 region is of medium intensity, but appears generally as very sharp. The band in the 820 region is strong in all cases.

It is thus obvious that the three monosubstituted types (1-, 2- and 4- or α,β and $\alpha\beta$) can be distinguished without difficulty.

1,6-Derivatives, Fig. 1e. The spectra of these compounds look like those of 1-substituted, except for the lack of absorption in the 750 region and the usually higher intensity in the 680 band.

1,8-Derivatives, not shown. It is generally not easy or even possible to obtain these compounds in as pure a condition as the sparingly soluble 1,6-isomers.[6,7] Their spectra resemble those of the latter compounds except for the lack of absorption in the 680 region that makes it easy to distinguish between the two types of derivatives, which almost without exception appear together when two substituents are directly introduced into pyrene.

2,7-Derivatives, Fig. 1f. These spectra are dominated by two intense and rather sharp bands in the regions 710 and 870, the latter band being related to the presence of four isolated hydrogens (H-1, H-3, H-6 and H-8). A weak band is present at low wave numbers in the 820 region. In the case of different substituents in the two β-positions two bands may arise in the 870 region.

1,3,6,8-Derivatives, Fig. 1g. The same regions are represented in these spectra as in those for the 2,7-derivatives. However, differences in band intensities make a differentiation possible. While in the 820 region the 2,7-derivatives show weak to medium absorption, strong bands are shown by the 1,3,6,8-derivatives. In the 710 region the behaviour is to the contrary.

From the above statements a set of empirical rules can be deduced that correlate the IR spectra of
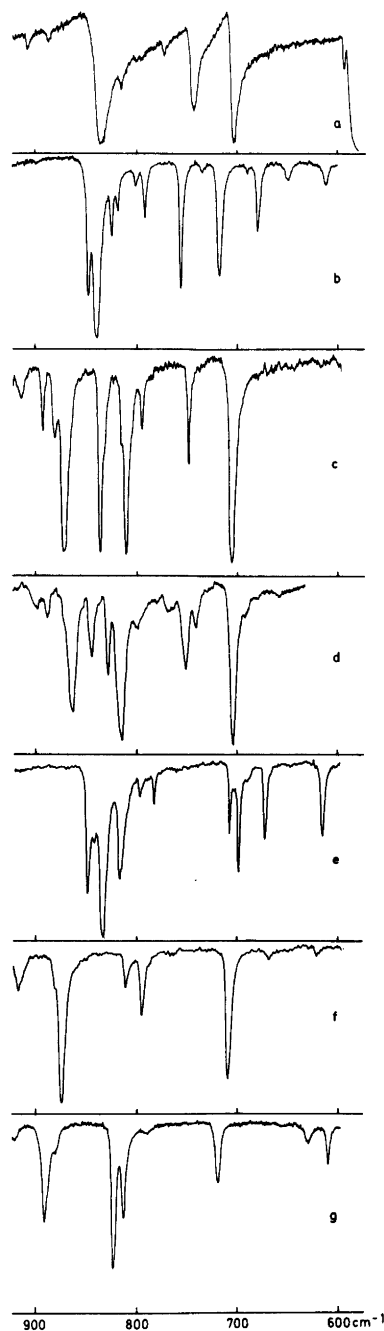

Fig. 1. Characteristic IR spectra of pyrene derivatives in the range $900-600$ cm^{-1}. (a) Pyrene. (b) 1-Pivaloylpyrene. (c) 2-*tert*-Butylpyrene. (d) 4-Bromopyrene. (e) 1,6-Dibromopyrene. (f) 2,7-Di-*tert*-butylpyrene. (g) 1,3,6,8-Tetraisopropylpyrene.

a majority of the known pyrene derivatives with their substitution patterns.

1. A band in the 680 region will indicate a substituent in an α-position (1-, 1,6-). The reverse statement is not generally valid (1,8-, 1,3,6,8-).

2. A medium or weak 710 band indicates two or more α-substituents. Otherwise this band is strong.

3. If no band appears in the 750 region, this suggests that the molecule is substituted in both ends (1,6-, 1,8-, 2,7- and 1,3,6,8-), but the statement is not generally valid (4,9-, 4,10-, 4,5,9- do not show any band in this region).

