

362. Fluorescence Spectra of Polycyclic Aromatic Hydrocarbons in Solution.

By (MISS) R. SCHOENTAL and E. J. Y. SCOTT.

The approximate mirror-image relation between the fluorescence spectrum of a compound and the bands of longest wave-length of its ultra-violet absorption spectrum, already observed in a number of cases, has been found to hold for a series of polycyclic aromatic hydrocarbons and some related compounds. In each case the fluorescence band of shortest wave-length was found to occupy approximately the same position as the longest absorption band. Regularities previously observed in the long-wave region of ultra-violet absorption spectra (cf. Braude, *Ann. Reports*, 1945, **42**, 105) have been found to apply to the fluorescence spectra of derivatives of polycyclic aromatic hydrocarbons.

Comparison of the fluorescence spectra of isomeric hydrocarbons, with different arrangements of the rings, has shown a correlation between the position of the spectrum and the number of quinonoid rings in the structure with the maximum number of Kekulé rings, *i.e.*, the structure which conforms to the Fries rule. Fluorescence spectra have been used in the elucidation of structure of derivatives of partly reduced polycyclic aromatic hydrocarbons.

FLUORESCENCE spectra have already been extensively used in the identification of polycyclic aromatic hydrocarbons and their derivatives, particularly in relation to biological problems (for references, see Berenblum and Schoental, *J.*, 1946, 1017). However, by comparison with ultra-violet absorption spectroscopy relatively little use has been made of the much simpler fluorescence spectroscopy, especially in regard to the relations between spectra and chemical constitution. Fluorescence is to some extent the reverse of absorption. It reflects energy changes which accompany the return of a π electron from the lowest vibrational level of the excited state to different vibrational levels of the ground state. Such a transition of a π electron which has remained in the excited state for about 10^{-8} second gives rise to a set of fluorescence bands. The constant spacing between them corresponds to the energy differences of the vibrational levels of the *ground* state, whereas the spacing of bands in the *absorption* spectra corresponds to the vibrational energy levels of the *excited* state (cf. Bowen, *Quart. Reviews*, 1947, **1**, 1).

Few quantitative measurements of the fluorescence spectra of aromatic compounds have been recorded hitherto. Of these, the spectrum of benzene has received most attention (*e.g.*, Henri, *J. Phys. Radium*, 1922, **3**, 181; Ingold and Wilson, *J.*, 1936, 941); it is very complicated, on account of the peculiar symmetry of this hydrocarbon. The reproductions of photographs of fluorescence spectra, recorded by small dispersion spectrographs, which have usually been published, are not suitable for accurate photometric examination. The degree of accuracy of fluorescence data depends on the sharpness of the bands. Not only is this a characteristic of some electronic transitions, but it is also associated with the state of "fluorescence purity" of the specimen. The criteria of purity for fluorescence spectrography are different from those for other purposes. Thus, small traces of strongly fluorescent impurity may completely vitiate the fluorescence spectrum of the compound, and care must be taken to exclude even weakly fluorescent impurity. On the other hand, contamination with non-fluorescent materials is usually of little importance. The fact that compounds of similar structure exhibit fluorescence spectra of similar pattern furnishes a useful guide to the reliability of the spectra. Thus, the persistence of a subsidiary set of bands in the spectra of a number of naphthofluorenes (Table I), prepared by different types of method, indicates that these bands are a characteristic feature of the spectra of hydrocarbons of this character.

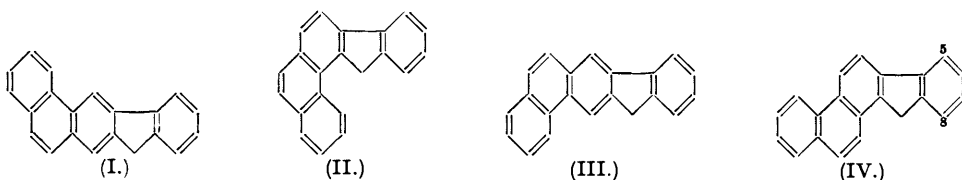
The specimens used in the present investigation were mostly samples which had been purified for elementary analysis, although some were submitted also to chromatography. The sharpness of the bands varied widely, however, and an accuracy of greater than ± 50 — 100 cm^{-1} is not claimed for the photometer readings. Data marked in the tables with an asterisk are regarded as falling below this standard. With some of the compounds examined it was not practicable to make quantitative intensity measurements, owing to low solubility or the minute amounts available. Very dilute solutions in light petroleum were employed. In a few cases the solubility in this solvent was too slight, and then benzene or liquid paraffin was used. The concentrations used were just sufficient to give the strongest bands of the fluorescence spectra, and, although some weaker bands may have been missed, this procedure avoided the risk of reabsorption due to overlap of fluorescence and absorption spectra with its attendant shift to the red of the first band (Sannié, *Biochem. J.*, 1936, **30**, 704; Bowen, *loc. cit.*). Precautions to exclude "oxygen

quenching" were not taken, as we were concerned mainly with the positions of the bands rather than their absolute intensities.

TABLE I.†

Compound.	Fluorescence maxima, $V' \times 10^{-2}$.		Absorption maximum of lowest wave-number, $V' \times 10^{-2}$.	Ref.	$(V'_a - V'_j) \times 10^{-2}$.
	(A.)	(B.)	(C.)		(D.)
Naphtho(2' : 1'-2 : 3)fluorene (I) ^a	276 262 248	269 254	—	—	—
Naphtho(1' : 2'-1 : 2)fluorene (II) ^a	275 261 247	269	—	—	—
Naphtho(1' : 2'-2 : 3)fluorene (III)	274 260 246	267 253	275.5	1	+1.0
Naphtho(2' : 1'-1 : 2)fluorene (IV)	273 259 245	266	274	4	+1.0
5-Methyl ,, ,, 	272.5 258.5 244.5	267 253	—	—	—
6-Methyl- ,, ,, 	272.0 258.0 244.5	265 251	—	—	—
7-Methyl- ,, ,, 	271.0 257.5 244.0	265 251	—	—	—
8-Methyl- ,, ,, 	272.5 258.5 244 *	265 251	—	—	—

^a For the synthesis of these compounds see Cook and Stephenson, this vol., p. 842.



