600. *Substituted Anthracene Derivatives. Part IV. The Ultra-violet Absorption Spectra of* meso-*Substituted* 1 : 2-*Benzanthracenes.*

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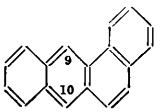
The ultra-violet absorption spectra of a number of *meso*-substituted 1 : 2-benzanthracenes have been examined. Benzanthracene has three main regions of absorption in the near ultra-violet, designated I, II, and III, respectively. Substitution in the *meso*-positions produces a shift in the positions of the bands to longer wave-lengths, the group II bands invariably being shifted to the greatest extent. The results are discussed in terms of the extent of conjugation of the substituent with the ring, and the influence of steric hindrance.

The ultra-violet absorption spectra of the polycyclic aromatic compounds have been extensively studied, particularly by Clar (" Aromatische Kohlenwasserstoffe," 1941), by Mayneord and Roe (*Proc. Roy. Soc.*, 1935, *A*, **152**, 299; 1937, *A*, **158**, 634), and by Jones (*Chem. Reviews*, 1943, **32**, 1; 1947, **41**, 353; *J. Amer. Chem. Soc.*, 1945, **67**, 2127). The fluorescence spectra of many aromatic compounds have also been examined (Schoental and Scott, *J.*, 1949, 1683). The accumulated facts have been of value, not only for the identification of unknown aromatic compounds, but also in the study of the inter-relationships of the compounds. Clar has drawn attention to the fact that there seems to be a relation between the position of the absorption bands and the chemical " reactivity " of the compound, and Schoental and Scott have pointed to a similar relationship between the position of the fluorescence bands and " reactivity." In the former case the " reactivity " was largely associated with the " Dewar " or " *para*-forms " of the hydrocarbon, and, in the latter, with the number of " quinonoid " rings. Unfortunately, very little information is available on the relative reactivity of polycyclic compounds, and we regard this relationship between wave-length of the absorption (or fluorescence) bands and " reactivity " as largely fortuitous. That there is no *direct* relationship of this nature is at once apparent from the fact that both electron-attracting and electron-donating substituents produce shifts in the position of the absorption (and fluorescence) bands to longer wave-lengths. This has been shown to be the case not only for substitution in benzene (see *e.g.*, Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714), but also for substitution in polycyclic compounds (Jones, *loc. cit.*). Moreover, Schoental and Scott (*loc. cit.*) observed similar shifts in the position of the fluorescence bands by both types of substituent. The nature and extent of the shifts produced by various substituents are still incompletely understood, however, and the present paper records the results of an investigation of the ultra-violet absorption spectra of a number of *meso*-substituted 1 : 2-benzanthracenes.

The absorption spectrum (Fig. 1) of 1 : 2-benzanthracene (I) has been recorded by several authors (Capper and Marsh, *J.*, 1926, 724; Clar, *Ber.*, 1932, **65**, 503; Mayneord and Roe, *loc. cit.*; Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148). All the results are in substantial agreement with the curve obtained in the present work. In the near ultra-violet there are twelve well-defined absorption bands, and the labels A . . . K, introduced by Jones, have been retained for easy reference. The twelve absorption bands fall into three main groups which, in agreement with Braude (*Ann. Reports*, 1945, **42**, 123), it is proposed to call I, II, and III, respectively. Group I includes the bands A, B, C, D, E, in the region of 2800 A. It is equivalent to the 2500 A. region of absorption in anthracene, and the 1800 A. region in benzene. Group II includes the bands F, G, H, I, in the region of 3400 A., equivalent to the 3400 A. region in anthracene and the 2000 A. region in benzene. Group III includes the bands I′, J, K, in the region 3800 A., and is equivalent to the 2550 A. region of absorption in benzene. The group III bands in anthracene are swamped under the group II absorption. These sub-divisions (Clar, *loc. cit.*; Braude, *loc. cit.*; Doub and Vandenbelt, *loc. cit.*; Klevens and Platt, *J. Chem. Physics*, 1949, **17**, 470; Platt, *ibid.*, p. 484; Jones, *loc. cit.*; Coulson, *Proc. Physical Soc.*, 1948, **60**, 257) now seem to be generally accepted, although the different authors have adopted various names (Table I) for the groups.



(I.)

FIG. 1.