4. A strong band in the 820 region will suggest a single β- or αβ-substituent (2-, 4-). However, 1,3,6,8-derivatives absorb fairly strongly in this region.

5. The 840 region shows a strong band in 1-, 2-, 1,6- and 1,8-derivatives. In 4-derivatives, however, this band is normally weak to medium but very sharp and totally absent in 2,7-derivatives.

6. Strong to medium absorption in the 870 region indicates the presence of isolated hydrogens in the molecule (2-, 4-, 2,7-, 1,3,6,8-).

7. If this band in the 870 region is rather strong, β-substituents are indicated (two isolated hydrogens in the same end of the molecule: 2-, 2,7-).

DISCUSSION

By use of these rules most pyrene derivatives among the seven types mentioned can be identified with regard to the substitution pattern. However, it should also be possible to obtain information about other types. The amount of information may be insufficient as the number of substituents gets very large. A few examples will be given.

In the IR spectrum of Fig. 2a the weak absorption at 674 cm^{-1} indicates α-substitution: 1- or 1,6-. The absence of a band in the 750 region suggests that both ends are substituted, but not as 1,8- or 1,3,6,8- that will show no absorption at 674 cm^{-1}. The very strong band at 880 cm^{-1} indicates a β-substituent. This will lead to the suggestion that a 1,7-derivative has been pictured (1-bromo-7-t-butylpyrene).

In the IR spectrum of Fig. 2b the band at 674 cm^{-1} again indicates 1- or 1,6-substitution. An absorption band at 746 cm^{-1} rules out the latter possibility. Since this band is rather weak a 2- or 4-derivative is possible. The band at 842 cm^{-1} is stronger than would be expected for a 4-substituted derivative. A 1,2-derivative, therefore, is suggested (1-amino-pyrene-2-sulfonic acid).
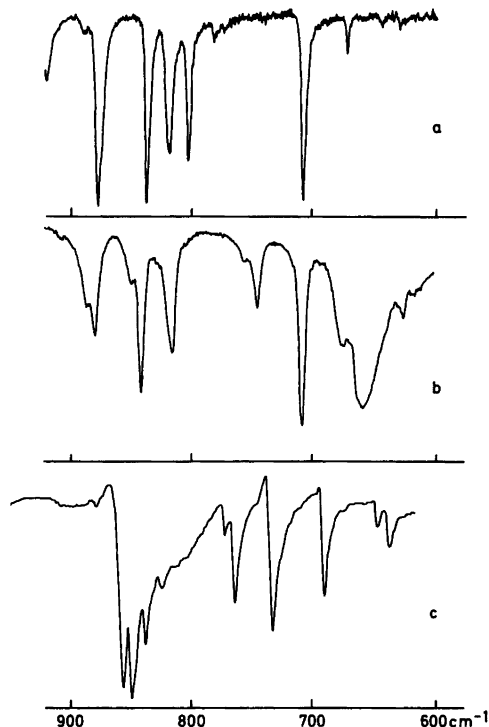
Fig. 2. IR spectra of pyrene derivatives in the range 900 – 600 cm^{-1}. (a) 1-Bromo-7-*tert*-butylpyrene. (b) 1-Amino-2-pyrenesulfonic acid. (c) 1,1'-Bipyrene.

The rules have been used to identify compounds containing more than one pyrene moiety. Compounds of this type are often difficult to identify by other spectroscopic methods such as ultra violet or NMR spectroscopy. 1,1'-Bipyrene,[8] Fig. 2c can serve as an example. It has not been possible by means of ^{1}H NMR spectra to establish whether the compound at hand was, as believed, a 1,1'-bipyrene or was a 1,2'-bipyrene. From the spectrum, it is seen that the absorptions fall clearly inside the ranges given for 1-substituted derivatives and thus leave no doubt about the structure.