The spectra examined ranged from 31,000 to 16,000 cm^{-1} . Although the positions of the fluorescence maxima are independent of the wave-length of the excited radiation, the intensity of fluorescence depends on the extinction coefficient and the intensity of the exciting radiation. The mercury line at 3650 Å . was used where possible, but in certain cases, indicated in the tables, it was necessary to use radiations of other wave-lengths for excitation.

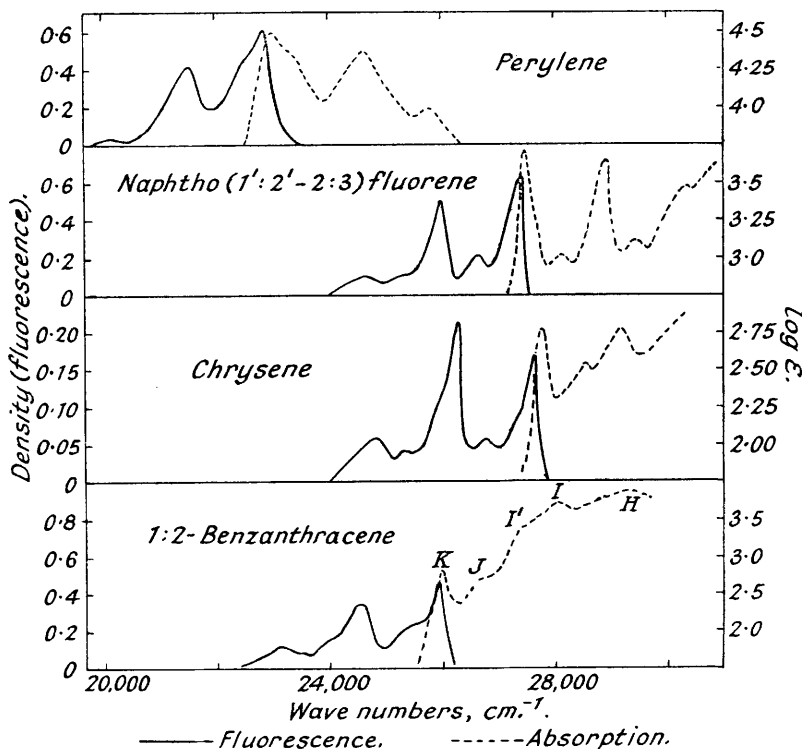
Discussion of Results.

(a) *General*.—As may be seen from Fig. 1 and Tables I to VII, the fluorescence spectra of polycyclic aromatic hydrocarbons in solution are relatively simple. They consist usually of one main set of 3—4 bands of diminishing intensity, equally spaced at about 1400 cm^{-1} and accompanied sometimes by a second interwoven set of equally-spaced, less intense, subsidiary bands. This second set of bands is associated usually with hydrocarbons containing angularly-condensed benzene rings. Thus, in the spectrum of anthracene, as in that of naphthacene, the maximum intensity almost coincides with the centre of the bands (slight duplication of the bands was observed in the anthracene spectrum by Sambursky and Wolfsohn, *Trans. Faraday Soc.*, 1940, **36**, 427, and Kortüm and Finkh, *Z. physikal. Chem.*, 1942, *B*, **52**, 263); but with 1 : 2-benzanthracene the subsidiary bands appear as inflections on the longer slopes of the main bands (Fig. 1), whereas in the cases of chrysene, 1 : 2 : 5 : 6-dibenzanthracene, and the naphthofluorenes they appear as distinct bands.

† For references and explanations of symbols used in Tables I—VI see p. 1696. For significance of asterisks see p. 1683.

Fig. 1 gives the fluorescence spectra of representative hydrocarbons, dissolved in light petroleum, together with their ultra-violet absorption bands of longest wave-length.* The absorption data, taken from the literature, were obtained usually in alcoholic solution. In general, the approximate mirror-image relation between the fluorescence and the absorption spectra (Lewschin, *Z. Physik*, 1931, 72, 368, 382) is quite striking. In some cases, e.g., with

FIG. 1.



Comparison of fluorescence spectra with the corresponding longest wave-length bands of the respective ultra-violet absorption spectra.

1:2-benzanthracene, this is somewhat obscured by the superposition in the absorption spectrum of additional bands which probably belong to another electronic transition. The absorption bands corresponding with the second and third fluorescence bands then appear only as inflexions. In cases of this kind comparison of the two spectra may assist in identifying the bands of the more complex absorption spectrum which are due to a particular electronic transition.

Tables II and III give the frequencies of the maxima of the fluorescence bands of a number of polycyclic aromatic hydrocarbons. The main system is given in column *A* and the subsidiary system in column *B*. For comparison, the frequency of the maximum of the longest absorption band, where it is known, is given in column *C*. Groups of isomeric hydrocarbons are tabulated together. The shortest fluorescence band is seen to coincide with the longest absorption band with a deviation not exceeding -300 cm.^{-1} (Tables II and III; column *D*). This deviation, although small, is probably greater than the limits of experimental error and greater even than the differences to be attributed to the use of different solvents for the two types of spectra (compare Seshan, *Trans. Faraday Soc.*, 1936, 32, 689, and Sambursky and Wolfsohn, *Phys. Review*, 1942, 62, 357).† Hausser, Kuhn, and Kuhn (*Z. physikal. Chem.*, 1935, B, 29, 417)

* In the figures and the tables wave-numbers are used, but for convenience reference is made in the text to wave-lengths. The expression "longest absorption band" is used to denote the ultra-violet absorption band of longest wave-length.

† The absence from the absorption spectrum of 1:2:6:7-dibenzpyrene of a band corresponding to the first fluorescence band may be due to the fact that absorption bands of lower intensity than $\log \epsilon = 2.5$ are not recorded for this compound.

TABLE II.

