

THE ULTRAVIOLET ABSORPTION SPECTRA OF AROMATIC HYDROCARBONS¹

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The ultraviolet absorption spectrum is of considerable value in the determination of the structure of an aromatic hydrocarbon. It has been used frequently for this purpose in synthetic organic chemistry, as well as in studies of natural products and of other substances of biological importance, such as the carcinogenic hydrocarbons.

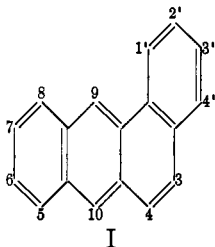
The influence of various structural factors on the absorption spectra of aromatic hydrocarbons is discussed, particularly with respect to changes produced in the spectra by the introduction of alkyl substituents, alicyclic groups, and alkene and cycloalkene groups. References to the absorption spectra of about three hundred and seventy hydrocarbons are collected in tables.

I. INTRODUCTION

This article is concerned primarily with an assessment of the possibilities and limitations of ultraviolet spectrophotometry as a method of characterizing aromatic hydrocarbons.

Although the mechanism of the absorption of ultraviolet light by organic molecules is still understood very imperfectly, much empirical knowledge has been accumulated, which has proved of considerable value in the elucidation of the structure of organic compounds (69, 71, 204). This is true particularly of substances which contain a simple chromophore, such as a carbonyl group, a conjugated diene, or an α,β -unsaturated carbonyl system, where the spectra are without fine structure and the chromophoric system can be identified by the position and intensity of the maximum, or occasionally two maxima, present.

The spectra of certain types of aromatic hydrocarbons, particularly those which contain several condensed benzene rings, may be exceedingly complex: e.g., the spectrum of 1,2-benzanthracene (I) (see figure 1). A dozen or more maxima may be present in the middle ultraviolet region between 2300 and 3900 Å. These maxima are usually attributed to several levels of vibrational activation associated with one or two primary electronic activation states, but



1,2-Benzanthracene

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details of the absorption process are still obscure. The absorption spectra of a great many hydrocarbons of this type have been measured; the spectra are characteristic of the particular system of fused aromatic rings involved and provide a reliable method for the identification of that ring system. Spectra of such a complex type cannot be described adequately by a list of the wave length and intensity of the maxima and minima, and similarities and differences between the spectra of two compounds can be discerned most readily if the two spectra are plotted on the same graph (figures 7 and 8). References to the spectra of unsubstituted hydrocarbons of this type are included in table 1. Alkyl, alicyclic, and alkene derivatives of these and other hydrocarbons are discussed elsewhere in this article.

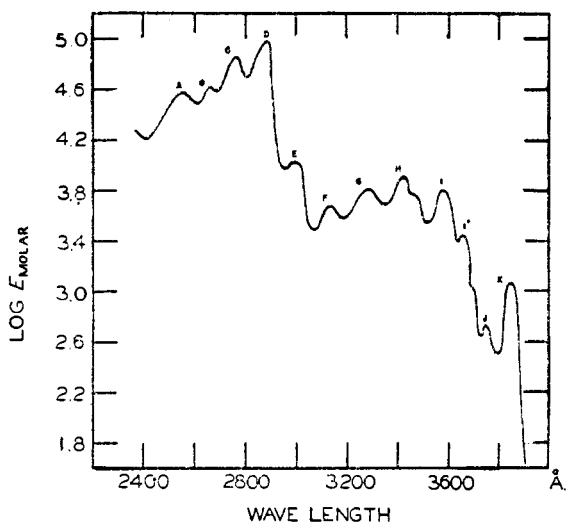
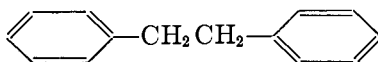
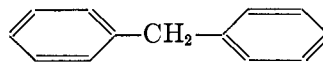


FIG. 1. Ultraviolet absorption spectrum of 1,2-benzanthracene in ethanol as solvent (132)

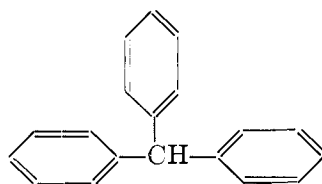
Polynuclear aromatic hydrocarbons in which phenyl groups are attached together through a single carbon-to-carbon linkage, as in diphenyl (LIIa), or in which the phenyl groups are linked through a chain of conjugated double bonds as in stilbene and 1,4-diphenylbutadiene, usually possess spectra of a much simpler type containing seldom more than three maxima (figure 2). If the phenyl groups are separated from one another by one or more methylene groups, there is negligible interaction between them, and aromatic systems in the same molecule, which are so separated, contribute additively to the total light absorption of the molecule. This is illustrated in figure 3, where the spectra of dibenzyl (II), diphenylmethane (III), and triphenylmethane (IV) are compared with that of a typical alkyl derivative of benzene.



II
Dibenzyl



III
Diphenylmethane



IV

Triphenylmethane

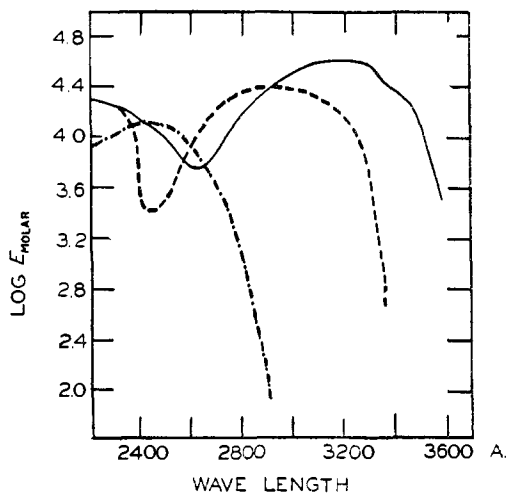


FIG. 2. Ultraviolet absorption spectra. —, 1,4-diphenyl-1,3-butadiene in ethanol as solvent (92); ----, *trans*-stilbene in ethanol as solvent (7); - · - ·, diphenyl in methanol as solvent (154).

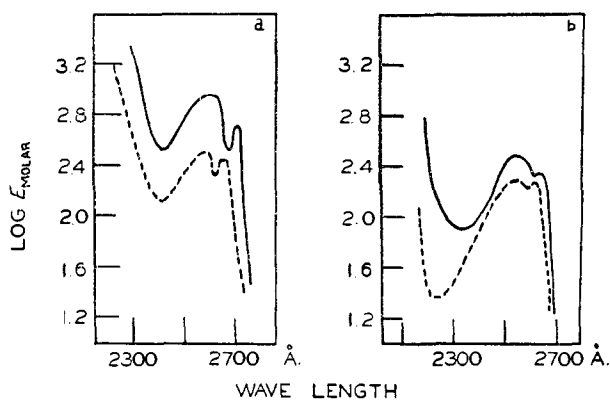


FIG. 3a. Ultraviolet absorption spectra. —, triphenylmethane in ethanol as solvent (217); ----, diphenylmethane in ethanol as solvent (217).

FIG. 3b. Ultraviolet absorption spectra. —, dibenzyl in methanol as solvent (154); ----, ethylbenzene in ethanol as solvent (97).

TABLE 1
References to the absorption spectra of unsubstituted aromatic hydrocarbons

COMPOUND		RING INDEX* NUMBER	REFERENCES
<i>A. One benzene ring:</i>			
C ₆ D ₆	Hexadeuterobenzene.....		(243 ^b)
C ₆ H ₆	Benzene.....	215	(10, 12 ^c , 18, 25, 29, 30, 35 ^{bd} , 36, 46, 59, 61, 71, 81, 94, 95, 99, 103, 104, 109, 110 ^{de} , 111, 112, 113, 115, 117, 121, 126, 138, 139, 140, 142, 144, 147, 149, 150, 152, 153, 157, 160, 161, 164, 166, 169, 170 ^f , 172, 173, 180, 184 ^{bd} , 189, 190, 191, 192, 197, 207, 224, 235, 244 ^b , 249, 250, 259, 260)
<i>B. Two benzene rings:</i>			
C ₁₀ H ₈	Naphthalene.....	1053	(9, 14 ^c , 29, 46, 55, 62, 81, 93, 103, 104, 109, 111, 115, 117, 150 ^e , 152 ^e , 157, 164, 169, 193, 202, 234 ⁱ , 248, 249, 250)
C ₁₂ H ₈	Biphenylene.....	1271	(34)
C ₁₂ H ₁₀	Diphenyl.....		(1, 18, 19, 37 ^b , 67, 71, 94, 95, 105, 111, 114, 115, 135, 154, 164, 186, 188, 193, 194, 197, 198, 204, 205, 207, 234, 247, 249, 250, 254)
C ₁₃ H ₁₀	Fluorene†.....	1775	(9, 26, 67, 131, 154, 170, 174, 207, 217, 234 ⁱ , 249)
<i>C. Three benzene rings:</i>			
C ₁₄ H ₁₀	Anthracene.....	2029	(14 ^c , 17 ^a , 25, 29, 33, 38, 41, 44, 46, 62, 66, 67, 90, 103, 104, 108, 109, 126, 148, 152, 155, 164, 169, 188, 202, 228, 234 ^j , 242, 246, 253)
C ₁₄ H ₁₀	Phenanthrene.....	2030	(8, 9, 14 ^c , 33, 38, 41, 45, 46, 50, 55, 67, 81, 98, 109, 112, 130, 152, 164, 169, 188, 202, 228, 234 ^j , 249)
C ₁₆ H ₁₀	Fluoranthrene.....	2568	(234 ^e)
C ₁₆ H ₁₂	1-Phenylnaphthalene.....		(131)
C ₁₆ H ₁₂	2-Phenylnaphthalene.....		(85, 131, 135)
C ₁₇ H ₁₂	1,2-Benzfluorene.....	2558	(14 ^c , 131, 170)
C ₁₇ H ₁₂	3,4-Benzfluorene.....	2560	(131, 170)
C ₁₈ H ₁₄	<i>o</i> -Diphenylbenzene.....		(198)
C ₁₈ H ₁₄	<i>m</i> -Diphenylbenzene (<i>m</i> -terphenyl).....		(94, 95, 198)
C ₁₈ H ₁₄	<i>p</i> -Diphenylbenzene (<i>p</i> -terphenyl).....		(94, 95, 198, 234)
C ₁₉ H ₁₄	9-Phenylfluorene.....		(217)
C ₁₉ H ₁₅	Triphenylmethyl (cation).....		(4, 90)
	(anion).....		(5, 90)
	(free radical).....		(5, 31, 90)
<i>D. Four benzene rings:</i>			
C ₁₆ H ₁₀	Pyrene†.....	2813	(14 ^c , 47, 91, 105, 169, 193, 202, 203, 234 ⁱ , 246, 249, 250)
C ₁₇ H ₁₂	7-Benzanthrene.....	2812	(51)
C ₁₈ H ₁₂	1,2-Benzanthracene.....	2805	(14 ^c , 33, 44, 132, 169, 227)
C ₁₈ H ₁₂	Chrysene.....	2806	(14 ^c , 28, 50, 55, 169, 227, 234 ^j , 249, 250)

TABLE 1—Continued

COMPOUND		RING INDEX* NUMBER	REFERENCES
<i>D. Four benzene rings:—Continued</i>			
C ₁₈ H ₁₂	3,4-Benzphenanthrene.....	2807	(170)
C ₁₈ H ₁₂	2,3-Benzanthracene (naphthacene)....	2804	(14 ^c , 46, 74 ^a , 106 ^b , 201, 203, 234 ^d)
C ₁₈ H ₁₂	Triphenylene.....	2808	(14 ^c , 55, 174)
C ₂₀ H ₁₄	9-Phenylanthracene.....		(33)
C ₂₀ H ₁₄	1,1'-Dinaphthyl.....		(2, 24, 188)
C ₂₀ H ₁₄	2,2'-Dinaphthyl.....		(2)
C ₂₁ H ₁₄	1',2'-Naphtho-2,3-fluorene.....	3157	(64, 170)
C ₂₁ H ₁₄	2',1'-Naphtho-1,2-fluorene.....	3161	(169)
C ₂₁ H ₁₄	1,2,3,4-Dibenzfluorene.....	3162	(174)
C ₂₁ H ₁₄	1,2,5,6-Dibenzfluorene.....	3165	(170)
C ₂₄ H ₁₆	Biacenaphthylidene (biacene, hepta- cyclyene).....	3673	(15)
C ₂₄ H ₁₈	4,4'-Diphenyldiphenyl (<i>p</i> -quater- phenyl).....		(1, 94, 95)
C ₂₄ H ₁₈	1,3,5-Triphenylbenzene.....		(234)
C ₂₅ H ₂₀	Tetraphenylmethane.....		(94)
<i>E. Five benzene rings:</i>			
C ₂₀ H ₁₂	3,4-Benzpyrene†.....	3382	(11, 14 ^c , 47, 137, 169, 171)
C ₂₀ H ₁₂	Perylene.....	3384	(14 ^c , 45, 68 ^a , 105, 106, 112, 188, 195 ^b , 196, 203, 234 ^e)
C ₂₂ H ₁₄	2,3,6,7-Dibenzanthracene (pentacene).....	3362	(46)
C ₂₂ H ₁₄	1,2,3,4-Dibenzanthracene.....	3367	(42, 44, 50, 55)
C ₂₂ H ₁₄	1,2,5,6-Dibenzanthracene.....	3369	(14 ^c , 42, 50, 73, 137, 157, 159, 169, 234 ^k)
C ₂₂ H ₁₄	1,2,6,7-Dibenzanthracene (2',3'-naph- tho-2,3-phenanthrene).....	3363	(43, 44, 50, 55)
C ₂₂ H ₁₄	1,2,7,8-Dibenzanthracene.....	3368	(51)
C ₂₂ H ₁₄	2,3,6,7-Dibenzphenanthrene (2',3'- naphtho-1,2-anthracene) (penta- phene).....	3364	(44, 46, 50, 53, 54)
C ₂₂ H ₁₄	1,2,7,8-Dibenzphenanthrene (picene).....	3370	(169, 226, 227)
C ₂₂ H ₁₄	1,2,6,7-Dibenzphenanthrene (2',3'- naphtho-1,2-phenanthrene).....	3365	(43, 44, 50, 55)
C ₂₂ H ₁₄	2,3,5,6-Dibenzphenanthrene (2',3'- naphtho-3,4-phenanthrene).....	3366	(56)
C ₂₅ H ₁₈	9,10-Diphenylanthracene.....		(105, 135, 202)
C ₃₀ H ₂₂	<i>p</i> -Quinquephenyl.....		(94)
<i>F. Six benzene rings:</i>			
C ₂₂ H ₁₂	Anthanthrene.....	3659	(50)
C ₂₂ H ₁₂	1,12-Benzperylene.....	3661	(45)
C ₂₄ H ₁₄	1,2,3,4-Dibenzpyrene†.....	3656	(47)
C ₂₄ H ₁₄	3,4,8,9-Dibenzpyrene†.....	3654	(47)
C ₂₄ H ₁₄	3,4,9,10-Dibenzpyrene†.....	3655	(47)
C ₂₄ H ₁₄	2',3'-Naphtho-3,4-pyrene†.....	3652	(47)
C ₂₄ H ₁₈	2,2'-Diphenyldiphenyl (2,2''-diphenylyldiphenyl).....		(1)
C ₂₆ H ₁₆	2',3'-Phenanthro-2,3-phenanthrene....	3644	(50)
C ₂₆ H ₁₆	2',1'-Anthraceno-1,2-anthracene.....	3645	(44, 50, 57)
C ₂₆ H ₁₆	2',3'-Phenanthro-1,2-anthracene (3,4- benzpentaphene).....	3646	(53)
C ₂₆ H ₁₆	1',2'-Anthraceno-1,2-anthracene.....	3647	(57)
C ₂₆ H ₁₆	1,2,3,4,5,6-Tribenzanthracene.....	3648	(50)
C ₂₈ H ₁₈	9,9'-Dianthryl.....		(17 ^g , 44, 135)