The absorption bands are not always single peaks but very often split up into more peaks or display shoulders, *e.g.* the bands at 703 and 700 cm^{-1} in 2-bromo-7-*tert*-butylpyrene. Bands originating in the substituents may cause troubles. Only few compounds with aromatic substituents have been included, as their spectra usually are rather complicated. Bellamy[2] has given a number of substituents which absorb in the frequency range of

Table 1. IR-frequencies (cm^{-1}) of pyrene derivatives in the six absorption regions centred about 870, 840, 820, 750, 710 and 680 cm^{-1}, respectively.[a] The six regions are quoted in the text by these numbers. Intensities are given in the usual manner as very strong (vs), strong (s), medium (m), weak (w), and very weak (vw).

#	Substituents. Identity[d] and positions	'870'		'840'		'820'		'750'		'710'		'680'	
Limits:		910	850	850	830	830	797	765	740	730	695	682	670
1	1-F				838s	828vs	820m		750w		704s		673w
2	Cl				835vs		815m		750m		704s		674w
3	Br			840s	834vs		818s		751m		703s		675w
4	I			837m	829s	810w	805w		743w		698m		669vw
5	OH			838s	830vs	828vs	820m	762m	751m		708s		676w
6	OCH_3			846s	840vs	830vs	818m	765w	756w		712s		675w
7	$OCH_2CH=CH_2$[b]				837s	830s	815m		752w		709m		673w
8	$OCOCH_3$				835s	830s	812w		753w		700m		670vw
9	SCH_3[b]				838s		815m	758m			709s		675w
10	$SCOCH_3$[b]				833s		813w		747w		702m		678vw
11	SCN			848s	840s	820s			748m		707s		679m
12	SS-(1-Py)[b]				831vs		811m		744m		701s		672w
13	NH_2				837m	830m	816w		755w		710m		674w
14	NH_2,H_2SO_4				838vs		812w	762w			707s		677w
15	$NHCOCH_3$				836s		814w	752w	745w		707m	682vw	
16	$N(CH_2)_5$[b]			842vs	837vs	818w	812w		755s	723s			679m
17	NHCONH-(1-Py)				837vs		817m		753m		708s		675m
18	NHCSNH-(1-Py)				841s	829m	817m	758w		712m	701m	680w	
19	NCS				835vs	822m	810s	754m	745w	706m	702s		673w
20	NO_2				843s	825s			752w		702s		675vw
21	N=N(O)-(1-Py)				832vs	823m			747w	711m	702m	686w	
22	CH_3				840vs		813w		750w		709s		678w
23	C_2H_5				837vs		813w		752w		715m		675w
24	$CH(CH_3)_2$				838vs	823m	815m		756s		717s	680m	
25	$C(CH_3)=CH_2$				838vs	825m	817w		750s		717m		678m
26	C_4H_9				837vs	825m	815w		748s		711s		674w
27	$C(CH_3)_3$				838vs	820s	813w		748s	720m			677m
28	$CH_2C(CH_3)_3$			845s	840s	825s	816m		756m		704m		677w
29	$(1-C_{10}H_{15})$[b]			848vs	840vs	829m	815w		754w	723m		680w	
30	$(1-C_{16}H_9)$			848vs	838vs	828s	818m		755m	722s		680m	
31	CH_2OH			847s	840vs	823w	815w	749m	741w	706m	698w		675w
32	$CHOHCH_3$			850s		827w	817w	763w	750w	722m	708w	681w	
33	$COH(CH_3)_2$				841s	828m	819m	758w		721m		681m	
34	CHO				842m	822m			752m		708s	681w	
35	$COCH_3$			843s	840s	827w	814w		755m	718s			678w
36	$C(CH_3)=NOH$[b]			848s	838s	832s	815m		743s		700s		674w
37	COC_2H_5			849m	837m	825w		757w			715m		677vw
38	$COC(CH_3)_3$[b]			850s	841vs	826m	820w	758s		720s		682w	
39	$CO(CH_2)_4CH_3$[b]			853m	841s		818w		754m	727w	712s	681vw	
40	$CO(CH_2)_{10}CH_3$[b]				842vs		820w	762m			714s		678vw
41	$CO(1-C_{10}H_{15})$[b]			847vs	842s	831s	820w	758w	751m		717s		677m
42	$CO(1-C_{16}H_9)$			847s	838vs	831m	818w	757w		719w	705s	680w	
43	$COCH_2OOCCH_3$				840vs		820w	761s	743w		711s	681w	
44	COOH			843s	833s		815m	737m	732m		700s		673vw
45	COOAg				836vs		820w		747m		708s		677vw
46	$CSSNH_4$				837vs		812w		750w		707m		673vw
47	CN				838vs	823m			755w		709s		678m
48	2-F		858m		833m		812w		753w		698m		
49	Br	870m	853vs		836vs		810s		750m	704m	699vs		
50	I	872w	856s		833s	822w	806m		747w	717w	697s		