Compound.	Exciting radiation.	Fluorescence maxima, $\nu'' \times 10^{-2}$. (A.)	Absorption maximum of lowest wave-number, $\nu' \times 10^{-2}$. (C.)	Ref.	$(V'_a - V'_f) \times 10^{-2}$. (D.)	$\Delta V'_f \times 10^{-2}$. (E.)	Number of quinonoid rings. (Q.)	Number of Kekulé resonance structures. (K.)	Carcinogenicity.
Naphthalene (V)	2, ^a	310	313.5	2, 4	+3.5	—	0	3	—
		300	297 *						
		289 *	286 *						
		288	280						
Phenanthrene (VI)	2, ^a	274.5	289.9	2, 4	+1.9	—	0	5	—
		261 *	266						
		265	—						
Anthracene (VII)	3	250.5	267.8	3, 4	+2.8	23	1	4	—
		236.5							
		223 *							
		283 *							
		276.5							
Triphenylene (VIII)	2, ^a	262.5	285.5	2	+2.5	-6.5	0	9	—
		248							
		245.5							
		231							
Chrysene (IX)	2	266 *	278	2, 4	+1.5	—	0	8	—
		259.5							
1 : 2-Benzanthracene (X)	3	245.5	260	3, 4, 5	+0.5	17.0	1	7	—
		231							
		212							
Naphthacene (XI)	3	197.5	211 ^b	3	-1.0	64.5	2	5	—
		266 *							
3 : 4 : 5 : 6-Dibenzphenanthrene (XII)	2, ^a	266 *	—	—	—	-2	0	13	—
		264 ^b							
Picene (XIII)	3	250.5	266 ^c	4	+2.0	—	0	13	—
		237.0							
		255.5							
Naphtho(2' : 3'-1 : 2)phenanthrene (XIV)	3	253.5	254.5 ^b	2	-1.0	8.5	1	11	—
		253.5							
1 : 2 : 7 : 8-Dibenzanthracene (XV)	3	254.0	253 ^b	6	-0.5	10.5	1	12	±
		240.0							
1 : 2 : 5 : 6-Dibenzanthracene (XVI)	3	225.5	253.0	4, 7	-1.0	10.0	1	12	++
		246							

51 s	Naphtho(2' : 3' : 2 : 3)phen- anthrene (XVII)	3	222.0	—	221 ^b	2	-1.0	42.0	2	9	—
			208.0								
			194.0								
	Pentacene (XVIII)	54	173 * ¹	—	172.5 ^b	8	-0.5	91.0	3	6	—
	1 : 2 : 3 : 4 : 5 : 6-Tribenz- anthracene (XIX)	3	257.5 244 * 230 *	(263)	257.5 ^b	9	0.0	—	1	22	—
	Phenanthro(3' : 2' : 2 : 3)phen- anthrene (XX)	3	230 215 201	—	231	10	1.0	—	2	16	—

^a Subscript refers to exposure time in hours; 54 = 5461 Å.

For explanation of 2 and 3 see Experimental.

^b Solution in benzene.

^c Solution in chloroform.

^d Solution in liquid paraffin.

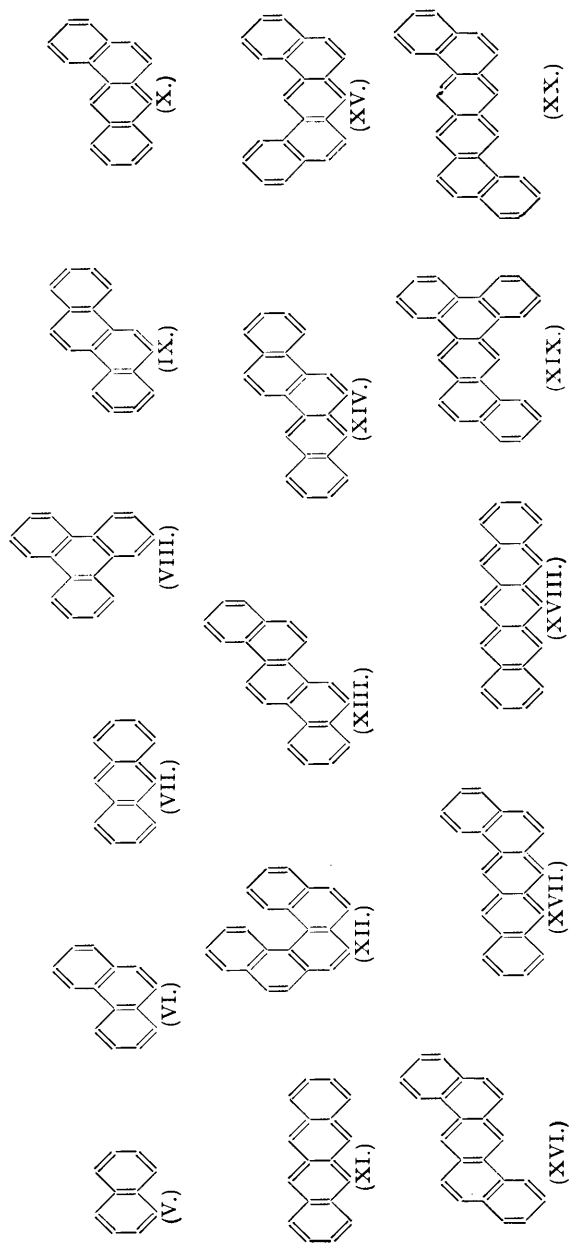
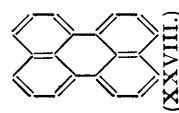
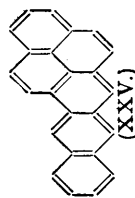
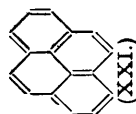
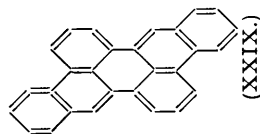
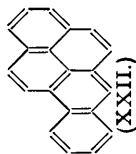
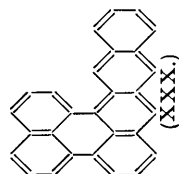
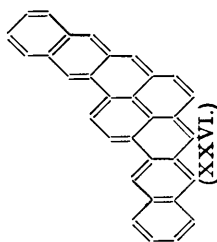
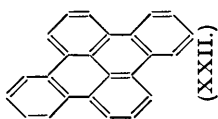
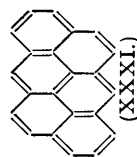
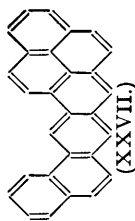
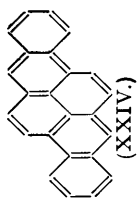


TABLE III.