Absorption spectrum of 1 : 2-*benzanthracene.*

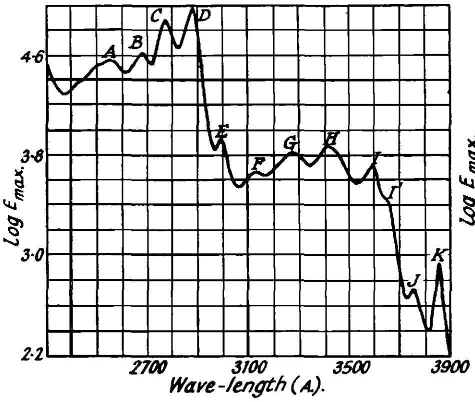


FIG. 2.

Curves showing the absorption spectra of 10-*cyano*-1 : 2-*benzanthracene* (———) *and* 10-*methyl*-1 : 2-*benzanthracene* (– – – –).

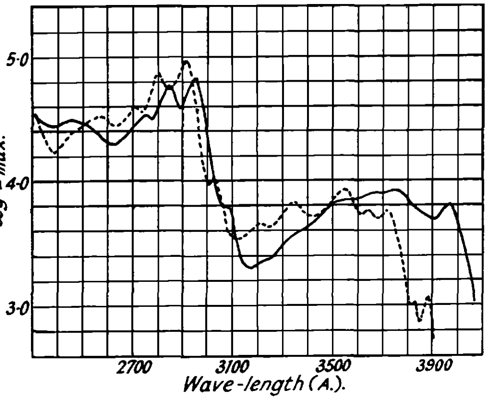


TABLE I.

Nomenclature of different regions of absorption.

Region of absorption, A.			Name of region.			
Benzene.	Anthracene.	1 : 2-Benz-anthracene.	Braude.	Clar.	Doub and Vandenbelt.	Klevens and Platt.
1800	2500	2800 (Bands A—E)	Group I	β-Bands	—	B_b
2000	3400	3400 (Bands F—I)	Group II	*para*-Bands	" Primary " bands	L_a
2550	—	3800 (Bands I′, J, K)	Group III	α-Bands	" Secondary " bands	L_b

There seems to be little doubt that group I bands (of anthracene) are associated with longitudinal polarisation, and group II bands with transverse polarisation. The fine structure in each group must represent vibrational sub-levels of electronic excitation, and it has been shown that the frequency differences between the various maxima in the group II region of the anthracene are very nearly constant, and equal to approximately 1400 cm.$^{-1}$ (Barnett, Cook, and Ellison, *J.*, 1928, 885; Jones, *Chem. Reviews*, 1947, **41**, 353). It does not seem generally known that similar constant frequency differences (which Jones associates with the C–H bending vibration) are to be found in the spectra of most polycyclic compounds, including that of 1 : 2-benzanthracene. The average frequency difference for the maxima in the group I region of 1 : 2-benzanthracene is 1490 cm.$^{-1}$; that for the group II maxima is 1300 cm.$^{-1}$; but that for the group III maxima is 700 cm.$^{-1}$. It is also noteworthy that the frequency difference between the fluorescence bands of benzanthracene and its derivatives is also constant, and is equal to approximately 1400 cm.$^{-1}$ (calculated from the results of Schoental and Scott, *loc. cit.*).

TABLE II.

Position of the maxima and corresponding intensities (log $E_{\text{max.}}$) *in the ultra-violet absorption spectra of* meso-*substituted* 1 : 2-*benzanthracenes* (*solvent, ethanol*).