Table 1. Continued.

No.	Substituent											
51	OH	868w	854s		832m		810m		752w		698s	
52	$OCH_2CH=CH_2$ [b]	877w	852s	845s	837s	815w	810m	760w	755m		703s	
53	$OCOCH_3$	891m	852m		833m		812m		749w	702m	695m	
54	SO_3Na		875s		838vs		815s		743m	705vs		
55	NH_2		855vs		837s		813m		758w	705vs		
56	$N(CH_2)_5$ [b]		856s		846s		830s		743w		701vs	
57	NO_2 [b]		879m		835m		816m		737w		695s	
58	CH_3		861m		838m		812w		758vw	706m		
59	$CH(CH_3)_2$		872s		838m		813m		752w	709s		
60	$C(CH_3)_3$ [b]		872vs		837vs		812vs		750m	707vs		
61	$(1-C_{10}H_{15})$ [b]		872s		841s		819s		755vw	711vs		
62	$(1-(2-(2-Py)-Ad))$ [b]	880m	875vs		843vs	820m	810w		750vw	711vs		673vw
63	C_6H_5		876vs		837s		817s		749s	705vs	695s	
64	CH_2OH		871vs		833s		810s		748w		702s	
65	$COCH_3$	881m	874m	845m	839m		817m	762vw	752vw	704s		
66	$COOH$	893s	882w		837s		817vs	765w	743m	711m	700vs	
67	$COOAg$	900w	888w		832m		814s		740w	720w	697s	
68	$COOCH_3$	891m	884w		834m		813s	760w	743m	704m	698s	
69	CN	875s	863m		842s		823s	762m		706s		673vw
70	4-F [b]		857m		834m[c]		824s		760w	716s	709m	
71	Cl [b]	897vw	872s		837m[c]		825s		759m		713s	
72	Br [b]	890vw	866s	846w	831m[c]		818vs		754m		707vs	
73	I [b]	886w	867m	837w	828w[c]		814s	753w	748m		706s	
74	OCH_3	875w	854s	840s	832s		815m		753w	713m	705s	676vw
75	NH_2	886vw	849m		835m[c]		823m		765vw		714m	
76	$N(CH_2)_5$ [b]	860m	853m		837m[c]	828m	820s	761w	758w	720s		688w
77	NO_2		886w		835w		824vs	768w	750vw	710s	701m	
78	CH_3		868s		840w[c]		820s	770w	755m	715s		675vw
79	$CH(CH_3)_2$ [b]	895w	875vs	857w	842s[c]		823vs	769w	760m	720vs		690m
80	CH_2OH [b]		872s		836w[c]		818s		758w	722m	709s	692w
81	$COCH_3$ [b]	887m	873w		839m[c]		830s	770w	761w	717s		686w
82	$COOH$		887m		837s[c]		821vs		742w	730m	708vs	
83	$COOCH_3$		888w		842w[c]	832w	824s		744w	718m	712s	
84	$COOC_2H_5$		868vw		840s[c]		832vs	761vw	747w	717vs	703w	
85	CN	895m	885w		835w[c]		820vs		754w	712vs		672w
86	1,2-NH_2, SO_3H	887w	880m	850vw	842s		817m		746w		708vs	675m
87	$CH_2CH=CH_2$,OH [b]	857vs	853vs		833vs	817vs	808m	752w	747m	708w	702m	678s
88	1,3-Br_2 [b]		863w	838w	834w		814m		749vw	702vw	696w	
89	$(CH(CH_3)_2)_2$ [b]		893w	844w	836s		818w	762w	758w	722w		
90	1,6-Br_2			850s	834vs		818s			710w	701m	675m
91	Br, $NH(CH_2)_5$ [b]			849m	841s		812m			712m	696w	670s
92	$(NH(CH_2)_5)_2$ [b]				842vs	816m	807w			727w	719vw	677s
93	$(C(CH_3)_3)_2$				841m		806w			730vw	708vw	678w
94	$(OCOCH_3)_2$				850m	832w	817w			717w		681w
95	$(CN)_2$				852vs	827vw	809w			712w		681w
96	1,7-F, $C(CH_3)_3$ [b]		871s		830m	816w	801m			704m		(667vw)
97	Br, $C(CH_3)_3$ [b]		879vs		838vs	820m	804s			709vs		674vw
98	$(NH(CH_2)_5)_2$ [b]		865m	848vs	833s	823w	817m			718s		674m
99	$COC(CH_3)_3$,$C(CH_3)_3$ [b]		876s	847m	841m	809m	799w			718m		678w
100	CO(1-Ad),(1-Ad) [b]		870m		839m		815w			715m		675w
101	1,8-Br_2				840s	828m	815s				695m	
102	Br, $NH(CH_2)_5$ [b]				843vs	828s	817m			717m		
103	$(NH(CH_2)_5)_2$ [b]				832s		817w			723w		
104	$(NH_2)_2$				837m		818m			708m		
105	$(C(CH_3)_3)_2$				844s	825m	808w			730w		
106	2,7-Br, $C(CH_3)_3$ [b]	875vs	854vs				802w			703vs	700vs	