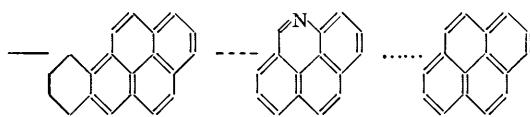
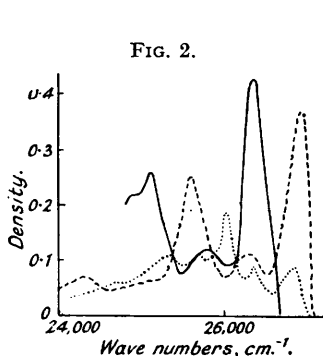
Compound.	Exciting radiation.	Fluorescence maxima, $V_f' \times 10^{-4}$, (A.)	Absorption maximum of lowest wave-number, $V_a' \times 10^{-4}$, (C.)	Ref. ($V_a' - V_f'$) $\times 10^{-4}$, (D.)	Number of Kekulé resonance structures, (K.)	Number of quinonoid rings, (Q.)	Carcinogenicity.
Pyrene (XXI)	2	268.5	269.5	1.0	6	1	—
		264					
		261					
		258					
		255*					
3:4-Benzpyrene (XXII)	3	248.0	248.0	0.0	9	1	+++
		234.0	245.0				
		220.5	232.0				
		229	241.0				
1:2:6:7-Dibenzpyrene (XXIII)	3	253.0	(261.5) ^b	—	20	1	—
		239.0					
		225.5					
3:4:8:9-Dibenzpyrene (XXIV)	3	223.0	221.5 ^b	-1.5	13	2	+++
		209.5					
Naphtho(2':3'-3:4)pyrene (XXV)	3	219	218.5 ^b	-0.5	12	2	—
		205					
		191					
Dinaphtho(2':3'-3:4)(2'':3''-9:10)pyrene (XXVI)	3	194	187	—	26	3	—
		180					
		167					
Phenanthro(9':2'-3:4)pyrene (XXVII)	3	229.5	—	—	21	2	—
		214.5					
		200*					
		215	230	1.5	9	1	—
Perylene (XXVIII)	3	238.5	230	1.5	9	1	—
		215					
		201					
2:3:8:9-Dibenzperylene (XXIX)	3	231	230.5 ^b	-0.5	25	1	—
		217					
		163*†					
Naphtho(2':3'-1:2)perylene (XXX)	57 ^a	232.5	231 ^b	-1.5	15	3	—
		219	229		10	2	—
Anthanthrene (XXXI)	3						

^b Solution in benzene.[†] Solution in liquid paraffin.^a Exciting radiation, 5770 Å.

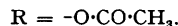
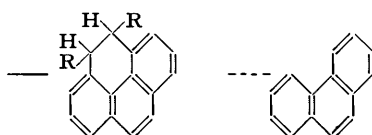
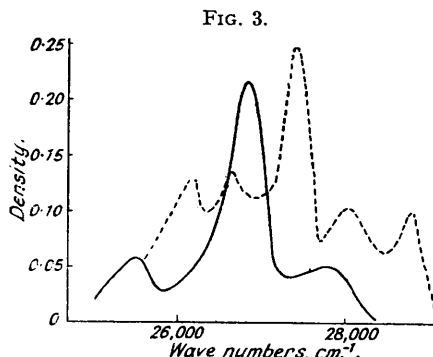


studied the relation between fluorescence and absorption spectra of a series of diphenylpolyenes and found the deviation of the coincident bands to increase with the number of double bonds. No such regularity was observed in our series of hydrocarbons. The spacings between the main bands of the fluorescence spectra are constant within the limits of experimental error, being about 1400 cm^{-1} . The spacings between the bands of the subsidiary systems are also the same, but with different compounds the two systems are shifted with respect to one another.

According to Fries's rule the arrangement of double bonds in the molecules of polycyclic aromatic hydrocarbons should be such as to lead to Kekulé structures for the maximum number of rings, with a corresponding minimum number of quinonoid rings. We have observed a relation between this minimum number of quinonoid rings and the positions of the fluorescence bands. It was found that the larger the number of such quinonoid rings in the molecule the greater was the shift of the spectrum towards the region of longer wave-length, as compared with isomeric hydrocarbons of which the structures could be represented entirely by Kekulé



Fluorescence spectra of 1':2':3':4'-tetrahydro-3:4-benzpyrene, 1-azapyrene, and pyrene.



Fluorescence spectra of 1:2-diacetoxy-1:2-dihydropyrene and phenanthrene.

forms. The magnitude of this shift (Table II, column *E*) is related approximately to the square of the minimum number of quinonoid rings. There is undoubtedly a general correspondence between this number of quinonoid rings and the degree of chemical reactivity of the compound, and hence it seems that there is a relation between the relative chemical reactivity of a compound and the position of its fluorescence bands. This suggests that the electronic transitions reflected in fluorescence are also concerned in the chemical reactions. From the theory of resonance, the greater the number of resonance forms the greater will be the stabilising resonance energy, and hence the lower the degree of chemical reactivity. Column *K* of Table II gives the number of resonance forms of each compound, in which for the sake of simplicity only Kekulé forms have been taken into account. It is seen that, for each series of isomeric hydrocarbons, a decrease in the number of resonance forms, with the implied increase in chemical reactivity, is associated with a shift of the fluorescence spectrum towards the red. Evidently the position of the spectrum is not the only criterion of chemical reactivity, for, if we consider the series of hydrocarbons, anthracene, 1:2-benzanthracene, and 1:2:5:6-dibenzanthracene, all of which contain a minimum of one quinonoid ring, the fluorescence spectra are seen to be shifted progressively towards the red as the number of rings increases, whereas the chemical reactivity diminishes. Possibly this last phenomenon is connected with steric inhibition at the *meso*-positions.