	A.	B.	C.	D.	E.	F.	G.	H.	I.	I′.	J.	K.
(*a*)	2560	2670	2770	2875	2995	3140	3265	3410	3585	3640	3750	3850
	4·56	4·61	4·89	4·99	3·95	3·67	3·81	3·87	3·72	3·46	2·73	2·95
(*b*)	2580	2680	2770	2870	2985	3190	3340	3440	3600	3670	—	3890
	4·57	4·69	4·89	4·93	3·77	3·64	3·82	3·85	3·75	3·63	—	3·20
(*c*)	2580	2680	2780	2880	—	3220	3360	3520	3630	3685	—	3890
	4·56	4·65	4·91	4·94	—	3·64	3·82	3·88	3·78	3·74	—	3·20
(*d*)	2585	2700	2800	2910	3010	3210	3350	3510	3640	3680	—	3880
	4·48	4·58	4·86	4·96	3·81	3·64	3·83	3·91	3·77	3·79	—	3·11
(*e*)	2570	2690	2790	2900	3010	3190	3330	3500	3630	3675	—	3870
	4·58	4·64	4·92	5·02	3·78	3·68	3·89	3·96	3·75	3·79	—	2·93
(*f*)	—	—	3930	3020	—	—	—	—	—	—	—	—
	—	—	4·6	4·65	—	—	—	—	—	—	—	—
(*g*)	2590	2700	2800	2910	—	3200	3340	3490	3620	3660	—	3870
	4·49	4·57	4·82	4·90	—	3·61	3·79	3·86	3·73	3·72	—	3·12
(*h*)	2600	2750	2860	2960	—	—	—	3510	—	—	—	3900
	4·49	4·52	4·72	4·77	—	—	—	3·78	—	—	—	3·48
(*i*)	2590	2710	2815	2925	3020	3240	3390	3555	3740	—	—	3910
	4·47	4·58	4·90	5·20	3·85	3·65	3·87	4·00	3·85	—	—	3·02
(*j*)	—	—	2920	3020	—	—	—	3830	—	—	—	—
	—	—	4·61	4·65	—	—	—	3·91	—	—	—	—
(*k*)	—	2740	2840	2950	3050	—	—	3750	—	—	—	3960
	—	4·53	4·77	4·84	3·83	—	—	3·93	—	—	—	3·80
(*l*)	2595	2700	2803	2913	3015	3205	3350	3510	3645	3685	—	3890
	4·60	4·68	4·94	5·06	3·91	3·69	3·89	3·96	3·82	3·84	—	2·16
(*m*)	2600	2700	2800	2910	3020	3200	3350	3510	3650	3690	—	3890
	4·53	4·60	4·87	5·06	3·92	3·65	3·84	3·94	3·77	3·79	—	3·09
(*n*)	2580	2680	2780	2880	—	—	3340	3500	3670	—	—	3875
	4·50	4·63	4·77	4·74	—	—	3·75	3·77	3·68	—	—	3·49
(*o*)	2600	2690	2790	2890	3010	3240	3390	3555	3680	3725	—	3910
	4·60	4·67	4·91	4·92	3·99	3·66	3·87	3·97	3·80	3·81	—	3·24
(*p*)	2640	2740	2850	2950	—	3300	3455	3620	3800	—	—	—
	4·57	4·59	4·83	4·90	—	3·63	3·86	3·99	3·88	—	—	
(*q*)	2610	2710	2810	2930	3030	3300	3450	3625	3810	—	—	—
	4·54	4·63	4·86	4·88	4·07	3·59	3·82	3·95	3·80	—	—	—
(*r*)	2600	2730	2835	2945	—	3270	3430	3570	3730	—	—	—
	4·55	4·63	4·72	4·80	—	3·69	3·94	4·06	3·97	—	—	—
(*s*)	2620	2720	2820	2930	—	3280	3420	3590	3770	—	—	—
	4·57	4·62	4·87	4·92	—	3·64	3·85	3·97	3·83	—	—	—
(*t*)	2640	2750	2850	2960	—	3310	3480	3640	3820	—	—	—
	4·52	4·59	4·85	4·89	—	3·61	3·86	4·00	3·87	—	—	—
(*u*)	2600	2750	2860	2960	—	—	—	3780	—	—	—	—
	4·42	4·58	4·81	4·82	—	—	—	4·01	—	—	—	—
(*v*)	—	—	(2850)	2945	—	—	—	3860	—	—	—	—
	—	—	4·58	4·68	—	—	—	3·95	—	—	—	—
(*w*)	2645	2735	2835	2945	—	(3250)	3440	3600	3760	—	—	—
	4·59	4·66	4·91	4·96	—	3·61	3·87	3·98	3·87	—	—	—