TABLE 1—*Concluded*

COMPOUND		RING INDEX* NUMBER	REFERENCES
<i>F. Six benzene rings:—Continued</i>			
C ₂₈ H ₁₈	9,9'-Diphenanthryl.....		(116)
C ₂₈ H ₁₈	1'-Phenyl-2',3'-indeno-3,4-pyrene.....		(47)
C ₃₀ H ₂₀	9,10-Diphenylnaphthacene.....		(75 ^a)
C ₃₀ H ₂₀	9,11-Diphenylnaphthacene.....		(75 ^a)
C ₃₀ H ₂₀	2,8-Diphenylchrysene.....		(168)
C ₃₆ H ₂₆	<i>p</i> -Sexiphenyl.....		(94)
<i>G. Seven benzene rings:</i>			
C ₂₄ H ₁₂	Coronene.....	3842	(187)
C ₂₈ H ₁₆	2,3,10,11-Dibenzperylene.....	3834	(45, 105)
C ₃₀ H ₁₈	3,4,9,10-Dibenzpentaphene.....		(53)
C ₃₄ H ₂₂	9,10-Di (1-naphthyl)anthracene.....		(52, 135)
C ₃₆ H ₁₈	Decacyclene.....	3954	(15)
<i>H. Eight benzene rings:</i>			
C ₄₂ H ₂₈	9,10,11,12-Tetraphenylnaphthacene (rubrene).....		(76 ^a , 114)
C ₄₈ H ₂₈	Fluorocyclene.....	3971	(15, 102, 252)
<i>I. Nine benzene rings:</i>			
C ₅₄ H ₃₈	<i>m</i> -Noviphenyl.....		(94)
<i>J. Ten benzene rings:</i>			
C ₅₄ H ₃₆	9,11-Diphenyl-10,12-bisdiphenylnaphthacene.....		(77 ^a)
C ₆₀ H ₄₂	<i>m</i> -Deciphenyl.....		(94)
<i>K. Eleven benzene rings:</i>			
C ₅₆ N ₄₆	<i>m</i> -Undeciphenyl.....		(94)
<i>L. Twelve benzene rings:</i>			
C ₆₆ H ₄₄	2,6,10,12-Tetraphenyl-9,11-bisdiphenylnaphthacene.....		(76 ^a)
C ₇₂ H ₅₀	<i>m</i> -Duodeciphenyl.....		(94)
<i>M-P. Thirteen-sixteen benzene rings:</i>			
C ₇₈ H ₅₄	<i>m</i> -Tredeciphenyl.....		(94)
C ₈₄ H ₅₈	<i>m</i> -Quatuordeciphenyl.....		(94)
C ₉₀ H ₆₂	<i>m</i> -Quindeciphenyl.....		(94)
C ₉₆ H ₆₆	<i>m</i> -Sedeciphenyl.....		(94)

^a Visible spectrum only.

^b Vapor-phase spectrum in medium ultraviolet (2200–4000 Å).

^c Spectrum of solution in concentrated sulfuric acid.

^d Spectrum of vapor in vacuum ultraviolet.

^e Spectra of vapor, and of solution in organic solvent.

^f Spectrum of solution at low temperature.

^g Spectrum of solid.

^h Spectrum of solution in concentrated sulfuric acid and in an organic solvent.

ⁱ Spectra of vapor, solution, and solid.

^k Spectra of solution and solid.

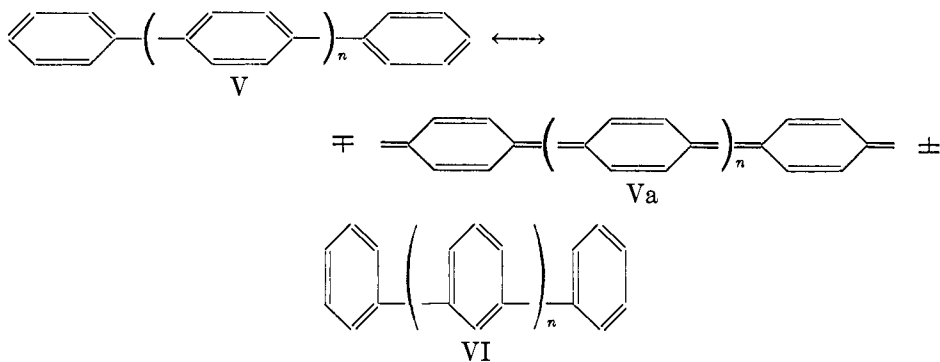
All other references are to spectra of solutions in organic solvents in the medium ultraviolet.

* This serial number serves to characterize further the ring system by reference to *The Ring Index* of A. M. Patterson and L. T. Capell. The Reinhold Publishing Corporation, New York (1940).

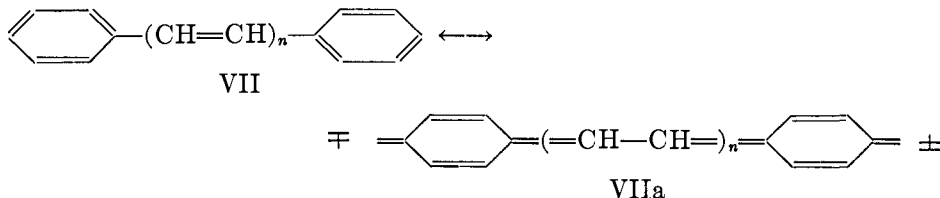
† Several earlier measurements of the spectrum of fluorene have been omitted, as later work has shown them to be inaccurate (9), owing to the presence of unsuspected impurities, possibly acenaphthylene.

‡ Some ambiguity concerning the numbering system of pyrene still remains. All the compounds in this table have been made to conform with the system used in this laboratory (see formula XIII), which is also that employed by Clar (47).

Attempts which have been made to establish relationships between the chemical structure of polynuclear aromatic hydrocarbons and their spectra have been successful only in certain limited cases. In a series of hydrocarbons which bear a certain structural resemblance to one another, definite and regular changes in passing from one hydrocarbon of the series to the next may sometimes be observed. Gillam and Hey (94) have examined the spectra of several *p*-polyphenyls (V) in which *n* has a value of 0, 1, 2, 3, and 4. All of these compounds possess similar spectra with a single broad maximum, the position of which is shifted to longer wave lengths as the length of the chain is increased. In the corresponding *m*-polyphenyl series (VI) the spectra of the members in which *n* has values of 1, 7, 8, 9, 10, 11, 12, 13, and 14 have been measured; here no change is observed in the position of the maximum on ascending the series, and the intensity agrees with that calculated on the assumption that each phenyl group contributes independently to the total absorption.

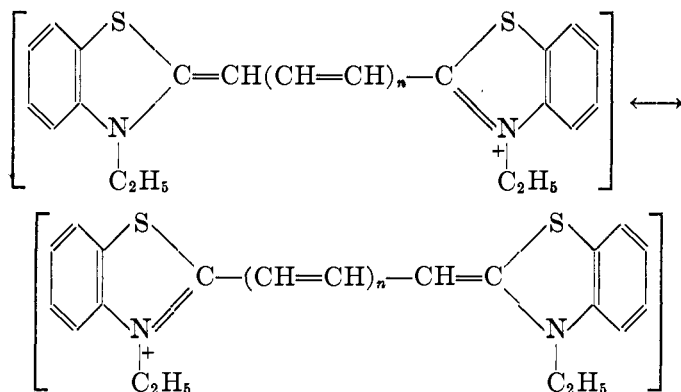


A second electronic structure (Va) may be written for the *p*-polyphenyls, and although this undoubtedly represents a condition of much higher energy than V, involving a separation of charge and the existence of the aromatic rings in a quinonoid form, it does permit the possibility of some resonance interaction to occur between the rings, and the *p*-polyphenyls can therefore be regarded as compounds of the same type as the α, ω -diphenylpolyenes (102) (VII).



In this latter series the quinonoid form (VIIa) differs less in energy from the benzenoid form, as only two benzenoid-quinonoid ring systems are concerned, and accordingly the α, ω -diphenylpolyenes may be considered as intermediate in character between the *p*-polyphenyls and the symmetrical heterocyclic carbocyanines for which two completely equivalent structures (VIII, VIIIa) can

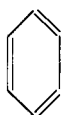
be written (27). In the symmetrical carbocyanines the addition of an extra double bond to the chain produces an enormous bathochromic shift (1000 Å.), i.e., the position of the absorption maximum is displaced to longer wave lengths by this amount. In the α,ω -diphenylpolyenes the effect is less, and in the *p*-polyphenyl series it is again diminished. It therefore appears that in the two hydrocarbon series V and VII the bathochromic effect of an added group



VIIIa

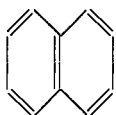
to the chain is influenced by the energy difference between the benzenoid and quinonoid structures which can be written for the molecule. In the *m*-polyphenyl series no bathochromic effect is observed, since meta-substitution makes a quinonoid form impossible; the linkage between the aromatic rings is completely aliphatic in character.

Some relationships between the structure and spectra can also be discerned in certain groups of hydrocarbons containing condensed aromatic ring systems. Clar (46) has examined the series benzene, naphthalene, anthracene, and naph-



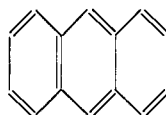
IX

Benzene



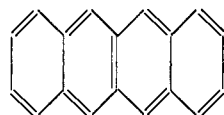
X

Naphthalene



XI

Anthracene



XII

Naphthacene

thacene (IX to XII) and has noted a progressive shift of certain regions of the spectra to longer wave lengths with the addition of each aromatic nucleus, accompanied by comparatively little change in the general appearance of the curve. The position of the absorption maximum of lowest frequency (ν_p) he finds will fit an equation of the type

$$\sqrt{\frac{R_p}{\nu_p}} = n$$

where R_p is a numerical constant and n an integer. Attention is drawn to certain resemblances between this relationship and Moseley's rule for atomic

spectra. In a later series of papers (48, 49, 50) Clar extends this analysis to other types of polynuclear aromatic hydrocarbons.

The relationships between structure and spectra illustrated above apply only to carefully selected groups of compounds, and no theory of general application has yet been developed which will account for the position and intensity of the various absorption maxima in terms of the molecular or electronic structure of an aromatic hydrocarbon molecule. Förster (89), Sklar (235, 237), and Spomer and coworkers (243, 244) have attempted to calculate the position of the absorption bands of benzene by quantum-mechanical methods, but the results so far obtained do not provide a precise interpretation of the spectra. The most promising method of attack would seem to be that based on the molecular orbital concept, the general principles of which have been reviewed by Price (199). Mulliken, in a series of papers (181, 183), has discussed the application of this principle to organic compounds including benzene (182), but although these studies may lead eventually to an understanding of the fundamental mechanism of the absorption of ultraviolet radiation by the bonding electrons of the molecule, such progress as has been recorded so far is of little value to those interested primarily in the use of absorption spectra as a means of identifying molecular structures.

It should be observed that the extensive analyses of the infrared and Raman spectra of benzene and the several deuterobenzenes which have been carried out by Ingold and coworkers (6) and by Wilson (255, 256) yield information concerning the modes of vibration of the atoms in the electronic ground state of the molecule but tell nothing of the mechanism of electronic activation.

The polynuclear aromatic hydrocarbons of the type which contain condensed rings and which give rise to spectra containing much fine structure include carcinogenic substances and other compounds of biological interest. It is this type of hydrocarbon for which the spectrographic method of structure determination is most effective. The study of these compounds may be approached empirically on the assumption that each system of condensed aromatic rings gives rise to its own characteristic spectrum.³

In many cases where resort is made to absorption spectra as a method of structure determination, the compound of uncertain structure may be some derivative of a hydrocarbon. It is important therefore to have some knowledge of the manner and extent to which various substituents modify the spectrum of the unsubstituted hydrocarbon, for only in those cases where the introduction of a particular substituent is known not to alter the spectrum significantly can the substitution product be compared directly with alternative possible parent hydrocarbons. In this article the discussion is limited to the effect of alkyl, alicyclic, and alkene substituents on the spectra of aromatic hydrocarbons, but

³ The differences between the spectra are in most cases sufficiently great to enable the particular ring system to be characterized directly by inspection of the absorption curve. In certain of the more complex condensed ring systems ambiguity is possible, but usually there is supporting evidence from analytical data or other sources which restrict the possible structure to one of a relatively small number of possibilities.

it is hoped that this may later be extended to include derivatives containing functional substituents, and to quinones.

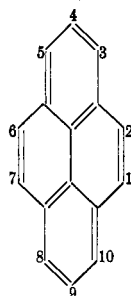
As might be anticipated, more extensive investigations have been made of derivatives of benzene than of polynuclear aromatic hydrocarbons (60, 178, 180, 191, 236, 237, 251). Many substituents appear to modify the spectrum of benzene to a much greater extent than they affect those of more complex hydrocarbons; this is true particularly of their effect on the intensity of absorption. The position and intensity of the main absorption maximum of some benzene derivatives in the middle ultraviolet (180) are compared with one of the maxima

TABLE 2
Effect of substituents on the absorption spectra of benzene and 1,2-benzanthracene

SUBSTANCE	MAXIMUM		INCREASE IN INTEN- SITY ON SUBSTITU- TION	SUBSTANCE	MAXIMUM*		INCREASE IN INTEN- SITY ON SUBSTITU- TION
	λ	E_{molar}			λ	E_{molar}	
	\AA .		<i>per cent</i>		\AA .		<i>per cent</i>
Benzene.....	2550	302		1,2-Benzanthracene.....	3410	7413	
<i>p</i> -Xylene.....	2680	479	59	9,10-Dimethyl-1,2-benz- anthracene.....	3640	8710	17.5
Benzoic acid....	2670	1778	430	7-Cholanthroic acid....	3625	7762	4.6
Phenol.....	2730	1778	430	3-Hydroxy-1,2-benzan- thracene.....	3380	8710	17.5
Anisole.....	2720	2239	580	3-Methoxy-1,2-benzan- thracene.....	3345	7943	7.1

* Maximum H (see figure 1).

of a similar derivative of 1,2-benzanthracene (I) in table 2 (132, 133). Whereas the molecular extinction of the benzene maximum may be raised by 59 to 480 per cent by the introduction of certain substituents, the same groups raise the intensity of the 1,2-benzanthracene maximum by only 4.6 to 17.5 per cent. The benzene molecule is much more sensitive to the disturbing influence of substituents than most polynuclear aromatic hydrocarbons, probably on account of its high symmetry. In view of this, one cannot predict the effect of a substituent on the spectrum of a polynuclear aromatic hydrocarbon from analogy with the effect of the same group on the benzene spectrum.