(b) *Hydrocarbons with Highly Condensed Ring-systems.*—The spectrum of pyrene (Table III; Fig. 2) consists of five narrow bands of close proximity and unequal spacing. The complexity of this spectrum suggested contamination of the specimen. However, the spectrum produced

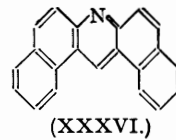
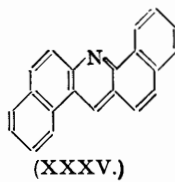
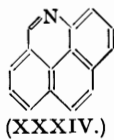
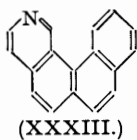
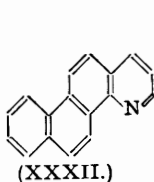
by a sample of pyrene from coal-tar was in no way different from that given by a sample isolated from products of petroleum cracking and purified exhaustively by chromatography, vacuum-sublimation, and recrystallisation. This spectrum closely resembled those already recorded for pyrene (Hieger, *Biochem. J.*, 1930, **24**, 505; Miescher *et al.*, *Biochem. Z.*, 1936, **287**, 189). The complexity of the spectrum is probably due to the high degree of molecular symmetry. The curves published by Förster and Wagner (*Z. physikal. Chem.*, 1937, **37**, B, 353) show that in the absorption spectrum of 4-methylpyrene there is a similar series of closely packed bands, but in the spectrum of the unsymmetrical 3-methylpyrene some of these bands were less prominent or absent. We have found that with other unsymmetrical derivatives of pyrene, such as 1-azapyrene and 1':2':3':4'-tetrahydro-3:4-benzpyrene (Fig. 2) there were also simplification of the pattern and modification of the spacing of the fluorescence bands. Thus the conclusion of Berenblum and Schoental (*loc. cit.*) that substitution does not materially affect the pattern of fluorescence spectra of the parent hydrocarbons seems invalid when a high degree of molecular symmetry is destroyed by substitution.

Comparison of the spectra of 1:2:6:7- and 3:4:8:9-dibenzpyrenes and of naphtho(2':3'-3:4)pyrene (Table III) showed that in the two last cases there is a considerable shift to the red. This is in agreement with the presence of a minimum of one quinonoid ring in the structure of the first compound, whereas the other two substances must have two such rings. Also the order of chemical reactivities, as expressed by the number of resonance forms (20, 13, 12) (Table III, column *K*) is in good agreement with the observed shifts of the spectra. It may be noted also that, whilst the number of quinonoid rings seems to define the position of the spectrum, within broad limits, the number of possible Kekulé structures reflects the amounts of the smaller shifts observed in isomers with the same number of quinonoid rings.

The positions of the bands in the spectrum of perylene do not agree with the structure with four Kekulé benzenoid rings usually assigned to this hydrocarbon. The simplicity of the spectrum (Fig. 1) and the frequency of the main band (22830 cm.^{-1})* are more in accord with a structure containing two quinonoid rings. Two examples of more complex perylene derivatives

TABLE IV.

Compound.	Exciting radiation.	Fluorescence maxima, $V' \times 10^{-2}$.		Main fluorescence maximum of corresponding hydrocarbon, $V'_{\text{Hom.}} \times 10^{-2}$.	$(V'_{\text{Het.}} - V'_{\text{Hom.}}) \times 10^{-2}$.
		(A.)	(B.)		
6-Azachrysene..... (XXXII)	2	276.5 262 248	269 254	276.5	0
6-Aza-3:4-benzphenanthrene (XXXIII)	2	268 255.5 243	263 250	—	—
1-Azapyrene..... (XXXIV)	2	269 255 242	263 249	268.5	+0.5
1:2:5:6-Dibenzacridine (XXXV)	2	253.5 240	247	254.0	-0.5
3:4:5:6-Dibenzacridine (XXXVI)	3	255 241 228	248 235	253.5	+1.5



* A similar value was obtained with an alcoholic solution by Seshan (*loc. cit.*). The position of the first band recorded by Ganguly (*Indian J. Physics*, 1944, **19**, 347) shows considerable displacement towards the red. Unequal spacing of the bands suggests that this displacement is due to concentration quenching.

are naphtho(2' : 3'-1 : 2)perylene* (having 15 resonance structures) and 2 : 3 : 8 : 9-dibenzperylene (with 25 resonance structures). The fluorescence spectrum of the highly reactive naphtho-perylene showed the expected shift towards the region of longer wave-length, whereas the spectrum of 2 : 3 : 8 : 9-dibenzperylene was shifted somewhat towards the region of shorter wave-length, as compared with perylene itself, with the same number of quinonoid rings (cf. Clar, *Ber.*, 1932, 65, 846).

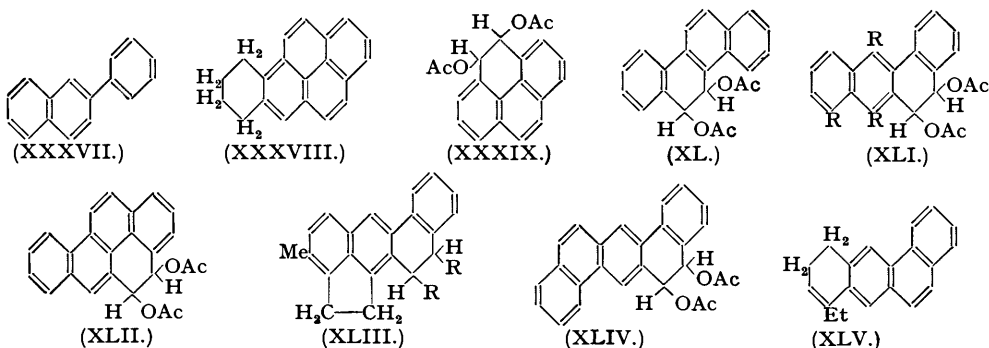
(c) *Aza-compounds*.—It is well known that replacement of a =CH- group of an aromatic ring by the isoelectronic nitrogen atom does not greatly influence the ultra-violet absorption spectrum of a compound. Hence it is not to be expected that the position of the fluorescence bands would

TABLE V.