(*a*) 1 : 2-Benzanthracene. (*b*) 9-Acetoxy-1 : 2-benzanthracene. (*c*) 9-Methoxy-1 : 2-benzanthracene. (*d*) 10-Acetamido-1 : 2-benzanthracene. (*e*) 10-Acetoxy-1 : 2-benzanthracene. (*f*) 10-Amino-1 : 2-benzanthracene. (*g*) 1 : 2-Benzanthracene-10-carboxylic acid. (*h*) 1 : 2-Benzanthracene-10-glyoxylic acid. (*i*) 10-Bromo-1 : 2-benzanthracene. (*j*) 1 : 2-Benz-10-anthraldehyde. (*k*) 10-Cyano-1 : 2-benzanthracene. (*l*) 10-Ethoxymethyl-1 : 2-benzanthracene. (*m*) 10-Hydroxymethyl-1 : 2-benzanthracene (and acetate). (*n*) 10-Nitro-1 : 2-benzanthracene. (*o*) 9 : 10-Diacetoxy-1 : 2-benzanthracene. (*p*) 9 : 10-Diethyl-1 : 2-benzanthracene. (*q*) 9 : 10-Dimethoxy-1 : 2-benzanthracene. (*r*) 9 : 10-Diphenyl-1 : 2-benzanthracene. (*s*) 10-Acetoxy-9-methyl-1 : 2-benzanthracene. (*t*) 10-Bromo-9-methyl-1 : 2-benzanthracene. (*u*) 10-Cyano-9-methyl-1 : 2-benzanthracene. (*v*) 9-Methyl-1 : 2-benz-10-anthraldehyde. (*w*) 9-Methyl-10-ethoxymethyl-1 : 2-benzanthracene.

Substituted polycyclic aromatic compounds have absorption spectra which, in general, are very similar to those of the parent hydrocarbons, except that the bands are displaced towards longer wave-lengths (bathochromic shift). The magnitude of the shift depends on the position of substitution and on the nature of the substituent. Jones (*J. Amer. Chem. Soc.*, 1940, **62**, 148) has already shown that the effect of a methyl substituent in benzanthracene is dependent on the position of substitution, and that the bathochromic shift is greatest for the *meso*-substituted derivatives. The influence of the nature of the substituent is shown by the work of Jones (*J. Amer. Chem. Soc.*, 1945, **67**, 2127) and by that now reported. All the compounds examined are *meso*-substituted benzanthracenes, and the wave-lengths and extinction coefficients of the various maxima (A. . . . K) are given in Table II.

The origin of the shift in the position of the absorption bands which results on the introduction of a substituent has always been somewhat obscure, but there now seems little doubt that it is largely to be associated with the mesomeric or resonance effect of the substituent : that is, with the degree of conjugation of the substituent with the ring system. Doub and Vandenbelt (*loc. cit.*), for example, have studied the shift produced both by *ortho-para*-directing and by *meta*-directing substituents on the absorption bands of benzene. In both series the magnitude of the shift parallels the magnitude of the mesomeric effect as estimated in other ways. The same conclusion, with respect to the methyl, hydroxyl, and methoxyl substituents was reached by Kiss, Molnár, and Sandorfy (*Compt. rend.*, 1948, **227**, 724).

The effect of a substituent on the absorption bands has sometimes been classified as follows : (i) a bathochromic effect; (ii) a conjugation effect; (iii) a fine structure effect; (iv) a steric effect. Although useful for the purposes of discussion, it must be remembered that this classification is entirely artificial. For example, Jones (*loc. cit.*, 1945) has discussed the conjugation effect only in terms of unsaturated substituents and those having a lone pair of electrons available for conjugation. There can be little doubt, however, that the major part of the shift produced by alkyl groups is determined by the very similar mechanism of hyperconjugation. It is noteworthy that the absorption spectra of cyano-derivatives are similar to those of the corresponding methyl derivatives, except that the absorption bands of the former are displaced to somewhat longer wave-lengths (see Fig. 2). Furthermore, the loss of fine structure which follows the introduction of certain substituents appears to be intimately connected with the extent of conjugation.

TABLE III.

Average frequency shift (m.$^{-1}$) *in each group of absorption and fluorescence bands produced by mono*-meso-*substitution in* 1 : 2-*benzanthracene.*

	Absorption.					Absorption.			
Substituent.	Group I.	Group II.	Group III.	Fluorescence.[b]	Substituent.	Group I.	Group II.	Group III.	Fluorescence.[b]
9-OAc	0·4	3·9	2·5	—	9-OMe	1·5	7·3	3·0	—
10-OAc	2·3	5·5	2·0	—	9-Me	4·3[a]	7·8[a]	—*	5·5
10-CO$_2$H ...	4·1	5·5	1·5	—	10-Me	4·8[a]	7·8[a]	4·6[a]	3·0
10-NHAc ...	3·5	6·8	3·2	—	10-CO·CO$_2$H	4·2	8·3	—*	—
10-CH$_2$·OEt	4·1	6·8	3·0	2·3	10-OMe ...	4·2[a]	9·2[a]	2·4[a]	—
10-CH$_2$·OH	4·2	6·8	3·2	2·5	10-Br	5·1	11·2	3·9	—
10-CH$_2$·OAc	4·2	6·8	3·2	2·5	10-CN	8·3	(26·5) *	7·2	—
10-NO$_2$	1·5	7·0	1·7	—	10-CHO ...	17·6	(32·1) *	—*	—
	1·3[a]	7·4[a]	2·4[a]		10-NH$_2$	17·9	? *	—*	—
10-NH$_3^+$ ...	3·4[a]	7·1[a]	3·3[a]	—		17·4[a]	(32·3) *[a]	—*	—