XIII

II. ALKYL DERIVATIVES

The substitution of an alkyl group for a hydrogen atom attached directly to the carbon atom of a chromophore usually produces a shift of the spectrum to longer wave lengths but does not otherwise alter the general appearance of the absorption curve. In the case of α,β -unsaturated carbonyl groups, Woodward (261) has shown that the magnitude of the bathochromic shift is independent of the position of substitution in the ethylenic double bond and is also independent of the size and nature of the alkyl group which is introduced; the shift is the same whether this be a simple methyl group or an alicyclic part of a sterol structure. In the case of the conjugated dienes both the position and the nature of the substituent modify the spectrum (26). The introduction of an alkyl substituent into a polynuclear aromatic hydrocarbon produces a bathochromic shift, but does not change the characteristic shape of the curve; the spectra of alkyl-substituted aromatic hydrocarbons may be related directly to the spectra of the corresponding unsubstituted hydrocarbon⁴. Conrad-Billroth (62) has developed a somewhat complex system of empirical rules based on a principle of vector analysis whereby the bathochromic effect produced in a given compound by certain substituents may be calculated. This was developed initially for the substitution of alkyl groups and halogens in benzene and has since been extended to naphthalene, anthracene, and pyrene derivatives (91).

Only in a few of the many series of polynuclear aromatic ring systems have a sufficient number of alkyl derivatives been examined to give some indication of the relation between the degree of bathochromic shift and the position of substitution. Askew (8) has published data on several alkylphenanthrenes, Morton and de Gouveia (176) and de Laszlo (150) on alkylnaphthalenes, Brode and Patterson (28) on alkylchrysenes, and Mayneord and Roe (169, 170) and Jones (132, 133) on alkyl-1,2-benzanthracenes.

The absorption spectrum of 1,2-benzanthracene (I), figure 1, contains twelve maxima, and the position and intensity of two of the more prominent maxima (D and H) of twenty-five alkyl and alicyclic derivatives of 1,2-benzanthracene are recorded in table 3, together with references from which fuller details of the spectra may be obtained. Inspection of table 3, supplemented by examination of the original curves, shows that in all of these derivatives the general character of the spectrum of the unsubstituted hydrocarbon is preserved. The resolution of the more prominent maxima (A B C D G H I) is not greatly influenced by the presence of the substituents, and the molar extinction coefficients of the D maximum all lie between 66,000 and 112,000, those of the H maximum between 6,000 and 10,000. The variations which are observed in the number of maxima which can be resolved are chiefly due to differences in the small bands in regions where the general slope of the absorption curve is steep (E and J), which also show greater variations in intensity than do the other maxima. Morton and de Gouveia (176) observed in the naphthalene series similar variations in maxima which occur in a general region of rapidly increasing intensity of absorption.

⁴ Certain exceptions to this statement are discussed on page 32.

These variations are of a minor character and do not prejudice the value of absorption spectra as a method of characterizing ring structures, since it is the general shape of the absorption envelope rather than details of one or two particular maxima which should form a basis for the comparison of hydrocarbon

TABLE 3
Position and intensity of the D and H maxima in the spectra of alkyl-1,2-benzanthracenes
Solvent, ethanol

COMPOUND	MAXIMUM D		MAXIMUM H		NUMBER OF MAXIMA RESOLVED	REFERENCES
	λ	E_{molar}	λ	E_{molar}		
	\AA .		\AA .			
1,2-Benzanthracene.....	2870	89100	3410	7410	12	(132)
1'-Methyl-1,2-benzanthracene.....	2875	79400	3410	7590	11	(132)
7-Methyl-1,2-benzanthracene.....	2880	83200	3410	6030	13	(169)
4-Methyl-1,2-benzanthracene.....	2885	91200	3420	6760	11	(132)
6-Methyl-1,2-benzanthracene.....	2890	79400	3440	6460	11	(169)
5-Methyl-1,2-benzanthracene.....	2890	85100	3460	8130	12	(132)
8-Methyl-1,2-benzanthracene.....	2900	91200	3460	7590	12	(132)
9-Methyl-1,2-benzanthracene.....	2905	87100	3515	7590	9	(132)
10-Methyl-1,2-benzanthracene.....	2915	95500	3545	8710	12	(132)
6-Isopropyl-1,2-Benzanthracene.....	2895	79400	3420	6460	11	(170)
10-Isopropyl-1,2-benzanthracene.....	2920	112200	3530	10000	10	(169)
6,7-Dimethyl-1,2-benzanthracene.....	2880	93300	3430	7080	11	(169)
5,8-Dimethyl-1,2-benzanthracene.....	2925	85100	3520	7590	10	(132)
5,10-Dimethyl-1,2-benzanthracene.....	2945	85100	3580	9330	10	(132)
8,10-Dimethyl-1,2-benzanthracene.....	2950	91200	3560	9330	11	(132)
9,10-Dimethyl-1,2-benzanthracene.....	2965	79400	3640	8710	9	(132)
10-Methyl-3'-isopropyl-1,2-benzanthracene.....	2940	97700	3530	8510	10	(133)
6,7-Cyclopenteno-1,2-benzanthracene....	2880	93300	3430	7080	9	(169)
5,6-Cyclopenteno-1,2-benzanthracene....	2930	93300	3520	7080	10	(169)
Cholanthrene.....	2950	75900	3580	8910	10	(85, 170)
22-Methylcholanthrene.....	2960	75900	3580	7590	10	(82)
20-Methylcholanthrene.....	2970	89100	3590	7940	10	(169)
6-Methylcholanthrene.....	2975	74100	3600	9330	10	(82, 133)
6,22-Dimethylcholanthrene.....	2985	66100	3600	6920	10	(82, 133)
6,20-Dimethylcholanthrene.....	2985	95500	3600	8320	10	(82, 133)
4,10-Dimethylene-1,2-benzanthracene....	2935	107000	3575	6920	12	(88)

spectra. In the naphthalene, chrysene, and phenanthrene series, the intensities of the main maxima are constant to within the same range as in the alkyl-1,2-benzanthracenes and the similarity of the shape of the absorption curve is equally well maintained.

The magnitude of the bathochromic shift produced by alkyl substitution is

influenced considerably by the position of the entering group, which usually affects all the maxima to the same relative degree. In table 3, the eight monomethyl derivatives of 1,2-benzanthracene are arranged in order of the increasing bathochromic effect on the D maximum (figure 1); the magnitude of the effect on the H maximum is in the same order, although the shape of the absorption curve suggests that the two maxima are probably associated with different primary electronic activation processes. Substitution at the 1'-position exerts the least effect ($\Delta\lambda_D = 5 \text{ \AA.}$), while substitution at the meso 9- and 10-positions produces the greatest shifts ($\Delta\lambda_D = 45 \text{ \AA.}$ for 10-methyl-1,2-benzanthracene and 95 \AA. for 9,10-dimethyl-1,2-benzanthracene). The spectra of the 1'-methyl derivative (XIV) and the 9,10-dimethyl derivative (XV), which represent the

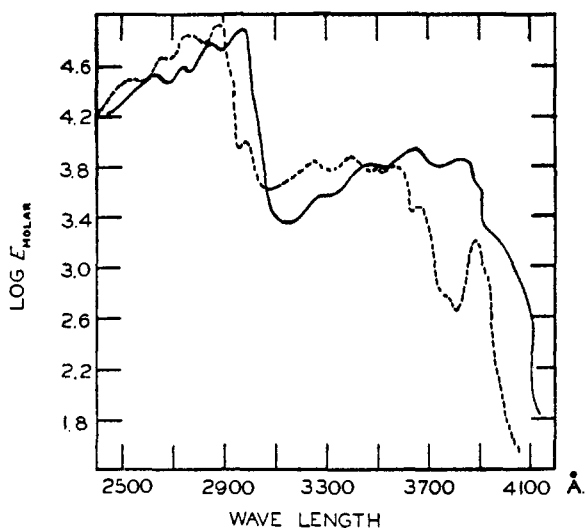
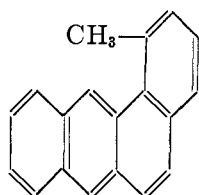


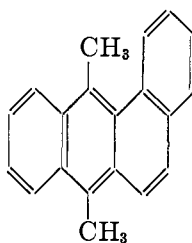
FIG. 4. Ultraviolet absorption spectra. —, 9,10-dimethyl-1,2-benzanthracene in ethanol as solvent (132); ----, 1'-methyl-1,2-benzanthracene in ethanol as solvent (132).

methyl compounds with minimum and maximum shifts, respectively, are given in figure 4. All the other eleven monomethyl- and dimethyl-1,2-benzanthracenes have spectra which lie between these two curves.



XIV

1'-Methyl-1,2-benzanthracene



XV

9,10-Dimethyl-1,2-benzanthracene

The effect of increase in the length of the alkyl side chain has been investigated in the benzene series by Pestemer and Gübitz (189), who have recorded the spectra of all the *n*-alkylbenzenes up to and including the *n*-hexyl derivative. The fine structure of the benzene spectrum is greatly reduced in the ethyl derivative and disappears in the higher members, except for one sharp peak on the long-wave-length side of the main maximum which persists throughout the series. The increase in the bathochromic shift becomes progressively less as the side chain lengthens.

The cause of this bathochromic shift is still obscure. Mulliken, Rieke, and Brown (183), from quantum-mechanical calculations based on the concept of molecular orbitals, consider that interaction between the electrons of the ring

TABLE 4
Comparison of the position and intensity of the absorption maxima of 3-aminopyrene hydrochloride and 3-methylpyrene†*

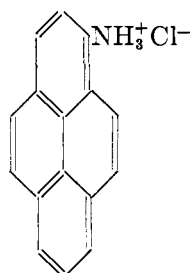
MAXIMA	WAVE LENGTH		INTENSITY (Log E_{molar})	
	—NH ₃ ⁺	—CH ₃	—NH ₃ ⁺	—CH ₃
	Å.	Å.		
A.....	2330	2330	4.68	4.68
B.....	2415	2415	4.92	4.94
C.....	2530	2540	4.06	4.06
D.....	2640	2650	4.40	4.42
E.....	2745	2760	4.64	4.77
F.....	2970	2970	3.62	3.64
G.....	3100	3120	4.02	4.06
H.....	3240	3270	4.44	4.44
I.....	3400	3435	4.56	4.58
J.....	3530	3550	3.04	3.25
K.....	3590	3620	2.86	2.90
L.....	3660	3680	2.56	2.64
M.....	3740	3765	2.64	2.97

* Solvent 2 *N* hydrochloric acid in 50 per cent aqueous ethanol.

† Solvent absolute ethanol.

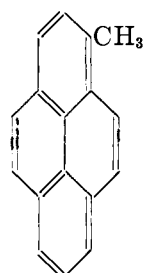
structure and those involved in the C—H linkages of the alkyl groups (hyper-conjugation) is insufficient to account for shifts of the observed order of magnitude. Price (199) considers that the dipole effect of the alkyl group may be involved, but, if this be so, it is difficult to understand why the absorption spectra of the positive ions of aromatic amines should resemble those of the parent hydrocarbon so closely (258, 263). The polar effect of the positive charge on the nitrogen atom must produce a greater electron displacement in the —C—NH₃⁺ linkage than the relatively weak dipole displacement in the —C—CH₃ linkage, yet, in several cases, the —NH₃⁺ substituent has been observed to produce bathochromic shifts in aromatic hydrocarbons no larger than those produced by introduction of a methyl substituent at the same position. This is illustrated in table 4, where the wave lengths and intensities of the maxima

of 3-aminopyrene hydrochloride (XVI) and 3-methylpyrene (XVII) are compared (263).



XVI

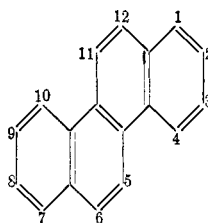
3-Aminopyrene hydrochloride



XVII

3-Methylpyrene

The positions at which the methyl group exerts its maximum bathochromic effect in the 1,2-benzanthracene series happen also to be the centers of maximum chemical reactivity in the typical aromatic substitution reactions and the positions most readily susceptible to oxidation. This suggests that the bathochromic effect of an alkyl substituent may be associated with the electron density at the point of substitution. This argument fails, however, if an attempt is made to use it to predict the effect of alkyl groups on the spectrum of chrysene.



XVIII

Chrysene

Chrysene (XVIII) forms two stable quinones, 5,6- and 6,12-chrysenequinones (83). From analogy with 1,2-benzanthracene it might be predicted that the 5-methyl- and 6-methyl-chrysenes should show greater bathochromic effects than the other monomethyl derivatives. The maximum shifts are actually observed in the spectra of 4- and 5-methyl-chrysenes (28); that of 6-methyl-chrysene is considerably less. Brode and Patterson (28) suggest that the greater bathochromic shifts of the 4- and 5-methyl-chrysenes are due to steric hindrance. Considerable interference exists between the hydrogen atoms and the methyl groups at the 4- and 5-positions, which might play a part in modifying the spectra; such hindrance will be greatly increased in the case of 4,5-dimethylchrysene, where changes in the spectrum of a greater magnitude have actually been observed (134).