Compound.	Exciting radiation.	Fluorescence maxima, $V'_f \times 10^{-2}$.	
		(A.)	(B.)
2-Phenyl-naphthalene (XXXVII)	2_1^a	292 *	289 *
		279 *	
		264 *	
1' : 2' : 3' : 4'-Tetrahydro-3 : 4-benzpyrene (XXXVIII)	2	263	257
		250	
1 : 2-Diacetoxy-1 : 2-dihydropyrene (XXXIX)	2	279 * ^b	—
		269	
		255	
1 : 2-Diacetoxy-1 : 2-dihydrochrysene (XL)	2	289 ^b	284 *
		275 *	268 *
		262 *	254 *
3 : 4-Diacetoxy-3 : 4-dihydro-1 : 2-benzanthracene (XLI; R = H)	2	287 ^b	—
		274	
		262 *	
6 : 7-Diacetoxy-6 : 7-dihydro-3 : 4-benzpyrene (XLII)	2	272 ^b	—
		258	
		244 *	
Diacetoxy-5 : 9 : 10-trimethyldihydro-1 : 2-benzanthracene (XLI; R = Me)	2	280 * ^b	—
		268 *	
6 : 7-Diacetoxy-20-methyl-7 : 6-dihydrocholanthrene (XLIII; R = OAc)	2	280 ^b	—
		267	
		253 *	
20-Methyl-6 : 7-dihydrocholanthrene (XLIII; R = H)	2	284 ^b	—
		270 ^b	
		256	
3 : 4-Diacetoxy-3 : 4-dihydro-1 : 2 : 5 : 6-dibenzanthracene (XLIV)	2	271 ^b	—
		257	
		243 *	
5-Ethyl-7 : 8-dihydro-1 : 2-benzanthracene (XLV)	3	273	—
		259	
		245 *	

^a Exposure time, hours.

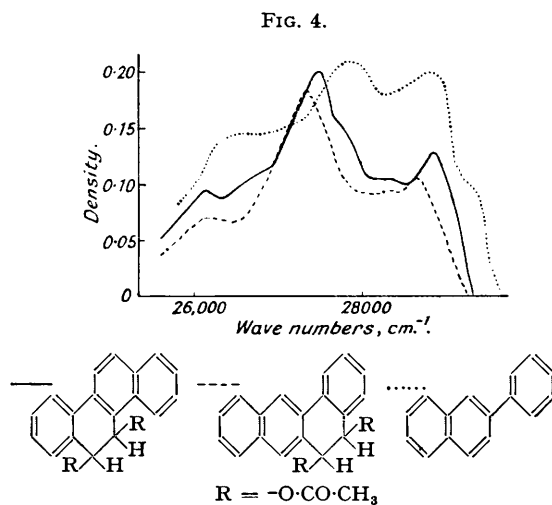
^b Solution in benzene; others in light petroleum.



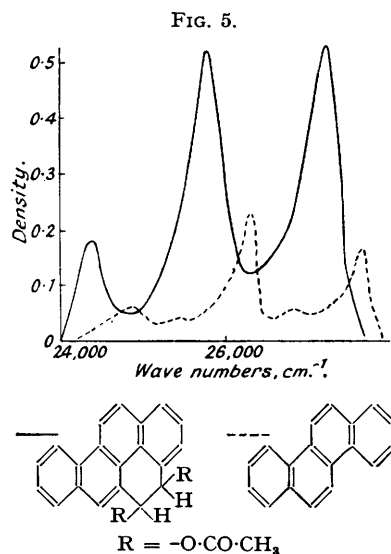
* Synthesised by Clar and Wright by a method not yet published.

be greatly affected, and this was found to be the case, although the intensity of fluorescence was considerably augmented. Thus, the fluorescence spectra of two dibenzacridines closely resembled those of the corresponding dibenzanthracenes (Table IV), and the same parallelism holds for chrysene and the corresponding 6-azachrysene. The case of pyrene and 1-azapyrene has already been discussed (Fig. 2 and Table IV).

(d) *Hydroaromatic Compounds*.—The approximate mirror-image relation between fluorescence and absorption spectra suggested the use of the former for identification of hydroaromatic compounds in appropriate cases. Compounds formed by partial hydrogenation of fused-ring aromatic compounds are difficult to free from the more intensely fluorescent, purely aromatic compounds, but the diacetates of the diols formed by oxidation of polycyclic aromatic hydrocarbons with osmium tetroxide (Cook and Schoental, *J.*, 1948, 170) provided convenient test materials (see Table V and Figs. 2, 3, 4, and 5). The fluorescence spectrum of 1:2-diacetoxy-1:2-dihydropyrene showed, as was to be expected, the main characteristics of that of phenanthrene, but is shifted towards the red by about 500 cm.^{-1} . The spectra of 1:2-diacetoxy-1:2-dihydrochrysene and 3:4-diacetoxy-3:4-dihydro-1:2-benzanthracene both resemble that of 2-phenylnaphthalene, with a shift towards the red. On account of the additional



Fluorescence spectra of 1:2-diacetoxy-1:2-dihydrochrysene, 3:4-diacetoxy-3:4-dihydro-1:2-benzanthracene, and 2-phenylnaphthalene.



Fluorescence spectra of 6:7-diacetoxy-6:7-dihydro-3:4-benzpyrene and chrysene.

substitution, 3:4-diacetoxy-5:9:10-trimethyl-3:4-dihydro-1:2-benzanthracene showed a greater displacement towards the region of longer wave-length. This spectrum is similar to that of the corresponding diacetate prepared from 20-methylcholanthrene, which may therefore be assumed to be the 6:7-diacetoxy-6:7-dihydro-compound. The spectrum of this likewise resembles that of 6:7-dihydro-20-methylcholanthrene, except that in the latter case the spectrum is displaced towards the region of shorter wave-length. The spectrum of the diacetate from 1:2:5:6-dibenzanthracene resembles that of naphtho(1':2'-2:3)fluorene, which indicates that the diacetoxy-groups have been added to the 3:4-positions. This was confirmed chemically by oxidation to the known 1:2:5:6-dibenz-3:4-anthraquinone (Cook, *J.*, 1933, 1594).

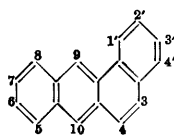
In the case of 3:4-benzpyrene the attack by osmium tetroxide might conceivably take place at the 1:2- or the 6:7-positions. The former would lead to a residual 1:2-benzanthracene system, the latter to a residual chrysene system. The spectrum resembled that of chrysene, but with a shift of 450 cm.^{-1} towards the red, indicating that oxidation had occurred at the 6:7-positions. The spectrum of 5-ethyl-7:8-dihydro-1:2-benzanthracene is of interest as it lies between those of phenanthrene and 1:2-benzanthracene.