* These bands cannot be identified with certainty owing to loss of fine structure. Values given in parentheses must be regarded as approximate. See also Table II.

[a] Values calculated from Jones's data (*loc. cit.*). [b] Values from Schoental and Scott (*loc. cit.*).

The various groups of absorption bands in polycyclic compounds are not equally affected by the presence of substituents, and Jones (*Chem. Reviews*, 1947, **41**, 353) used this fact in his interpretation of the directions of polarisation in the anthracene molecule. On the other hand, vibrational sub-levels in each group are shifted approximately to the same extent, and it is therefore reasonable to average the frequency shifts in the absorption bands of each group. In Table III, the average shifts in each of three groups (I, II, and III) of bands, and the average shifts in the fluorescence bands, for all the mono-*meso*-substituted 1 : 2-benzanthracenes which have now been examined, have been collected. The group II bands are invariably shifted to the greatest extent, and the substituents have therefore been arranged in order of the magnitude of their effect on this group of bands. With two or three exceptions, the shift in group I and group III absorption bands, and in the fluorescence bands, also increases in approximately the same order. If Doub and Vandenbelt's conclusions (*loc. cit.*) are valid, the order of increasing bathochromic shift is also the order of increasing conjugation of the substituent with the benzanthracene ring. It is not to be expected that this order will be the same as that derived by Doub and Vandenbelt for substituents in the benzene ring system, for in the present series of compounds the steric interference between the substituent and the *peri*hydrogen atoms, and with the " benz- " ring (in the case of 9-substituted derivatives) is sometimes very considerable (see Figs. 3, 4, and 5). This steric interference prevents the assumption of a co-planar configuration, which is usually considered to be a fundamental requirement for conjugation, and, indeed, according to Jones (*loc. cit.*, 1945), a 9-methoxy-group is strained even when rotated at 90° to the plane of the ring. However, consideration of steric interference solely in terms of the rotation of the substituent, ignores the fact that the group may be displaced *as a whole* either above or below the plane of the ring system. Evidence that displacements of this type do occur has accumulated in recent years (Newman and Hussey, *J. Amer. Chem. Soc.*, 1947, **69**, 978, 3023; Ball and Waring, *Chem. and Ind.*, 1949, 321; Everard and Sutton, *J.*, 1949, 2312). It seems likely that such displacements occur in many of the present compounds, for examination of Tables II and III indicates that in no case is conjugation entirely prevented by steric hindrance. All the substituents give rise to shifts in all groups of absorption bands, although it must be admitted that the magnitude of the shifts is sometimes only a fraction of that which occurs in the absence of steric hindrance.

FIG. 3.
9-*Methyl*-1 : 2-*benz*-10-*anthraldehyde*.

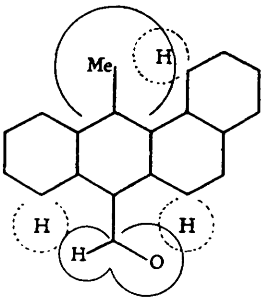


FIG. 4.
9 : 10-*Dimethoxy*-1 : 2-*benzanthracene*.

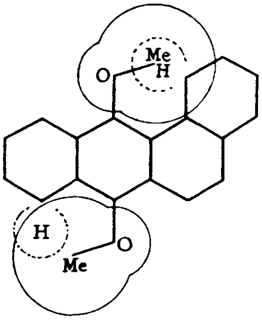
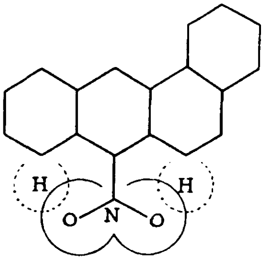


FIG. 5.
10-*Nitro*-1 : 2-*benzanthracene*.