Table 1. Continued.

No.	Compound									
107	$(NH(CH_2)_5)_2$[b]	867vs	854s			819w			710s	
108	$(C(CH_3)_3)_2$		875vs			813w			711s	
109	$(C(CH_3)_2C_2H_5)_2$	897m	878vs			801m			716vs	
110	$(1\text{-}C_{10}H_{15})_2$[b]		876vs			817m			714vs	
111	$4,9\text{-}(CH_3)_2$	892m	869s						717vs	675w
112	$(C_2H_5)_2$	906s	881vs						721vs	677w
113	$4,10\text{-}(CH_3)_2$	879s	859w	839w					718s	
114	$(C_2H_5)_2$	884m	859w	840w					715m	
115	$1,2,7\text{-}F,(C(CH_3)_3)_2$[b]		877s			806w			729s	687w
116	$Cl,(C(CH_3)_3)_2$[b]		874s			801m			717s	678w
117	$Br,(C(CH_3)_3)_2$[b]		873s			798m			712s	677w
118	$1,3,6\text{-}Br_3$[b]		873w	838s	822m	810s			693m	
119	$1,3,7\text{-}Br_2,COOH$	900w	866m		815m	811s	763w		691m	
120	$Br_2,COOCH_3$	897w	863w		816m	809m	755w		693w	
121	$4,5,9\text{-}(CH_3)_3$	906w	869m	838vw					713s	
122	CH_3,C_2H_5,CH_3	900m	867s	843w				720s	715m	
123	$C_2H_5,(CH_3)_2$	906m	870m	840vw				716vs	708m	
124	$1,6,2,7\text{-}Br_2,t\text{-}Bu_2$		871s		813w	798m			717m	674w
125	$1,3,5,8\text{-}(CH(CH_3)_2)_4$[b]	891s	877s	840m	821vs	816s	743m			
126	$(CH(CH_2)_5)_4$[b]	892w	870m	841w	820s	813w	745w			
127	$1,3,6,8\text{-}D_4$		909m		827s	812w			715m	
128	Br_4		872s		811m	809s			(687w)	
129	$(SO_3Na)_4$		912w			813w			695m	
130	$(NO_2)_4$		873s			808s			712w	
131	$(CH(CH_3)_2)_4$		892m		824s	815m			721w	
132	$(CH(CH_2)_4)_4$[b]		887m			820m			717w	
133	$(CH(CH_2)_5)_4$[b]		870m		818m	805w			710w	
134	$2,4,7,9\text{-}(CH(CH_2)_4)_4$[b]	893s	872m							
135	$1,3,4,6,8\text{-}(CH(CH_3)_2)_5$[b]	890m	885w			818m				
136	$1,3,5,7,9\text{-}(CH(CH_3)_2)_5$[b]	883m	870s							
137	$(CH(CH_2)_4)_5$[b]	880m	869w							