(e) *Homologues of 1:2-Benzanthracene*.—The fluorescence spectra of nine of the twelve possible monomethyl-1:2-benzanthracenes are recorded in Table VI. The patterns resemble

TABLE VI.

Compound.	Fluorescence maxima, $V'_f \times 10^{-2}$. (A.)	Absorption maximum of lowest wave-number, $V'_a \times 10^{-2}$. (C.)	$(V'_a - V'_f) \times 10^{-2}$. (D.)	$\Delta V'_f \times 10^{-2}$. (E.)	$\Delta V'_a \times 10^{-2}$. (F.)	Carcinogenicity.
1:2-Benzanthracene (XLVI)	259.5 245.5 231	260	+0.5	—	—	—
Derivatives thereof:						
9-Methyl	254 240 *	254.5 *	+0.5	5.5	5.5	++
10-Methyl	256 242 229	257	+1.0	3.5	3	++
3-Methyl	256.5 243 229	—	—	3.0	—	+
1'-Methyl	257 243 230	258	+1.0	2.5	2	—
8-Methyl	257 243 229	259	+2.0	2.5	1	—
6-Methyl	257.5 243 *	259	+1.5	2.0	1	+
7-Methyl	257.5 243 229	260	+2.5	2.0	0	+
5-Methyl	258.5 244 230	259	+0.5	1.0	1	++
4-Methyl	258.5 245 230	259.5	+1.0	1.0	0.5	+

closely that of the spectrum of the parent hydrocarbon, with shifts towards the red. The extent of the shift (column E) varies with the position of substitution and runs parallel to the shift of the longest absorption band (column F). In discussing the effect of methyl substituents in different positions, Jones (*J. Amer. Chem. Soc.*, 1940, **62**, 148; *Chem. Reviews*, 1943, **32**, 1) emphasised particularly the shift exhibited by another band (band H; cf. Fig. 1), which was shifted to the greatest extent in the case of 10-methyl-1:2-benzanthracene. It would appear, however, that band K, equivalent to the shortest fluorescence band, is of greater importance, and this shows the greatest shift in the case of 9-methyl-1:2-benzanthracene. The next largest shifts are shown by the 10-methyl and then the 3-methyl isomers. It may be of significance that these are the most reactive positions of the unsubstituted molecule, position 10 being much more reactive than position 9, possibly on account of steric hindrance at the latter position. It is of interest also that in their most recent calculations, using the method of molecular orbitals, Berthier, Coulson, Greenwood, and Pullman (*Compt. rend.*, 1948, **226**, 1906) assigned the highest value for the free valency index to position 9. Their calculated values for other positions do not, however, correlate with the shift in fluorescence spectrum caused by methyl substitution at those positions.



(XLVI.)

The fluorescence spectra of seven dimethyl-1:2-benzanthracenes have been examined (Table VII). Substitution at both *meso*-positions led to a remarkably large shift, which was followed by that for the 5:6-dimethyl compound. Substitution in the β -positions of the benzanthracene system seemed to have little effect, and even caused shifts towards the region of shorter wave-length. Thus, whereas the shift to the red of the benzanthracene spectrum was 200 cm^{-1} in the case of the 6- and 7-monomethyl derivatives, it was only 150 cm^{-1} with the 6:7-dimethyl compound. Higher-alkyl groups at position 5 of the benzanthracene molecule produced shifts of the spectrum not appreciably different from that caused by methyl. This is seen in Table VII, which gives also the effect of substituents other than alkyl groups at position

TABLE VII.

Compound.	Fluorescence maxima of main bands, $V'_f \times 10^{-2}$.		Shift of first band from that of (XLVI), $\Delta V'_f \times 10^{-2}$.	Carcinogenicity.	
1 : 2-Benzanthracene (XLVI).....	259.5	—	—	—	
Derivatives thereof :					
2' : 6-Dimethyl	257.5	243	229	2.0	—
2' : 7-Dimethyl	255.5	242	228	4.0	—
3' : 6-Dimethyl	258.0	243	230	1.5	—
3' : 7-Dimethyl	257.5	243	229	2.0	—
5 : 6-Dimethyl	253 *	—	—	6.5	++
6 : 7-Dimethyl	258.0	244	230	1.5	+
9 : 10-Dimethyl.....	247 *	—	—	12.5	+++
5-Ethyl	259	245	230	0.5	+
5- <i>n</i> -Propyl	258.5	245	230	1.0	+
5- <i>iso</i> Propyl	258.5	245	230	1.0	+
5-Phenyl	256.5	243 *	—	3.0	±
5-Carboxy	249 *	—	—	10.5	—
10-Acetoxyethyl	256.5	243	229	3.0	+
10-Ethoxyethyl	257	243	229	2.5	+
10-Hydroxyethyl	256.5	243	229	3.0	+
10-Cyano	252.0	238	225	7.5	—
4'-Amino	237 *	—	—	2.2	—
4'-Methoxy	254	240	226.5	5.5	—

5 and 10. The cyano-group, with its triple bond conjugated with an aromatic ring, caused larger shifts than did alkyl groups. Polar substituents also have considerable influence on the fluorescence spectrum, causing not only a considerable shift, but also diffuseness. This is exemplified by 5-carboxy- and 4'-amino-1 : 2-benzanthracenes.

Comparison of Fluorescence Intensities.

In a few cases sufficient material was available for quantitative assessment of the fluorescence intensities. The method of Berenblum and Schoental (*Biochem. J.*, 1942, **36**, 86) of matching intensities of bands on photographic plates was used, but visual estimations were replaced by photometric readings (see Experimental). Comparison was made of the similar spectra of closely related compounds. In the case of two nitrogenous compounds (6-azachrysene, 1-azapyrene), the intensities were about 10 times as great as those of the related hydrocarbons. The fluorescence intensities of three isomeric pentacyclic hydrocarbons, each containing one quinonoid ring in its structure [1 : 2 : 7 : 8-dibenzanthracene, 1 : 2 : 5 : 6-dibenzanthracene, and naphtho-(2' : 3'-1 : 2)phenanthrene], were in the ratio 1 : 10 : 300. The amount of variation in such closely related compounds is noteworthy. It should be stated that, on account of weak intensities, long exposures were required and diffuse spectra were obtained with triphenylene, 3 : 4 : 5 : 6-dibenzphenanthrene, and 1 : 2 : 7 : 8-dibenzanthracene; consequently, only approximate positions of the maxima of one main band are recorded for the spectra of these compounds and of those of the photolabile pentacene and naphtho(2' : 3'-1 : 2)perylene.