[These scale diagrams are based on the dimensions given by Jones, *loc. cit.*, 1945.]

FIG. 6.
Curves showing the absorption spectra of 5-*phenyl*-1 : 2 : 3 : 4-*dibenzpyrene* (III, ——) *and* 9 : 10-*diphenyl*-1 : 2-*benzanthracene* (II, - - - -).

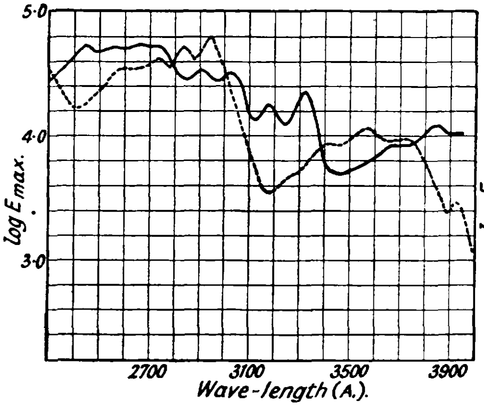
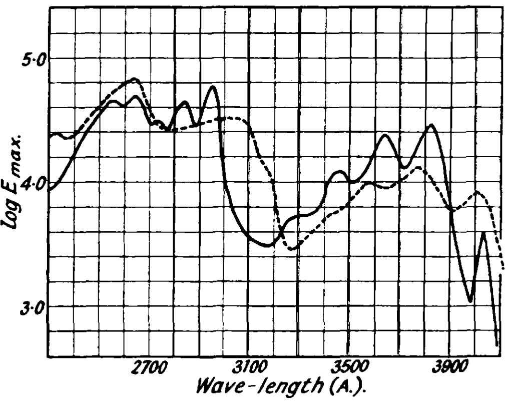
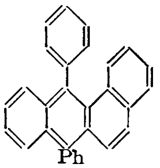
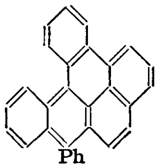


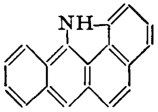
FIG. 7.
Curves showing the absorption spectra of 3 : 4-*benzpyrene* (V, ——; *after Mayneord and Roe*, loc. cit.) *and* 1′ : 9-*imino*-1 : 2-*benzanthracene* (IV, - - - -).

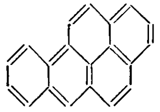


With the 9- and the 10-acetoxy-derivative, with 10-acetamido-1 : 2-benzanthracene, and with 1 : 2-benzanthracene-10-carboxylic acid, the steric effect must be considerable, and these substituents can only be conjugated with the ring system to a small extent. It is noteworthy that the shifts produced by the acetoxy- and methoxy-groups in the 9-position are much less than those produced by the same substituents in the 10-position, where the steric hindrance (although still large) is not so marked (see Fig. 4). On the other hand, the shift produced by the nitro-group is surprisingly small when compared with that observed in benzene, and the steric hindrance does not seem to be sufficiently marked to explain the difference (Fig. 5). It is interesting in this connection that Doub and Vandenbelt also found the nitro-group to be exceptional in some of their generalisations.


(II.)


(III.)


(IV.)


(V.)

The effect of phenyl substituents on the spectra of anthracene and similar compounds has already received considerable attention from spectroscopists (Hirshberg and Haskelberg, *Trans. Faraday Soc.*, 1943, **39**, 45; Hirshberg, *ibid.*, 1948, **44**, 285; Jones, *Chem. Reviews*, 1943, **32**, 1). In 9 : 10-diphenyl-1 : 2-benzanthracene (II) the two phenyl groups produce a slight shift, although this is very much less than would be expected in the absence of steric interference. It is interesting to compare the spectrum of this compound with that of the very closely related 5-phenyl-1 : 2 : 3 : 4-dibenzpyrene (III), from which it differs only by two hydrogen atoms. As expected, there is relatively little similarity between the two spectra. On the other hand, 1′ : 9-imino-1 : 2-benzanthracene (IV) is related to 3 : 4-benzpyrene (V) in the same way as pyrrole is to benzene, or carbazole is to phenanthrene, and although the two curves have certain differences, there are also some close similarities. The −NH− group does therefore simulate a −CH:CH− group to some extent, although much less closely than does a −S− group.

Experimental.—The ultra-violet absorption spectra were all determined, in absolute ethanol, by means of a Beckman DU Spectrophotometer.

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