[a] A great deal of the compounds exhibit more than one band in a particular region. When characteristic of the type of substitution pattern or when a choice is not reasonably made, they are shown in the table. Also shown are some irregular bands, which cannot be explained. A number of further bands, which cannot be disregarded on impurity grounds, are quoted below under the serial number of the compound. Also quoted here are some bands originating in the substituent. [b] Synthesis unpublished. See Ref. 9. [c] A very sharp band. [d] $Py=C_{16}H_9=$pyrenyl. $Ad=C_{10}H_{15}=$adamantyl. Bands not shown in the table: (1) 888m. (3) 709m (C−Br?). (4) 702w. (5) 893m. (8) 788vw. (13) 790vw. (14) 886s, 877s, 795vw, 697w. (15) 777vw, 670vw. (16) 863vw, 851vw, 795vw. (18) 856m. (20) 918w, 882m (C−NO$_2$), 798m, 730w, 692w. (23) 792w. (24) 690vw. (25) 892s. (28) 800m. (31) 720w (O−H def.?). (34) 784w (C−H def.?). (37) 787vw. (38) 795vw. (39) 770vw. (41) 797w, 789w. (42) 791w. (43) 782w. (44) 772w. (45) 793w. (46) 771w. (48) 850w. (49) 728w. (50) 793w. (52) 857s. (53) 798w. (54) 802w. (55) 903w. (56) 856 may partly be due to the piperidino group, 808w (piperidino?). (57) 790vw, 760vw, 724vw. (59) 897vw, 886vw, 800vw. (60) 894w, 882w. (63) 767w, 760w, 705vs or 695s may be due to phenyl. (65) 825w, 809w. (66) 792vw. (67) 779w, 771w. (68) 904w. (69) 904w, 813w. (70) 782w. (73) 798w. (74) 898vw. (76) 800w. (77) 908w, 797w. (79) 905vw. (81) 904w. (82) 903m, 782w, 701m. (83) 782vw. (84) 785m. (85) 915w. (90) 785w. (91) 856 (piperidino), 830vs, 826s. (92) 862m (piperidino). (93) Spectrum poorly resolved, bands very broad. (94) Like (93), 910m, 778w. (95) Like (93). (98) 859s (piperidino). (101−110) One or two weak bands between 794 and 761. Besides: (101) 692m, 849m (1,6-Br$_2$). (102) 862w (piperidino). (103)856w (piperidino). (111) 875m, 778s. (112) 814m, 766s. (113) 902w, 778s. (114) 898vw, 800w, 763w, 756w. (115) 827vw, 815w, 795w. (116) 824vw, 810w, 792w. (117) 821vw, 807w, 790w. (118) 802w. (119) 834w, 792w, 723vw, 703w (OH-def.). (120) 834vw, 789w, 723vw. (121) 898w, 888w, 783s. (122) 896w, 888w, 788s. (123) 899w, 889w, 786vs. (125) 714w. (126) 735vw (cyclohexane?). (127) 668vw. (128) 671m (C-Br?). (129) 737m. (130) 678m. (134) 737vw. (135) 898w, 837vw, 807vw. (136) 731vw, 672vw.

interest. We have noted that the piperidino ring system gives rise to an absorption in the range between 860 and 840 cm^{-1}. Similar absorptions have been observed in spectra of some substituted naphthalene derivatives such as 1,5-, 1,6- and 2,6-dipiperidino naphthalene.[9] In spite of the presence of these extra bands it is usually possible to analyze the spectra. In Fig. 1e the absorption band at 620 cm^{-1} is due to a carbon — bromine vibration and in Fig. 2b the band at 660 cm^{-1} originates from the sulfonic acid group.