TABLE 5

References to the absorption spectra of alkyl derivatives of aromatic hydrocarbons

COMPOUND		REFERENCES
<i>A. Benzene chromophore; one benzene ring:</i>		
C ₇ H ₈	Toluene.....	(10, 12 ^a , 19, 29, 61, 71, 105, 111, 112, 115, 138, 152, 160, 161, 166, 179, 180, 189, 206, 221, 249, 250, 259)
C ₈ H ₁₀	Ethylbenzene.....	(3, 10, 97, 105, 123, 160, 166, 189, 204, 205, 206, 208, 214, 215, 219, 249, 250, 258)
C ₈ H ₁₀	<i>o</i> -Xylene.....	(39, 61, 105, 111, 115, 138, 160, 179, 180, 204, 209, 216, 259)
C ₈ H ₁₀	<i>m</i> -Xylene.....	(39, 61, 105, 108, 111, 115, 138, 160, 179, 180, 221, 259)
C ₈ H ₁₀	<i>p</i> -Xylene.....	(29, 39, 61, 105, 109, 111, 115, 138, 160, 179, 180, 259)
C ₉ H ₁₂	<i>n</i> -Propylbenzene.....	(10, 71, 105, 119, 189, 197)
C ₉ H ₁₂	1,2,3-Trimethylbenzene (hemimellitene).....	(61, 179)
C ₉ H ₁₂	1,2,4-Trimethylbenzene (pseudocumene).....	(10, 61, 179, 260)
C ₉ H ₁₂	1,3,5-Trimethylbenzene (mesitylene).....	(10, 13 ^a , 61, 105, 198, 241, 260)
C ₁₀ H ₁₄	<i>n</i> -Butylbenzene.....	(10, 105, 108, 189)
C ₁₀ H ₁₄	1,2,3,4-Tetramethylbenzene (prehnitene).....	(61)
C ₁₀ H ₁₄	1,2,3,5-Tetramethylbenzene (isodurene).....	(61, 179)
C ₁₀ H ₁₄	1,2,4,5-Tetramethylbenzene (durene).....	(61, 155, 179)
C ₁₀ H ₁₄	1-Methyl-4-isopropylbenzene (<i>p</i> -cymene).....	(21)
C ₁₀ H ₁₄	Diethylbenzene (mixed isomers).....	(10)
C ₁₁ H ₁₆	<i>n</i> -Amylbenzene.....	(10, 105, 189)
C ₁₁ H ₁₆	Pentamethylbenzene.....	(61, 179)
C ₁₂ H ₁₈	<i>n</i> -Hexylbenzene.....	(105, 189)
C ₁₂ H ₁₈	Hexamethylbenzene.....	(61, 71, 78, 106, 152, 179, 230, 231, 234)
C ₁₂ H ₁₈	Triethylbenzene (mixed isomers).....	(10)
C ₁₈ H ₃₀	Hexaethylbenzene.....	(231)
C ₂₄ H ₄₂	<i>n</i> -Octadecylbenzene.....	(108)
<i>B. Benzene chromophore; two benzene rings:</i>		
C ₁₈ H ₁₂	Diphenylmethane.....	(19, 37, 94, 106, 111, 112, 115, 152, 154, 167, 185, 197, 204, 205, 207, 215, 217, 234 ^b , 241, 247, 249, 250)
C ₁₄ H ₁₄	Dibenzyl.....	(3, 7, 94, 106, 111, 153, 154, 204, 205, 212, 215, 234 ^b , 241, 250)
C ₁₈ H ₁₈	1,4-Diphenylbutane.....	(204, 205, 212, 215)
C ₁₆ H ₁₈	<i>p, p'</i> -Dimethyldibenzyl.....	(213)
C ₁₈ H ₂₂	1,6-Diphenylhexane.....	(212, 215)
C ₁₈ H ₂₂	<i>p, p'</i> -Diethyldibenzyl.....	(213)
C ₁₆ H ₂₄	Dimesitylmethane.....	(241)
C ₂₆ H ₂₆	1,8-Diphenyloctane.....	(215)
C ₂₆ H ₂₆	<i>sym</i> -Dimesitylethane.....	(241)
C ₂₂ H ₃₀	1,4-Dimesityl- <i>n</i> -butane.....	(241)

TABLE 5—Continued

COMPOUND		REFERENCES
<i>C. Benzene chromophore; three benzene rings:</i>		
C ₁₉ H ₁₆	Triphenylmethane.....	(94, 112, 152, 185, 217, 234)
C ₁₉ H ₁₆	Phenyl- <i>p</i> -diphenylmethane.....	(247, 249, 250)
<i>D. Benzene chromophore; four benzene rings:</i>		
C ₂₅ H ₂₀	Tetraphenylmethane.....	(94)
<i>E. Diphenyl chromophore:</i>		
C ₁₄ H ₁₄	2,2'-Dimethyldiphenyl.....	(186)
C ₁₄ H ₁₄	3,3'-Dimethyldiphenyl.....	(186)
C ₁₄ H ₁₄	4,4'-Dimethyldiphenyl.....	(186)
C ₁₆ H ₁₈	2,2', 4,4'-Tetramethyldiphenyl.....	(186)
C ₁₈ H ₂₂	2,2', 4,4', 6,6'-Hexamethyldiphenyl (dimesityl).....	(186, 198)
<i>F. Naphthalene chromophore:</i>		
C ₁₁ H ₁₀	1-Methylnaphthalene.....	(104, 111, 115, 150 ^b , 165, 193, 248, 249)
C ₁₁ H ₁₀	2-Methylnaphthalene.....	(104, 111, 115, 150 ^b , 165)
C ₁₂ H ₁₂	1,6-Dimethylnaphthalene.....	(40, 150 ^b)
C ₁₂ H ₁₂	2,6-Dimethylnaphthalene.....	(40, 150 ^b)
C ₁₂ H ₁₂	2,7-Dimethylnaphthalene.....	(150 ^b)
C ₁₃ H ₁₄	1,3,5-Trimethylnaphthalene.....	(176)
C ₁₃ H ₁₄	1,3,8-Trimethylnaphthalene.....	(176)
C ₁₃ H ₁₄	2,3,5-Trimethylnaphthalene.....	(176)
C ₁₃ H ₁₄	1-Methyl-5-ethylnaphthalene.....	(176)
C ₁₃ H ₁₄	1-Methyl-6-ethylnaphthalene.....	(176)
C ₁₃ H ₁₄	1-Methyl-7-ethylnaphthalene.....	(176)
C ₁₅ H ₁₈	1,6-Dimethyl-4-isopropylnaphthalene (cadalene).....	(176)
C ₁₇ H ₁₄	1-Benzyl-naphthalene.....	(51, 248, 249, 250)
C ₂₂ H ₁₈	<i>sym</i> -Di-1-naphthylethane.....	(2)
C ₂₂ H ₁₈	<i>sym</i> -Di-2-Naphthylethane.....	(2)
<i>G. Anthracene chromophore:</i>		
C ₁₅ H ₁₂	2-Methylantracene (tectonene).....	(105, 202)
C ₁₅ H ₁₂	9-Methylantracene.....	(253)
C ₁₆ H ₁₄	9,10-Dimethylantracene.....	(253)
C ₁₆ H ₁₄	9-Ethylantracene.....	(253)
C ₁₇ H ₁₆	9-Methyl-10-ethylantracene.....	(253)
C ₂₂ H ₂₆	9,10-Diisobutylnanthracene.....	(167)
<i>H. Phenanthrene chromophore:</i>		
C ₁₅ H ₁₂	1-Methylphenanthrene.....	(96)
C ₁₅ H ₁₂	9-Methylphenanthrene.....	(8)
C ₁₆ H ₁₄	1,2-Dimethylphenanthrene.....	(8)
C ₁₆ H ₁₄	1,3-Dimethylphenanthrene.....	(8)
C ₁₆ H ₁₄	1,7-Dimethylphenanthrene (piman- threne).....	(8)
C ₁₆ H ₁₄	1,8-Dimethylphenanthrene.....	(8)
C ₁₆ H ₁₄	1,9-Dimethylphenanthrene.....	(8, 14 ^a)
C ₁₆ H ₁₄	2,3-Dimethylphenanthrene.....	(8)
C ₁₆ H ₁₄	2,5-Dimethylphenanthrene.....	(8)
C ₁₆ H ₁₄	4,9-Dimethylphenanthrene.....	(8)
C ₁₆ H ₁₄	1-Ethylphenanthrene.....	(8)

TABLE 5—Continued

COMPOUND		REFERENCES
<i>H. Phenanthrene chromophore:—(Continued)</i>		
C ₁₇ H ₁₆	1,2,7-Trimethylphenanthrene.....	(8)
C ₁₇ H ₁₆	1,3,7-Trimethylphenanthrene.....	(8)
C ₁₇ H ₁₆	1,4,7-Trimethylphenanthrene.....	(8)
C ₁₇ H ₁₆	1,6,7-Trimethylphenanthrene.....	(8)
C ₁₇ H ₁₆	1,2,8-Trimethylphenanthrene (methyl- pimanthrene).....	(8, 233)
C ₁₇ H ₁₆	7-Methyl-1-ethylphenanthrene (homo- pimanthrene).....	(8)
C ₁₈ H ₁₆	3'-Methylcyclopentenophenanthrene....	(100, 233)
C ₁₈ H ₁₆	7-Methylcyclopentenophenanthrene....	(141)
C ₁₈ H ₁₈	1-Methyl-7-isopropylphenanthrene (retene).....	(8)
C ₁₉ H ₂₀	1-Ethyl-7-isopropylphenanthrene (homoretene).....	(8)
<i>I. Chrysene chromophore:</i>		
C ₁₉ H ₁₄	1-Methylchrysene.....	(28)
C ₁₉ H ₁₄	2-Methylchrysene.....	(28)
C ₁₉ H ₁₄	3-Methylchrysene.....	(28)
C ₁₉ H ₁₄	4-Methylchrysene.....	(28)
C ₁₉ H ₁₄	5-Methylchrysene.....	(28, 134)
C ₁₉ H ₁₄	6-Methylchrysene.....	(28)
C ₂₀ H ₁₆	4,5-Dimethylchrysene.....	(134)
C ₂₀ H ₁₆	5,6-Dimethylchrysene.....	(134)
<i>J. 1,2-Benzanthracene chromophore: see table 3</i>		
<i>K. Pyrene chromophore:</i>		
C ₁₇ H ₁₂	2-Methylpyrene.....	(169)
C ₁₇ H ₁₂	3-Methylpyrene.....	(91, 263)
C ₁₇ H ₁₂	4-Methylpyrene.....	(91, 263)
<i>L. Other chromophores:</i>		
C ₉ H ₁₀	<i>o</i> -Methylstyrene.....	(216, 218)
C ₁₀ H ₁₀	1-Methyl-1,2-indene.....	(218)
C ₁₀ H ₁₂	α -Methyl- <i>o</i> -methylstyrene.....	(218)
C ₁₀ H ₁₂	<i>p</i> -Methylpropenylbenzene.....	(210)
C ₁₁ H ₁₂	1-Methyl-3,4-dihydronaphthalene.....	(218)
C ₁₄ H ₁₄	7-Methylperinaphthene.....	(67, 263)
C ₁₅ H ₁₄	α -Methylstilbene.....	(7, 71, 90, 152, 154, 204, 206, 214)
C ₁₅ H ₁₄	<i>p</i> -Methylstilbene.....	(7, 152)
C ₁₆ H ₁₆	α,β -Dimethylstilbene (two isomers)....	(7, 90, 146, 152, 204, 249)
C ₂₀ H ₁₆	1',10-Dimethyl-2,3-benzanthracene....	(86)
C ₂₁ H ₁₄	8(or 9?)-Methyl-3,4-benzpyrene.....	(174)
C ₂₁ H ₁₄	2-Methyl-3,4-benzpyrene.....	(137)
C ₂₂ H ₁₆	7-Methylnaphthafuorene.....	(174)
C ₂₂ H ₁₆	2'-Methyl-1,2,5,6-dibenzanthracene....	(20)
C ₂₃ H ₁₆	3'-Methyl-1,2,5,6-dibenzanthracene....	(20)
C ₂₄ H ₁₈	7,7'-Dimethyl-2',3'-naphtho-3,4-phen- anthrene.....	(56)
C ₂₄ H ₁₈	9,10-Dimethyl-1,2,5,6-dibenzanthra- cene.....	(169)

TABLE 5—*Concluded*

COMPOUND		REFERENCES
C ₂₄ H ₁₈	6,7'-Dimethyl-2',3'-naphtho-1,2-anthracene.....	(54)
C ₂₄ H ₁₈	7,7'-Dimethyl-2',3'-naphtho-1,2-anthracene.....	(44, 54)
C ₂₅ H ₂₀	3,9,10-Trimethylpicene.....	(226)
C ₂₅ H ₂₂	5-Methyl-8-isopropyl-2',1'-naphtho-1,2-fluorene.....	(169)

^a Spectrum of solution in concentrated sulfuric acid.

^b Spectra of vapor and of solution in an organic solvent.

All other references are to spectra of solution in organic solvents in the medium ultraviolet.

Attempts to relate the magnitude of the bathochromic effect to steric factors in a similar manner fail completely in the 1,2-benzanthracene series. The bathochromic shift produced by a methyl substituent at the unhindered 10-position is greater than that caused by substitution at the hindered 9-position, while in 1'-methyl-1,2-benzanthracene, in which the steric relationship between the methyl group and the hydrogen at 9 is similar to that in 4-methyl- and 5-methyl-chrysenes, the observed bathochromic shift is actually *less* than for any other position which has been measured. In the spectra of 9-thiocyano- and 9-thiocyano-10-methyl-1,2-benzanthracenes the steric factors apparently do become significant, owing to the greater size of the substituent group (136). It can only be concluded that neither dipole effects, hyperconjugation, the chemical reactivity of the position of substitution, nor steric factors alone can explain adequately the relative magnitude of these bathochromic shifts.

In table 5 references to the spectra of alkyl derivatives of aromatic hydrocarbons are collected.

III. ALICYCLIC DERIVATIVES

Absorption spectra have been used extensively in the elucidation of the structure of hydrocarbons derived from natural products and in determining the positions of attack of hydrogen atoms during the partial hydrogenation of polynuclear aromatic hydrocarbons. This is illustrated in figures 5 and 6, where the absorption curves of several partial hydrogenation products of 20-methylcholanthrene and 10-methyl-1,2-benzanthracene (XIX to XXIII) are compared with the spectra of the corresponding unsubstituted aromatic parent hydrocarbons (85) (XIXa to XXIIIa). Pestemer and Manchen (193) showed that the so-called dihydropyrene and tetrahydropyrene obtained by partial hydrogenation of pyrene have spectra which are identical with those given by mixtures of 48 per cent hexahydropyrene and 52 per cent pyrene, and 75 per cent hexahydropyrene and 25 per cent pyrene, respectively, and are therefore only mixtures.

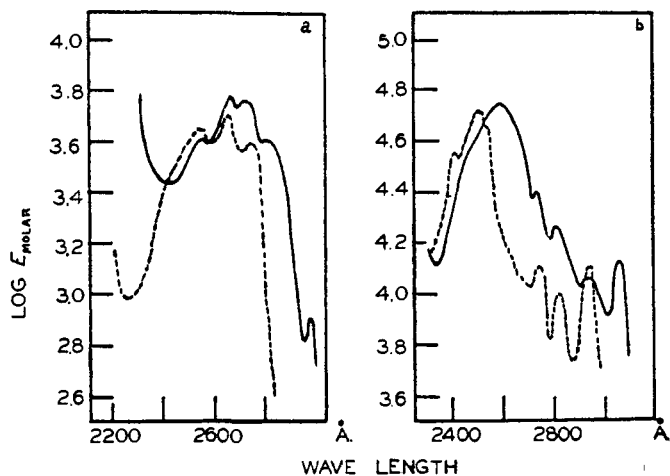


Fig. 5a. Ultraviolet absorption spectra. —, compound XX in ethanol as solvent (85); ----, curve calculated for an equimolecular mixture of benzene and naphthalene.