The fluorescence intensity of 3 : 4 : 8 : 9-dibenzpyrene is about six times that of 1 : 2 : 6 : 7-dibenzpyrene, but as the positions of the spectra differ they are not strictly comparable. The exceedingly intense fluorescence of perylene could be recorded with a 3-minutes' exposure in a concentration of 0.1 μg . per ml. It may be noted that there is no direct relation between the carcinogenic activity of some of the compounds and the position or intensity of the fluorescence spectrum.

EXPERIMENTAL.

Fluorescence Spectra in the Region 31,000—25,000 cm^{-1} (3000—4000 \AA).—Radiation from a mercury-vapour lamp S (Kelvin, Bottomley, and Baird), enclosed in a black box, was condensed by a 500-ml. silica flask containing a 10% solution of nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$). This filter absorbed the mercury lines at 3650 and 4047 \AA ., excitation being effected mainly by the 2537—2650 \AA . group, designated as 2 in the tables. A reduced image of the lamp was formed about 5 mm. from the slit of a Hilger medium quartz spectrograph (slit, 0.1 mm.) which was inclined at 80° to the path of the light. At the slit of the spectrograph was placed a quartz cell (1 \times 1 cm.) containing the solution to be examined. Exposures varied usually from 5 to 15 minutes, but were as long as several hours in specific cases which have been mentioned. Ilford Special Rapid plates were used.

Fluorescence Spectra in the Region 27,000—22,000 cm^{-1} (3700—4500 \AA).—Radiation from a 250-watt Mazda Compact Source Mercury Lamp was condensed by two quartz lenses (focal lengths, 6'' and 8'') and then passed through a Wood's filter. The excitation radiation (3650—3663 \AA .) is designated as 3

in the tables. An image of about 3 mm. in height was formed close to the spectrograph, oriented as described in the preceding paragraph. Exposures were about 3 minutes. Ilford Panchromatic plates were used.

Fluorescence Spectra in the Region 25,000—17,000 cm.⁻¹ (4000—6500 Å).—Radiation from the same source as recorded in the preceding paragraph was used, but the Wood's filter was replaced by appropriate glass filters so as to give the green or yellow mercury light.* The quartz spectrograph was replaced by a Hilger medium glass spectrograph. Exposures, lasting from 3 to 10 minutes, were made on Ilford Panchromatic plates.

Procedure.—Solutions of the compounds in redistilled light petroleum (b. p. 60—80°) were prepared and the concentrations adjusted by visual observation in ultra-violet light so that there was no appreciable quenching. A number of spectra was photographed on the same plate, interspersed with mercury emission spectra to facilitate measurements. The positions of the bands were measured using a Hilger microphotometer (slit, 0.2 mm.). The plate was initially oriented in the holder so that the mercury lines on each side of the fluorescence spectra were correctly aligned. Measurements were made every 0.5 mm. from the ultra-violet edge of one of the mercury lines (3342 or 3650 Å.) until the whole spectrum had been traversed. For accurate determinations, readings were taken every 0.05 mm. near the heads of the bands. From a distance calibration table, obtained from an iron-arc spectrum, the wave-lengths of the heads of the bands could be obtained.

When the glass spectrograph was used, a wave-length scale was imprinted above and below each spectrogram. Microphotometric readings were taken every 20 Å. For accurate readings, the distance of the head of the band from a line on the scale was measured, and the wave-length then found by interpolation.

To measure the density of the bands, a reading was taken initially of an unexposed part of the plate. The resistance in series with the photocell was adjusted so that this reading corresponded to the maximum deflection on the scale (50 cm.). Readings were then taken as already described and the logarithms of the values so obtained were subtracted from $\log_{10} 50$. Density curves were obtained by plotting \log_{10} density against wave-numbers.

Quantitative comparisons of fluorescence intensities were made by matching the intensities of spectrograms produced by serial dilution of the compound under examination with that of a standard solution of 3:4-benzopyrene, photographed on the same plate under standardised conditions. The ratio of the concentrations required to give the same photographic density was taken as an inverse measure of the relative fluorescence intensities.

Tables.—References to ultra-violet absorption spectra in Tables I, II, III, IV, and VI are: (1) Mayneord and Roe, *Proc. Roy. Soc., A*, **158**, 634; (2) Clar and Lombardi, *Ber.*, 1932, **65**, 1411; (3) Clar, *ibid.*, p. 503; (4) Mayneord and Roe, *Proc. Roy. Soc., A*, **152**, 299; (5) Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148; (6) Clar, "Aromatische Kohlenwasserstoffe," Berlin, 1941, p. 147; (7) Clar and Lombardi, *Gazzetta*, 1932, **62**, 539; (8) Clar, *Ber.*, 1936, **69**, 607; (9) Clar, "Aromatische Kohlenwasserstoffe," Berlin, 1941, p. 148; (10) Nichol *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 376; (11) Clar, *Ber.*, 1936, **69**, 1671; (12) *Ber.*, 1943, **76**, 609; (13) *Ber.*, 1932, **65**, 846; (14) *Ber.*, 1932, **65**, 846; cf. Schanenstein, and Bürgermeiser, *Ber.*, 1943, **76**, 208; (15) Clar, *Ber.*, 1940, **73**, 596.

Unless otherwise specified, the solutions used were in light petroleum (b. p. 60—80°), and the exciting radiation was 3650 Å. ν denotes wave-number in cm.^{-1} .

We are much indebted to Professor J. W. Cook, F.R.S., for supplying a large proportion of the compounds used in this investigation and for his interest, kind help, and suggestions, and we have received also much valuable advice from Dr. Stotherd Mitchell in regard to the spectroscopic techniques. We thank the British Empire Cancer Campaign for a grant (to R. S.), the Carnegie Trust for the Universities of Scotland for a Scholarship (to E. J. Y. S.), and Dr. G. M. Badger, Dr. E. Clar, and Miss E. F. M. Stephenson for gifts of hydrocarbons.