The relatively narrow limits within which most of the bands are observed indicate, as has been found for other aromatic hydrocarbons,[2,4] that the influence of substituents on band positions are small. The band associated with isolated hydrogen seems to be the most sensitive in the 900 – 600 cm^{-1} range. It has been pointed out[2] that heavy substitution in benzene with strongly polar substituents (NO_2, SO_3H) can move the band out of the normal range towards higher frequencies. Sodium pyrene-1,3,6,8-tetrasulfonate and 1,3,6,8-tetranitropyrene both have weak absorptions about 910 cm^{-1}. Their spectra are, however, otherwise difficult to interpret.

The occurrence of a band in the 680 region seems to depend on the symmetry of the molecule. The spectrum of pyrene whether recorded in a solvent or in potassium bromide shows no absorption in this region, nor is the band observed in the Raman spectrum according to Mecke and Klee.[10] Only by irradiation of single crystals or polycrystalline films by polarized light has a weak absorption been observed,[10,11] which on account of the insensitivity of band positions to substitution reasonably is identified with the 680 region band of some pyrene derivatives.

A number of papers[10–13] have dealt with the assignment of the fundamental vibrations of pyrene. The assignments have been based on experimental techniques[10,11] or on a comparison of spectra with predictions made by forcefield calculations.[11,13] Substituted compounds have also been taken into account in the assignment of spectra of pyrene and naphthalene.[10,14]

The behaviour of the 680 region band that is absent in the spectra of pyrene, 1,3-, 1,8-, and 1,3,6,8-derivatives (point group D_{2h}, C_{2v}, C_{2v} and D_{2h}, respectively), but observed for 1- and 1,6-substituted pyrenes (point group C_s and C_{2h}) indicates that this band instead of being assigned a B_{2u} species[11] must be assigned an A_u species. This assignment is furthermore in good agreement with

calculations done by Bree et al.,[13] who predict a fundamental of A_u symmetry at 660 cm^{-1}.

EXPERIMENTAL

IR spectra (KBr) were recorded on a Beckman Infra Red Spectrometer, Model IR-18, and wave numbers were measured on linear expanded spectra (20 cm^{-1}/cm).

Some of the pyrene derivatives included were synthesized according to literature descriptions. The syntheses of the others[9] will be described at a later date.

REFERENCES

1. Wiberley, S. E. and Gonzales, R. D. *Appl. Spectrosc. 15* (1961) 174.
2. Bellamy, L. J. *Infra Red Spectra of Complex Molecules*, Wiley, New York 1958.
3. Katritzky, A. R. *Q. Rev. Chem. Soc. 13* (1959) 353.
4. Colthup, N. B., Daly, L. H. and Wiberley, S. E. *Introduction to Infra Red and Raman Spectroscopy*, Academic, New York 1964.
5. Martin, R. H. *Tetrahedron 20* (1964) 897.
6. Vollmann, H., Becker, H., Corell, M. and Streek, H. *Ann. 531* (1937) 1.
7. Grimshaw, J. and Trocha-Grimshaw, J. *J. Chem. Soc. Perkin Trans. 1* (1972) 1622.
8. Lund, H. and Berg, A. *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd. XXII* (1946) 10.
9. Berg, A., Lund, H., Hansen, P. E., Blaabjerg, O., Sørensen, N. E. and Johansen, S. R. *Unpublished results.*
10. Mecke, R. and Klee, W. E. *Z. Elektrochem. 65* (1961) 327.
11. Neto, N. and di Lauro, C. *Spectrochim. Acta Part A 26* (1970) 1175.
12. Califano, S. and Abbondanza, G. *J. Chem. Phys. 39* (1963) 1016.
13. Bree, A., Kydd, R. A., Misra, T. N. and Vilkos, V. V. B. *Spectrochim. Acta Part A 27* (1971) 2315.
14. Claverie, N. and Garrigou-Lagrange, C. *J. Chim. Phys. 61* (1964) 889.