Fig. 5b. Ultraviolet absorption spectra. —, compound XXI in ethanol as solvent (85); ----, phenanthrene in ethanol as solvent (169).

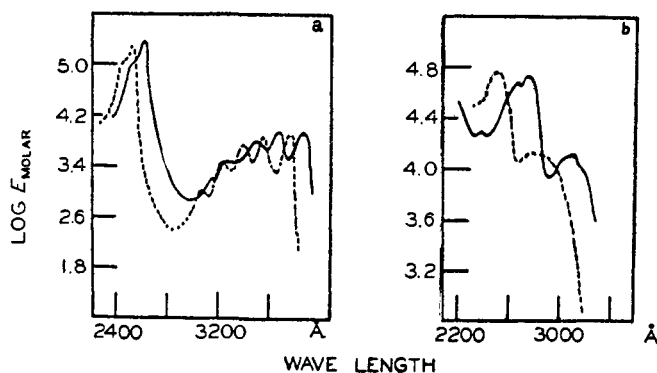
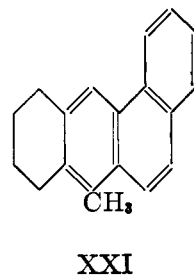
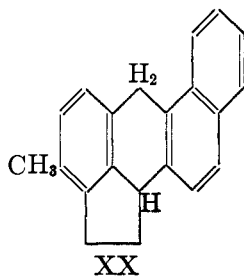
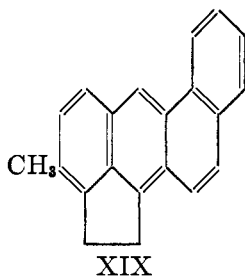
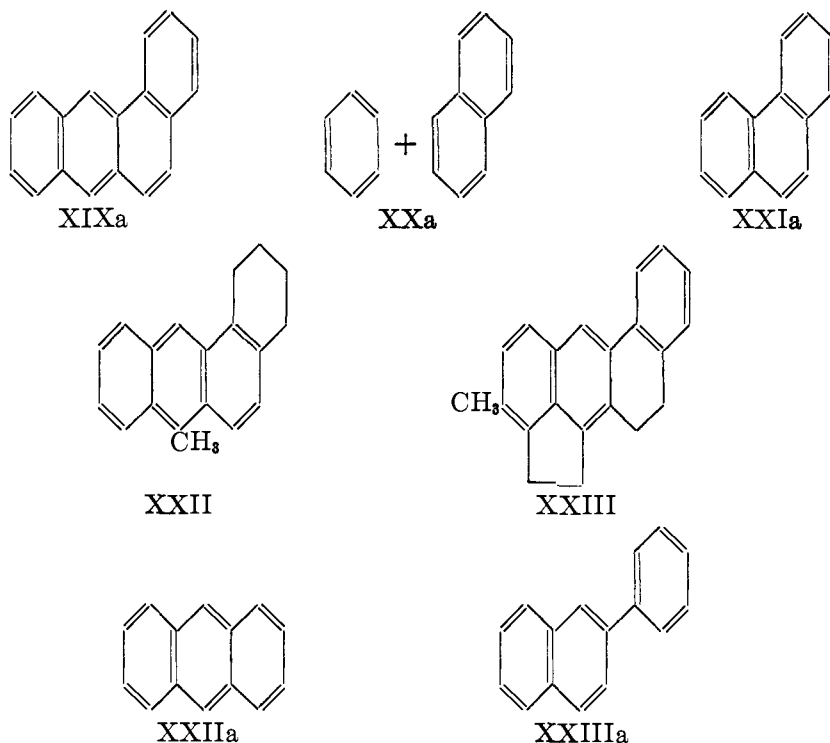


Fig. 6a. Ultraviolet absorption spectra. —, compound XXII in ethanol as solvent (85); ----, anthracene in ethanol as solvent (169).

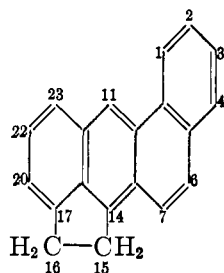
Fig. 6b. Ultraviolet absorption spectra. —, compound XXIII in ethanol as solvent (85); ----, 2-phenylnaphthalene in ethanol as solvent (85).





It is of considerable importance to examine the influence of alicyclic rings on the spectra of aromatic hydrocarbons, since in the use of spectra for such purposes it is assumed that the presence of alicyclic rings does not greatly alter the spectrum of the parent aromatic hydrocarbon structure.

The spectra of 5,6-cyclopenteno-1,2-benzanthracene, 6,7-cyclopenteno-1,2-benzanthracene, and of several alkyl derivatives of cholanthrene (XXIV) are included in table 3; all of these resemble the spectrum of 1,2-benzanthracene with as close a degree of similarity as is shown by the simpler alkyl derivatives, although the bathochromic shift is frequently greater than in the case of the corresponding dimethyl derivative.



XXIV
Cholanthrene

TABLE 6

References to the absorption spectra of aromatic hydrocarbons and related compounds containing alicyclic substituents

COMPOUND		STRUCTURAL FORMULA	REFERENCES
<i>A. Benzene chromophore:</i>			
C ₉ H ₁₀	Hydrindene.....	XXXVI	(71, 175, 204, 214, 216, 218)
C ₁₀ H ₁₂	Tetralin.....		(71, 100, 159, 176)
C ₁₄ H ₁₂	9,10-Dihydroanthracene.....		(66, 155)
C ₁₄ H ₁₈	1,2,3,4,5,6,7,8-Octahydroanthracene.....		(33, 108, 155)
C ₁₄ H ₁₈	1,2,3,4,9,10,11,12-Octahydrophenanthrene.....		(9)
C ₁₄ H ₁₈	1,2,3,4,5,6,7,8-Octahydrophenanthrene.....		(9)
C ₁₈ H ₁₆	Hexahydrochrysene (<i>cis</i> and <i>trans</i> isomers).....	XLVII	(9)
C ₁₈ H ₂₀	9,9-Diethyl-9,10-dihydroanthracene.....		(167)
C ₁₈ H ₂₂	Dodecahydrochrysene.....	XXV	(9)
C ₁₈ H ₂₄	Dodecahydrotriphenylene.....		(9, 55)
C ₂₂ H ₂₈	9,9-Diisobutyl-9,10-dihydroanthracene.....		(167)
C ₂₂ H ₂₈	9,10-Dibutyl-9,10-dihydroanthracene.....		(167)
C ₂₂ H ₂₈	9,10-Diisobutyl-9,10-dihydroanthracene.....		(167)
C ₂₄ H ₃₂	9,10-Diisooamyl-9,10-dihydroanthracene.....		(167)
C ₂₇ H ₄₂	Neoergostatriene.....	XXVI	(101, 169)
C ₃₀ H ₄₄	9,10-Dioctyl-9,10-dihydroanthracene.....		(167)
C ₂₈ H ₄₀	9,10-Di- <i>n</i> -propyl-9,10-di- <i>n</i> -butyl-9,10-dihydroanthracene.....		(167)
C ₃₀ H ₄₄	9,9,10,10-Tetraisobutyl-9,10-dihydroanthracene.....		(167)
C ₃₄ H ₅₂	9,9,10,10-Tetraisoamyl-9,10-dihydroanthracene.....		(167)
C ₂₇ H ₄₀ O	Neoergosterol.....		(69, 71, 79, 80, 127)
C ₂₇ H ₄₀ O	<i>epi</i> -Neoergosterol.....		(71, 257)
C ₂₈ H ₄₂ O	<i>epi</i> -Neoergosteryl methyl ether..		(257)
C ₁₈ H ₂₂ O ₂	Δ ^{5,7,9} -Estratrienol-3-one-17.....		(107 ^a)
C ₁₉ H ₂₆ O ₂	XLVIII	(225)
C ₁₉ H ₁₈ O ₃	XLIX	(66)
C ₂₃ H ₂₆ O ₃	Trihydrostrophanthidin.....		(79)
C ₂₃ H ₂₈ O ₃	Trihydroperiplogenin.....		(79)
C ₂₃ H ₂₈ O ₃	Dihydrotrianhydrostrophanthidin.....		(79)
<i>B. 1,2-Dihydronaphthalene chromophore:</i>			
C ₁₅ H ₁₈	1-Methyl-1,2,3,4,11,12-hydrophenanthrene.....		(96 ^b)

TABLE 6—Continued

COMPOUND		STRUCTURAL FORMULA	REFERENCES
<i>B. 1, 2-Dihydronaphthalene chromophore: (Cont.)</i>			
C ₂₇ H ₃₈	Neoergostapentaene.....	XXXa	(101, 169)
C ₂₇ H ₄₀	Neoergostatetraene.....	XXXb	(101, 169)
C ₁₈ H ₂₀ O	$\Delta^{3,5,7,9}$ -Estratetraeneone-17.....		(107 ^a)
<i>C. Diphenyl chromophore:</i>			
C ₁₄ H ₁₂	9,10-Dihydrophenanthrene.....	LIV	(9, 67, 135)
C ₁₅ H ₁₂	4,5-Methylene-9,10-dihydrophenanthrene.....	LV	(135)
<i>D. Naphthalene chromophore:</i>			
C ₁₂ H ₁₀	Acenaphthene.....		(193, 234 ^c , 249)
C ₁₃ H ₁₂	4,5-Benzhydrindene.....		(67, 131, 169)
C ₁₄ H ₁₄	1,2,3,4-Tetrahydrophenanthrene.....	XXVII	(9, 98)
C ₁₆ H ₁₆	Hexahydropyrene.....	L	(193)
C ₁₇ H ₁₈	7,8-Dihydrophenalyl-7-spirocyclopentane.....	XXVIII	(9)
C ₂₁ H ₁₈	9,10-Dihydro-22-methylcholanthrene.....	XX	(85 ^c)
C ₂₄ H ₂₀	9,10-Dimethyl-9,10-dihydro-1,2,5,6-dibenzanthracene.....		(169)
C ₂₆ H ₂₄	9,9,10,10-Tetramethyl-9,10-dihydro-1,2,5,6-dibenzanthracene.....	XXIX	(170)
<i>E. 1-Phenylnaphthalene chromophore: see discussion on pages 27, 34</i>			
<i>F. 2-Phenylnaphthalene chromophore:</i>			
C ₁₈ H ₁₄	5,6-Dihydrochrysene.....	XXXI	(174)
C ₂₀ H ₁₈	5,8-Dimethyl-3,4-dihydro-1,2-benzanthracene.....	XXXII	(87)
C ₂₁ H ₁₈	6,7-Dihydro-20-methylcholanthrene.....	XXIII	(85, 87, 131, 135)
<i>G. Anthracene chromophore:</i>			
C ₁₉ H ₁₈	1',2',3',4'-Tetrahydro-10-methyl-1,2-benzanthracene.....	XXII	(85)
<i>H. Phenanthrene chromophore:</i>			
C ₁₇ H ₁₄	1,2-Cyclopentenophenanthrene...		(8, 65, 100, 169)
C ₁₇ H ₁₄	2,3-Cyclopentenophenanthrene...		(174)
C ₁₇ H ₁₄	1,10-Trimethylenephenanthrene...		(51)
C ₁₈ H ₁₆	2'-Methyl-1,2-cyclopentenophenanthrene.....		(100, 233)
C ₁₉ H ₁₈	3',7-Dimethyl-1,2-cyclopentenophenanthrene.....		(141)
C ₁₉ H ₁₈	5,6,7,8-Tetrahydro-10-methyl-1,2-benzanthracene.....	XXI	(85)
C ₂₀ H ₁₈	Hexahydropyrene.....	LI	(41)
<i>I. 1,2-Benzanthracene chromophore:</i>			
C ₁₉ H ₁₂	1',9-Methylene-1,2-benzanthracene.....	XL	(132)
C ₂₀ H ₁₄	Cholanthrene.....	XXIV	(14 ^d , 85, 170)
C ₂₀ H ₁₄	10-Methyl-1',9-methylene-1,2-benzanthracene.....		(133)

TABLE 6—*Concluded*

COMPOUND		STRUCTURAL FORMULA	REFERENCES
<i>I. 1, 2-Benzanthracene chromophore: (Continued)</i>			
C ₂₀ H ₁₄	4,10-Dimethylene-1,2-benzanthracene.....	XLII	(88)
C ₂₁ H ₁₆	6-Methylcholanthrene.....		(82, 133)
C ₂₁ H ₁₆	20-Methylcholanthrene.....	XIX	(14 ^d , 169)
C ₂₁ H ₁₆	22-Methylcholanthrene.....		(82)
C ₂₁ H ₁₆	5,6-Cyclopenteno-1,2-benzanthracene.....		(169)
C ₂₁ H ₁₆	6,7-Cyclopenteno-1,2-benzanthracene.....		(169)
C ₂₂ H ₁₈	6,20-Dimethylcholanthrene.....		(82, 133)
C ₂₂ H ₁₈	6,22-Dimethylcholanthrene.....		(82, 133)
<i>J. Chrysene chromophore:</i>			
C ₁₉ H ₁₂	4',5-Methylenechrysene.....	XLI	(133)
<i>K. Triphenylene chromophore:</i>			
C ₂₁ H ₁₆	Cyclopentenotriphenylene.....		(174)
<i>L. 3,4-Benzpyrene chromophore:</i>			
C ₂₂ H ₁₄	4,5-Dimethylene-3,4-benzpyrene.		(11)
<i>M. Phenol chromophore:</i>			
C ₁₈ H ₂₀ O ₂	Equilin.....		(72, 170)
C ₁₈ H ₂₂ O ₂	Estrone.....		(72, 107, 170, 222, 223, 257)
C ₁₉ H ₂₂ O ₂	Estradiol-3,17.....		(120, 128, 170)
C ₁₉ H ₂₄ O ₃	1-Methylestradiol.....		(128)
C ₂₀ H ₂₆ O ₃	1-Methylestradiol-17 methyl ether		(128)
C ₂₀ H ₂₄ O ₃	Estradiol-17 acetate.....		(128)
C ₂₁ H ₂₆ O ₃	1-Methylestradiol-17 acetate.....		(128)
<i>N. 2-Naphthol chromophore:</i>			
C ₂₇ H ₃₆ O	Tetradehydroneoergosterol.....		(69, 71, 122)
C ₁₈ H ₁₈ O ₂	Equilin.....		(69, 72, 120)
C ₂₇ H ₄₀ O ₂	Dihydrotetradehydroneoergosteryl acetate.....		(257)
<i>O. 2,3-Benzfluorenone chromophore:</i>			
C ₂₀ H ₁₄ O	4,4'-Trimethylene-2,3-benzfluorenone.....		(84)

^a The intensity of the carbonyl chromophore is too small to influence the spectrum in this compound.

^b Spectrum covers only a restricted wave-length range.

^c The contribution of the benzene chromophore is small.

^d Spectrum of solution in concentrated sulfuric acid.

^e Spectra of vapor, and of solution in an organic solvent.

The data on a large number of compounds containing alicyclic rings are summarized in table 6. The spectra of these compounds have been compared with those of the relevant parent chromophoric systems; in most cases the agreement in the appearance of the curves is sufficiently close to leave no reasonable doubt as to the nature of the chromophore present. As typical examples, the absorption curves of dodecahydrochrysene (XXV) and neoergostatriene (XXVI) are compared with that of benzene in figure 7, while those of 1,2,3,4-

tetrahydrophenanthrene (XXVII) and 7,8-dihydrophenalyl-7-spirocyclopentane (XXVIII) are compared with the naphthalene spectrum in figure 8.

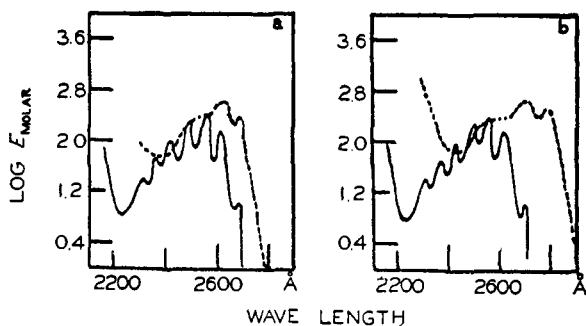
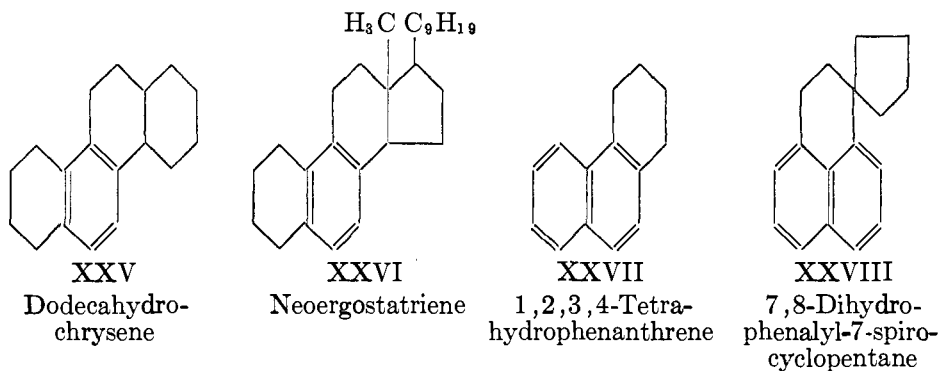


Fig. 7a. Ultraviolet absorption spectra. ----, dodecahydrochrysene in ethanol as solvent (9); —, benzene in ethanol as solvent (169).

Fig. 7b. Ultraviolet absorption spectra. ----, neoergostatriene in ethanol as solvent (169); —, benzene in ethanol as solvent (169).

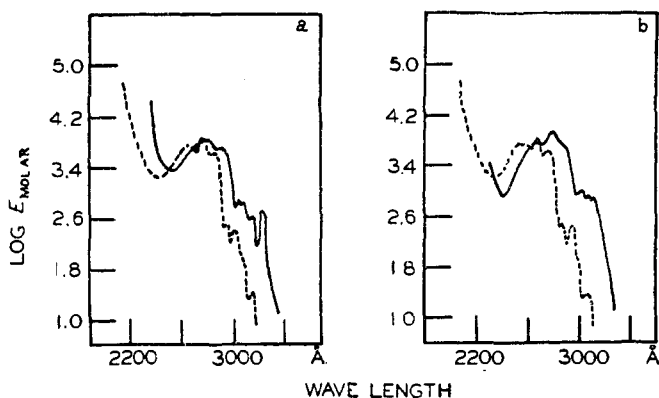
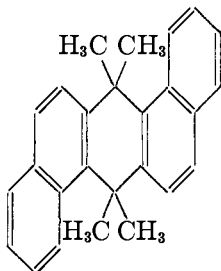


Fig. 8a. Ultraviolet absorption spectra. —, naphthalene in ethanol as solvent (9); ----, 1,2,3,4-tetrahydronaphthalene in ethanol as solvent (9).

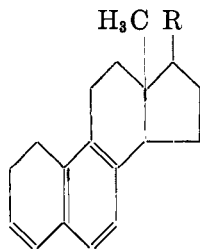
Fig. 8b. Ultraviolet absorption spectra. —, naphthalene in ethanol as solvent (9); ----, 7,8-dihydro-7-spirocyclopentane in ethanol as solvent (9).

The spectrographic data have been used as a criterion of structure of certain of the examples included in table 6, while in other cases the structure is known definitely from evidence not involving the spectrum. If the molecule contains two similar but separated chromophoric groups (XXIX), allowance must be made for the doubling of the absorption intensity implicit in the calculation of the molecular extinction coefficient. Certain of the chromophoric groups in-



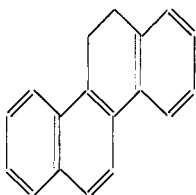
XXIX

cluded in table 6 call for further discussion. The absorption spectrum of 1,2-dihydronaphthalene (LXXVII) shows a close and unexpected similarity to that of naphthalene. This chromophore occurs in neoergostatetraene (XXXa) and neoergostapentaene (XXXb) where, however, certain differences from the naphthalene spectrum are observed in the further ultraviolet. The absorption

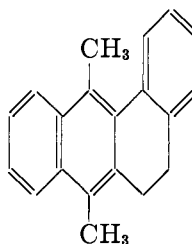
XXXa (R = C₉H₁₉)XXXb (R = C₉H₁₇)

of naphthalene increases to a maximum near 2300 Å. (Log $E \approx 5$), while the spectra of XXXa and XXXb have two maxima of lower intensity in this region. Morton and de Gouveia (176) did not extend their measurements of the spectrum of 1,2-dihydronaphthalene sufficiently far into the ultraviolet to observe this region. It is evident that more data on compounds of this type are needed before it can be decided whether the differences between the naphthalene and the 1,2-dihydronaphthalene spectra are sufficient to enable a distinction between these particular unsaturated systems to be made on purely spectrographic grounds.

Certain alicyclic derivatives of 2-phenylnaphthalene (XXIII, XXXI, XXXII) have spectra which resemble that of 2-phenylnaphthalene, but the spectra of some alicyclic derivatives of 1-phenylnaphthalene (XXXIII, XXXIV) differ

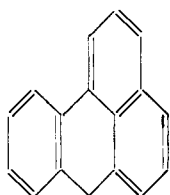


XXXI

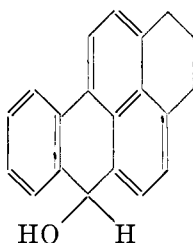


XXXII

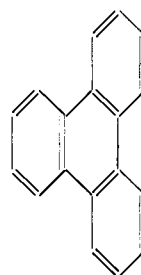
considerably from that of 1-phenylnaphthalene itself and thus appear to be exceptions to the rule that such substituents do not alter the spectral type. This is most probably due to the influence of steric factors, which are discussed more fully on page 32. The spectra of triphenylene (174) (XXXV) and of cyclopentenotriphenylene both resemble that of phenanthrene quite closely.



XXXIII

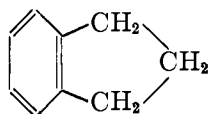


XXXIV

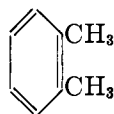
XXXV
Triphenylene

In addition to the few exceptions mentioned above, minor changes in the spectra of aromatic hydrocarbons may also occur if the closure of the alicyclic ring cannot be completed without deformation of the normal bond lengths and valence angles. Presumably such deformations set up strains in the structure which may influence the spectrum by restricting the modes of vibration of the atoms and also by altering the relative energies associated with the different canonical structures contributing to the ground and excited states of the molecule. The main consequence of such strain appears to be the enhancement of the fine structure of the absorption bands, and such effects have been observed in several instances.

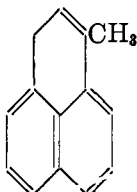
Ramart-Lucas and Hoch (204, 216) compared the spectra of hydrindene (XXXVI) and *o*-xylene (XXXVII) and observed that, although the *o*-xylene spectrum is devoid of fine structure, the hydrindene spectrum has two fine structure bands (figure 9). In the case of the alicyclic carbonyl compounds, both cyclobutanone and cyclopentanone exhibit fine structure in hexane solution (204, 262), while the spectra of the open-chain aliphatic ketones and the cyclic ketones with larger rings are smooth curves under the same conditions. The spectrum of 7-methylperinaphthene (263) (XXXVIII) shows structure, while that of 1-propenylnaphthalene (XXXIX) does not (figures 15 and 16).



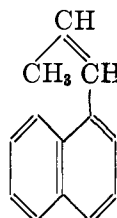
XXXVI
Hydrindene



XXXVII
o-Xylene



XXXVIII
7-Methylperinaphthene



XXXIX
1-Propenylnaphthalene

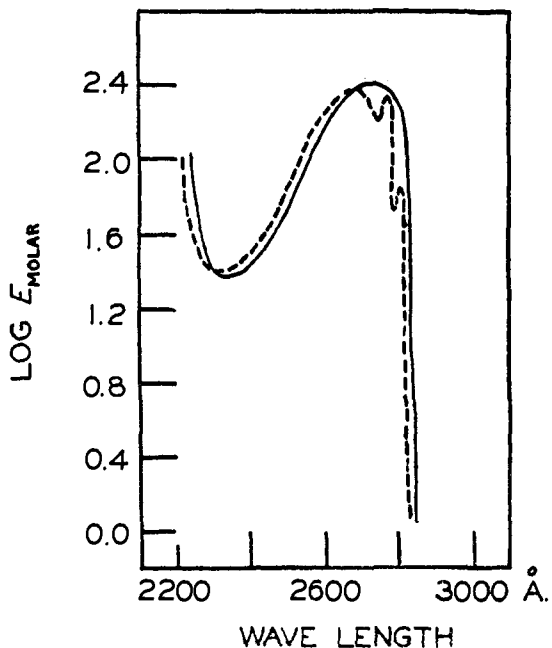
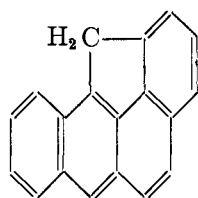


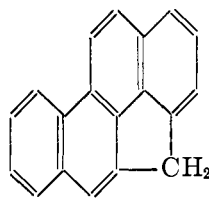
FIG. 9. Ultraviolet absorption spectra. —, *o*-xylene in hexane as solvent (216); ----, hydrindene in hexane as solvent (216).

Striking examples of this effect are provided by 1',9-methylene-1,2-benzanthracene (XL) and 4,5-methylenechrysene (XLI), both of which exhibit very highly developed fine structure. In XL there is also a change in the character of the absorption in the region between 2800 and 3000 Å., where the D maximum of 1,2-benzanthracene (figure 1) is replaced by a system of two maxima of lower intensity (figure 10a). The introduction of the bridge methylene group involves a deformation of the bond angles by about 12° to close the five-membered ring,



XL

1',9-Methylene-1,2-benzanthracene



XLI

4,5-Methylenechrysene

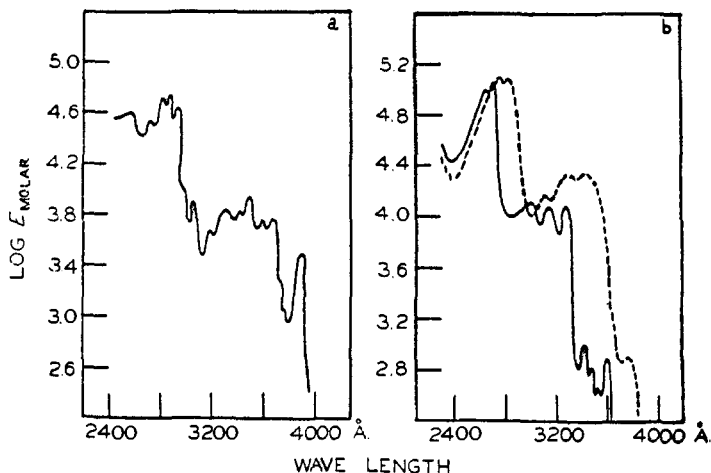
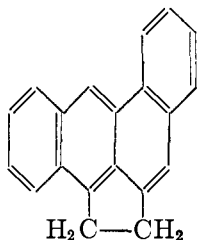


FIG. 10a. Ultraviolet absorption spectrum of 1',9-methylene-1,2-benzanthracene in ethanol as solvent (132).

FIG. 10b. Ultraviolet absorption spectra. —, 4,5-methylenechrysene in ethanol as solvent (134); ----, 4,5-dimethylchrysene in ethanol as solvent (134).

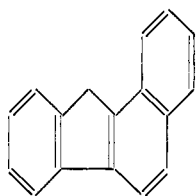
assuming a planar structure for the molecule. In fluorene (124, 125) there is evidence from dipole-moment measurements that, in solution, this strain is distributed among the aromatic as well as the aliphatic bonds, but no information is available concerning the molecular geometry of XL and XLI. Although the dimethylene bridge of 20-methylcholanthrene and of cholanthrene does not produce this effect, it has recently been observed that in 4,10-dimethylene-1,2-benzanthracene (XLII) (72) there is more structure present in the 3000–4000 Å. region than in the parent hydrocarbon.



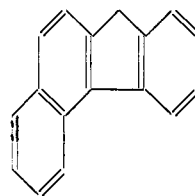
XLII

4,10-Dimethylene-1,2-benzanthracene

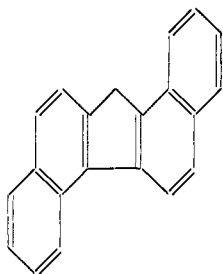
The alicyclic derivatives XL and XLI may be regarded as derivatives of fluorene. The spectra of several other hydrocarbons related to fluorene have been regarded as of a distinct chromophoric type and are included in table 1; among these are 1,2-benzfluorene (XLIII), 3,4-benzfluorene (XLIV), 1,2,5,6-dibenzfluorene (XLV), and 1',2'-naphtho-2,3-fluorene (XLVI), which may be considered as methylene derivatives of 2-phenylnaphthalene, 1-phenylnaphthalene, 1,2'-dinaphthyl, and 2-phenylphenanthrene, respectively. The spectra



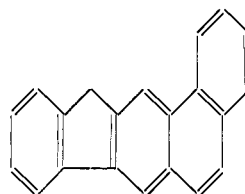
XLIII
1,2-Benzfluorene



XLIV
3,4-Benzfluorene

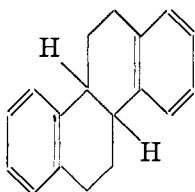


XLV
1,2,5,6-Dibenzfluorene

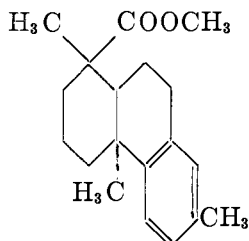


XLVI
1',2'-Naphtho-2,3-fluorene

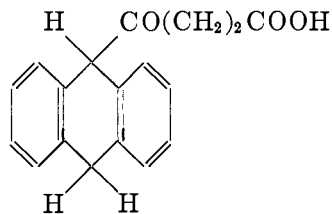
of XLIII and XLIV differ markedly from the spectra of the respective parent aromatic hydrocarbons; the spectra of the parent hydrocarbons corresponding to XLV and XLVI have not been measured. In all of these substances, the methylene linkage holds together two parts of the molecule which would otherwise be joined only by a single carbon-to-carbon bond; consequently, the addition of the methylene group must greatly modify the rigidity of the molecule. In 4,5-methylenechrysene and 1',9-methylene-1,2-benzanthracene the methylene linkage is attached to a system of condensed aromatic rings in which there is already very great steric restriction, and accordingly it is not surprising that the introduction of the methylene bridge causes much greater changes in the spectra of structures such as XLIII to XLVI than in XL and XLI.



XLVII



XLVIII



XLIX

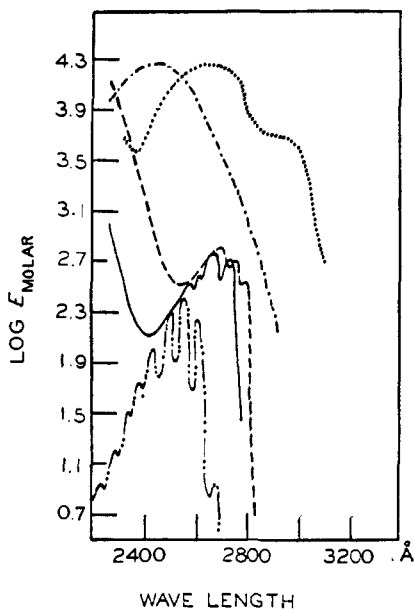
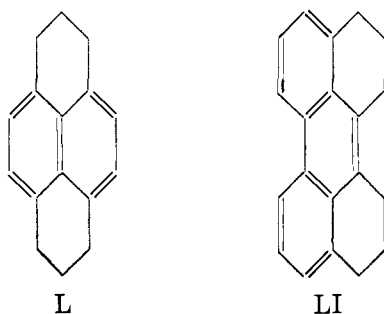


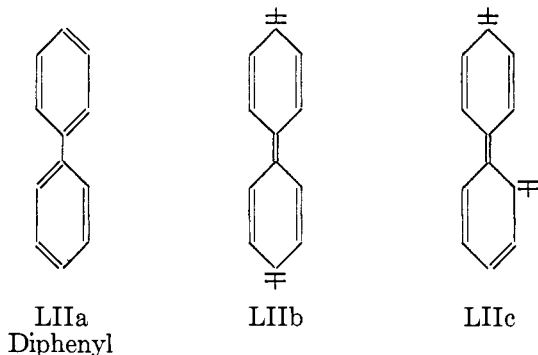
FIG. 11. Ultraviolet absorption spectra. —, 2 moles of mesitylene in ethanol as solvent; ----, dimesityl in ethanol as solvent (198); - · - ·, diphenyl in methanol as solvent (154); · · · ·, 9,10-dihydrophenanthrene in ethanol as solvent (135); - - - - ·, benzene in ethanol as solvent (169).

IV. ARYL DERIVATIVES

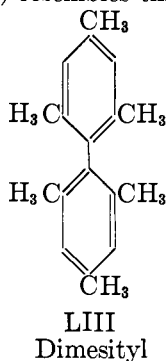
Several of the polynuclear aromatic hydrocarbons listed in table 1 may be regarded as aromatic hydrocarbons containing aryl substituents. The simplest of these is diphenyl.

A comparison of the spectra of diphenyl and benzene shows that they differ greatly from one another (figure 11), and considerable interaction must take place between the electronic systems of the two aromatic rings across the coannular bond, which cannot have the purely aliphatic character suggested by the conventional formula (LIIa). Evidence of this is provided also by x-ray diffraction measurements (70), which show that the length of the coannular bond is 1.48 Å. in comparison with 1.54 Å. for the aliphatic carbon-carbon link and 1.39 Å. for

a purely aromatic bond (22). It has been inferred that the coannular linkage in diphenyl has considerable double-bond character and that structures of the type LIIb and LIIc are contributing significantly to the ground state of the molecule (32).



Studies of the spectra of alkyl derivatives of diphenyl (186, 198) have shown that such groups may be introduced at the meta and para positions without changing the spectrum, apart from producing the normal bathochromic shift and minor changes in intensity. Substitution of methyl groups at the ortho positions, on the other hand, causes a profound change in the spectrum; thus the spectrum of dimesityl (LIII) resembles that of mesitylene rather than that



of diphenyl (figure 11). Structures such as LIIb and LIIc must be planar, and if, owing to steric interference, the two benzene rings are prevented from taking up a coplanar configuration, the contributions of these resonance forms to the molecular structure will be greatly reduced, and substances that contain ortho substituents behave as though the coannular bond were very largely aliphatic in character. This explanation of the anomalous effect of methyl substituents at the ortho positions is supported by the fact that the spectra of 9,10-dihydrophenanthrene (LIV) and 4,5-methylene-9,10-dihydrophenanthrene (LV) (135), in which the ortho-substituted methylene and dimethylene bridges hold the two aromatic rings in or near a coplanar configuration, possess the diphenyl type of spectra.

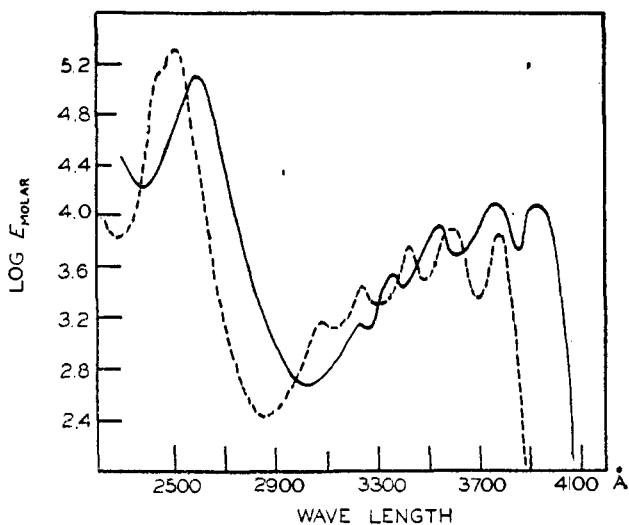
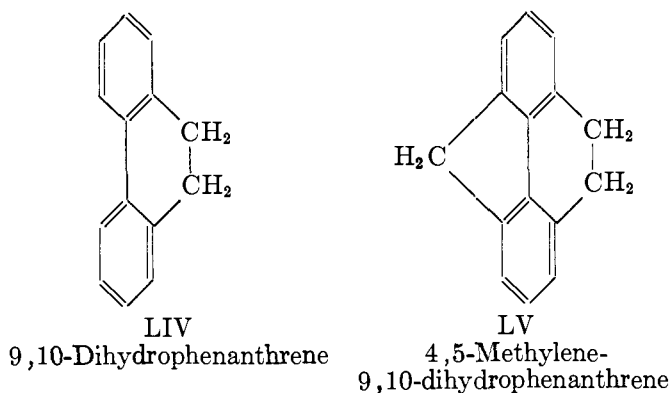


FIG. 12. Ultraviolet absorption spectra. —, 9,10-diphenylanthracene in ethanol as solvent (202); ----, anthracene in ethanol as solvent (169).

The spectra of several aryl-substituted polynuclear aromatic hydrocarbons exhibit effects which can be attributed to steric factors that act to prevent the aryl substituents from taking up a configuration coplanar with the rest of the conjugated system. The spectra of 9-phenylanthracene (LVI), 9,10-diphenylanthracene (LVII) (figure 12), and 9,10-di(1-naphthyl)anthracene (LVIII) are all very similar to that of unsubstituted anthracene (135), in spite of the very considerable change in the nature of the unsaturated system. Steric interference may occur in these compounds between the hydrogen atoms of the ortho positions of the meso-aryl substituents and the hydrogen atoms at the 1- and 8-positions of the anthracene ring system. Theoretically such compounds might be expected to possess spectra equivalent to the summation of the spectra of the meso-aryl substituents and anthracene. In the case of the phenyl derivatives the intensity of the benzene contribution is negligible. The di(1-naphthyl)

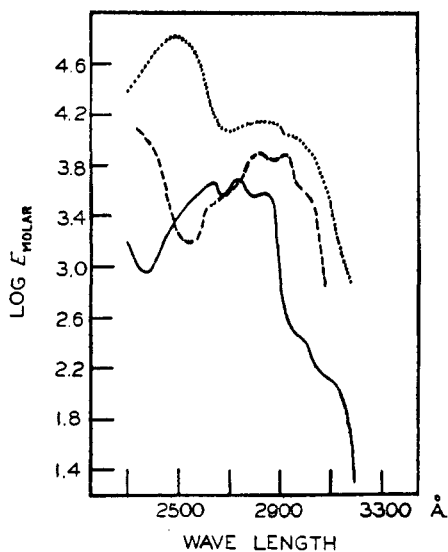
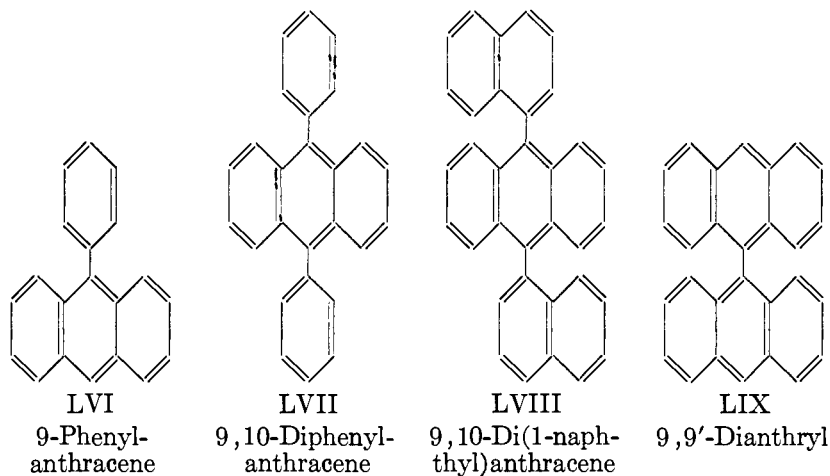
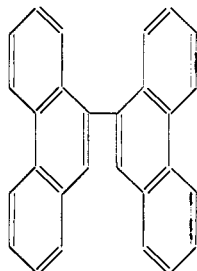


FIG. 13. Ultraviolet absorption spectra. —, curve calculated for 1 mole of naphthalene and 1 mole of benzene; ----, 1-phenylnaphthalene in ethanol as solvent (131); ····, 2-phenylnaphthalene in ethanol as solvent (135).

derivative does show some structure which has been attributed to the naphthalene component (135), while the intensity of the absorption of 9,9'-dianthryl (LIX) is very close to twice that of anthracene.

Further examples of this effect are provided by the similarity between the spectra of phenanthrene and 9,9'-diphenanthryl (LX) (116) and between those of 1-phenylnaphthalene and an equimolecular mixture of naphthalene and benzene (figure 13). In the case of 2-phenylnaphthalene (XXIIIa), where there is no steric restriction, the spectrum differs greatly from that calculated on the assumption that the benzene and naphthalene chromophores behave inde-

pendently. The similarity between the spectra of 2-phenylnaphthalene and 6,7-dihydromethylcholanthrene (XXIII) (85, 135) may be cited as evidence in support of an approximately planar structure for 2-phenylnaphthalene (figures 6b and 13), because in 6,7-dihydromethylcholanthrene the phenyl group is held in or near the plane of the naphthalene ring by a dimethylene bridge.

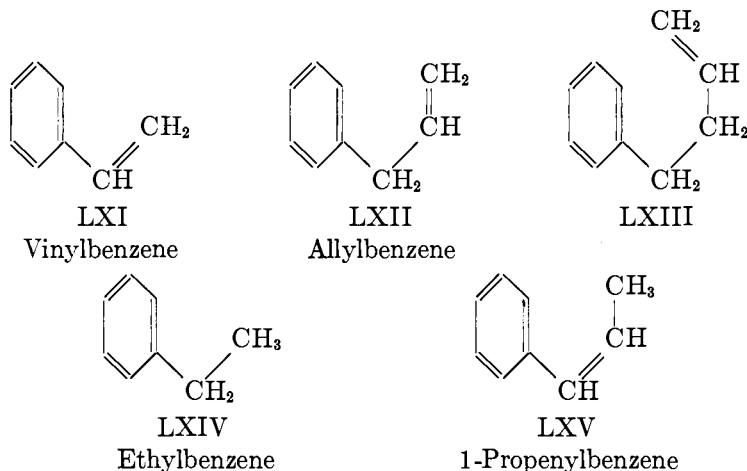


LX

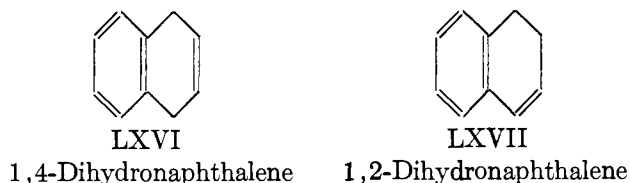
9,9'-Diphenanthryl

V. ALKENE, CYCLOALKENE, AND ALKYNE DERIVATIVES

Very little information is available concerning the effect of alkene side chains on the spectra of aromatic hydrocarbons, and that is restricted almost entirely to the benzene and the naphthalene series. Ramart-Lucas (204) compared the spectra of LXI, LXII, LXIII, and LXIV, and observed that the spectrum only differs appreciably from that of ethylbenzene in the case of LXI, where the ethylenic link is conjugated with the aromatic system. In the case of LXI, however, the change is considerable, the intensity increases more than tenfold



in the region near the maximum (figure 14). Similar observations have been recorded by Hillmer and Schorning (119), who compared the spectra of allylbenzene (LXII) and 1-propenylbenzene (LXV). The spectrum of 1,4-dihydronaphthalene (LXVI) is benzenoid, while that of 1,2-dihydronaphthalene (LXVII) is not (176).



In view of the fact that substituents usually modify the spectrum of benzene to a greater extent than they influence those of polynuclear aromatic hydro-

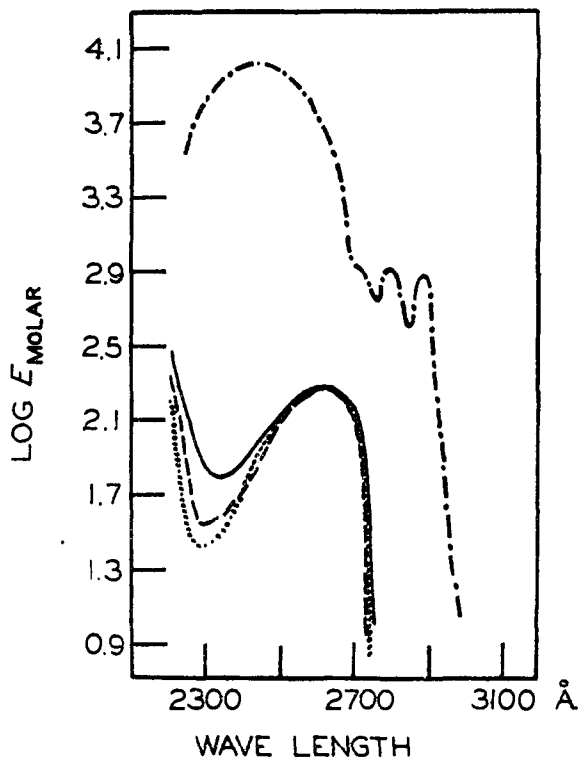


FIG. 14. Ultraviolet absorption spectra. —, allylbenzene in ethanol as solvent (204); ----, 4-phenyl-1-butene in ethanol as solvent (204); ····, ethylbenzene in ethanol as solvent (204); —·—·, styrene in ethanol as solvent (204).

carbons, it may be anticipated that the introduction of conjugated alkene substituents into polynuclear hydrocarbons may produce less pronounced effects. The spectra of 1-allylnaphthalene (LXVIII), 1-methylnaphthalene, and 1-propenylnaphthalene (LXIX) are compared in figure 15 (193). The effect of conjugation of the side-chain double bond with the naphthalene ring is less marked than its influence on the benzene chromophore; it may be noted that the conjugated compound shows no fine structure. Closure of the side chain to form a ring, as in 7-methylperinaphthene (67, 236) (XXXVIII), leads to a

considerable bathochromic shift and the appearance of fine structure. In acenaphthylene (LXX), in which the alkene substituent is conjugated with the

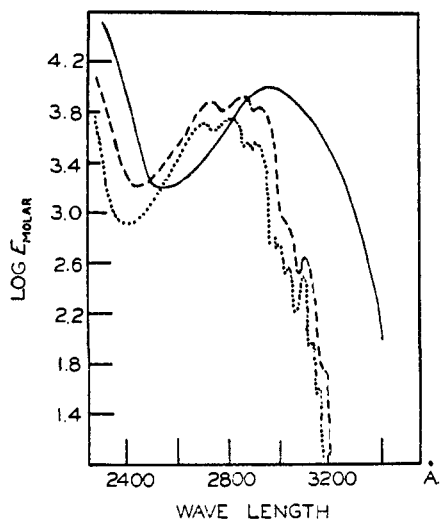
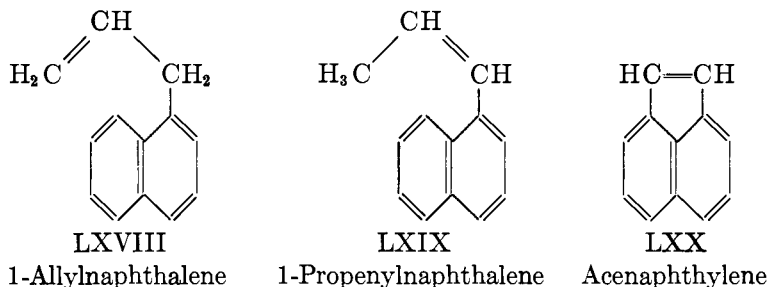
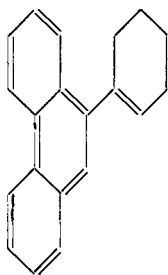


FIG. 15. Ultraviolet absorption spectra. —, 1-propenylnaphthalene in ethanol as solvent (197); ----, 1-allylnaphthalene in ethanol as solvent (193); ····, 1-methylnaphthalene in ethanol as solvent (193).

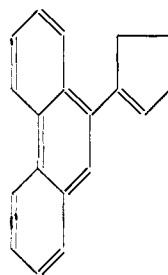
naphthalene system at two points, the spectrum differs considerably, particularly at wave lengths below 2800 Å. (figure 16). The variations among these alkene naphthalene derivatives are of interest, but as yet there are insufficient data for any general conclusions to be drawn from them which might be of value in the elucidation of the structure of unknown compounds which may belong to one of these types.

The spectra of two interesting substances containing cycloalkene substituents, 9-cyclohexenylphenanthrene (LXXI) and 9-cyclopentenylphenanthrene (LXXII), have been reported by Henri and Bergmann (116), who observe that LXXII has a spectrum which differs considerably from that of phenanthrene, as would be anticipated in view of the altered conjugated system. The cyclohexenyl derivative (LXXI) has a spectrum which is very similar to that



LXXI

9-Cyclohexenylphenanthrene



LXXII

9-Cyclopentenylphenanthrene

of phenanthrene. Calvin (32) considers that steric factors of the type discussed on page 32 may account for this difference; it may be possible, however, that the double bond in LXXI has moved out of conjugation with the aromatic

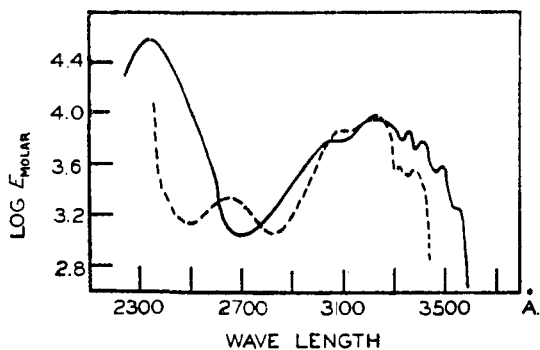
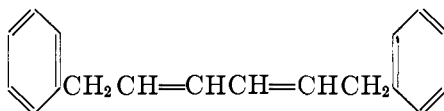


FIG. 16. Ultraviolet absorption spectra. —, 7-methylperinaphthene in ethanol as solvent (263); ----, acenaphthene in ethanol as solvent (67).

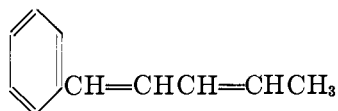
ring during the synthesis. Bergmann and Bergmann (16) cite evidence against this hypothesis which does not definitely exclude it.

In compounds such as LXII and LXVIII, where the side-chain double bond is "insulated" from the aromatic system by one or more methylene groups, there can be no doubt that it makes an additive contribution to the total absorption of the molecule; this, however, will occur in the vacuum ultraviolet region. If the side chain should contain a conjugated diene separated from the aromatic system, its additive contribution should be considerable; an example of this is provided by 1,4-dibenzylbutadiene (71, 238) (LXXIII). Where the



LXXIII

1,4-Dibenzylbutadiene



LXXIV

1-Phenyl-1,3-pentadiene

TABLE 7

References to the absorption spectra of aromatic hydrocarbons containing alkene and cycloalkene substituents

COMPOUND		REFERENCES
A. Benzene derivatives:		
C ₈ H ₈	Styrene	(3, 7, 13 ^a , 71, 95, 97, 123, 143, 153, 191, 197, 204, 205, 206, 208, 211, 238)
C ₉ H ₈	Indene	(71, 175, 207, 216, 218, 245)
C ₉ H ₁₀	Allylbenzene	(3, 71, 119, 197, 204, 205, 207, 210, 211)
C ₉ H ₁₀	Propenylbenzene	(71, 119, 197, 206, 207, 210)
C ₉ H ₁₀	<i>o</i> -Methylstyrene	(216, 218)
C ₉ H ₁₀	2-Phenyl-1-propene	(211)
C ₁₀ H ₁₀	1,2-Dihydronaphthalene	(176, 218)
C ₁₀ H ₁₀	1,4-Dihydronaphthalene	(176)
C ₁₀ H ₁₀	1-Methyl-1,2-indene	(218)
C ₁₀ H ₁₀	1-Phenyl-1,3-butadiene	(238)
C ₁₀ H ₁₂	α -Methyl- <i>o</i> -methylstyrene	(218)
C ₁₀ H ₁₂	4-Phenyl-1-butene	(3, 204, 205, 211)
C ₁₀ H ₁₂	4-Methylpropenylbenzene	(210)
C ₁₁ H ₁₂	1-Methyl-3,4-dihydronaphthalene	(218)
C ₁₁ H ₁₂	1-Phenyl-1,3-pentadiene	(197)
C ₁₁ H ₁₄	5-Phenyl-1-pentene	(211)
C ₁₂ H ₁₄	2,3,4,5-Tetrahydrodiphenyl	(197)
C ₁₂ H ₁₄	6-Phenyl-1-hexene	(211)
C ₁₃ H ₁₆	1-Ethylidene-2,2-dimethylhydrindene	(218)
C ₁₃ H ₁₈	7-Phenyl-1-heptene	(211)
C ₁₄ H ₁₂	<i>cis</i> -Stilbene	(7, 90, 151, 154, 239)
C ₁₄ H ₁₂	<i>trans</i> -Stilbene	(7, 37, 71, 90, 94, 106, 111, 118, 151, 152, 153, 154, 206, 210, 214, 238, 239, 249)
C ₁₄ H ₁₂	<i>asym</i> -Diphenylethylene	(31, 111, 156, 210, 232)
C ₁₄ H ₁₈	1-Ethylidene-2,2-dimethyltetralin	(218)
C ₁₅ H ₁₂	9-Ethylidene fluorene	(217)
C ₁₅ H ₁₄	α -Methylstilbene	(7, 71, 90, 152, 154, 204, 206, 214)
C ₁₅ H ₁₄	<i>p</i> -Methylstilbene	(7, 152)
C ₁₅ H ₁₄	1-Phenyl-1-(<i>p</i> -tolyl)ethylene	(204, 210)
C ₁₅ H ₁₄	1-Phenyl-2-(<i>p</i> -tolyl)ethylene	(210)
C ₁₅ H ₁₄	1,1-Diphenyl-1-propene	(210)
C ₁₅ H ₁₄	1,2-Diphenyl-1-propene	(210)
C ₁₆ H ₁₂	Benzylideneindene	(175)
C ₁₆ H ₁₄	1,4-Diphenyl-1,3-butadiene	(37, 71, 92, 102, 105, 106, 111, 118, 201, 238)
C ₁₆ H ₁₆	α,β -Dimethylstilbene (two isomers)	(7, 90, 146, 152, 204, 249)
C ₁₆ H ₁₆	<i>sym</i> -Dibenzylethylene	(71, 154, 238)
C ₁₆ H ₁₆	Distyrene	(97)
C ₁₆ H ₁₈	2,3-Diphenyl-2-butene (two isomers)	(220)
C ₁₆ H ₂₄	<i>n</i> -Octylstyrene	(211)
C ₁₈ H ₁₄	3,3'-Diindenyl	(245)
C ₁₈ H ₁₄	Cinnamylideneindene	(175)
C ₁₈ H ₁₆	1,6-Diphenyl-1,3,5-hexatriene	(71, 102, 105, 201, 238)

TABLE 7—*Concluded*

COMPOUND		REFERENCES
C ₁₈ H ₁₈	1,4-Dibenzyl-1,3-butadiene.....	(71, 238)
C ₂₀ H ₁₆	1-Styrylacenaphthalene.....	(263)
C ₂₀ H ₁₆	Triphenylethylene.....	(7, 19, 206)
C ₂₀ H ₁₈	1,8-Diphenyl-1,3,5,7-octatetraene.....	(71, 102, 105, 201, 238)
C ₂₀ H ₂₀	1,6-Dibenzyl-1,3,5-hexatriene.....	(71, 238)
C ₂₂ H ₂₀	1,10-Diphenyl-1,3,5,7,9-dodecapentaene.....	(71, 102, 238)
C ₂₄ H ₂₂	1,12-Diphenyl-1,3,5,7,9,11-dodecahexaene.....	(71, 102, 105, 201, 238)
C ₂₆ H ₁₆	Dibiphenyleneethylene.....	(33, 245)
C ₂₆ H ₂₀	Tetraphenylethylene.....	(7, 102, 154, 249)
C ₂₆ H ₂₄	1,14-Diphenyl-1,3,5,7,9,11,13-tetradecaheptaene.....	(71, 102, 238)
C ₂₈ H ₂₀	1-Phenyl-3-diphenylmethyleneindene.....	(23)
C ₃₀ H ₂₂	2,8-Diphenyl-6b,12b-dihydrochrysene.....	(168)
C ₃₀ H ₂₄	3-Diphenylmethylene-1,5-diphenyl-1,4-pentadiene.....	(156)
C ₃₄ H ₂₈	3-Diphenylmethylene-1,5-distyryl-1,4-pentadiene.....	(156)
C ₃₅ H ₂₆	Pentaphenylcyclopentadienal.....	(262)
C ₃₆ H ₂₆	1,12-Diphenyl-4,6,7,9-diphenylene-1,3,5,7,9,11-dodecahexaene.....	(245)
<i>B. Naphthalene derivatives:</i>		
C ₁₂ H ₈	Acenaphthylene.....	(67)
C ₁₃ H ₁₂	1-Allylnaphthalene.....	(193)
C ₁₃ H ₁₂	1-Propenylnaphthalene.....	(193)
C ₁₄ H ₁₄	7-Methylperinaphthene.....	(67, 263)
C ₂₀ H ₁₆	1-Phenyl-4-(1)-naphthyl-1,3-butadiene.....	(92)
<i>C. Derivatives of other aromatic hydrocarbons:</i>		
C ₁₉ H ₁₆	9-Cyclopentenylphenanthrene.....	(32, 116)
C ₂₀ H ₁₈	9-Cyclohexenylphenanthrene.....	(32, 116)
C ₃₆ H ₂₄	3,9-Diphenyldivinylperylene.....	(195)
<i>D. Cumulene derivatives:</i>		
C ₂₈ H ₂₀	Tetraphenyl-1,2,3-butatriene.....	(23, 145)
C ₃₀ H ₁₆	Tetraphenyl-1,2,3,4,5-hexapentaene.....	(145)
C ₃₀ H ₂₀	Dibiphenylene-1,2,3,4,5-hexapentaene.....	(145)

^a Spectrum of solution in concentrated sulfuric acid.

TABLE 8

References to the absorption spectra of aromatic hydrocarbons containing alkyne substituents

COMPOUND		REFERENCES
C ₈ H ₆	Phenylacetylene.....	(123, 177)
C ₁₄ H ₁₀	Diphenylacetylene (tolane).....	(58, 102)
C ₁₆ H ₁₀	Diphenyldiacetylene.....	(102)
C ₁₆ H ₁₄	4,4'-Dimethyltolane.....	(58)
C ₁₈ H ₁₈	4,4'-Diethyltolane.....	(58)
C ₁₈ H ₁₈	3,3',4,4'-Tetramethyltolane.....	(58)
C ₂₀ H ₂₂	4,4'-Di- <i>n</i> -propyltolane.....	(58)
C ₂₂ H ₂₆	4,4'-Di- <i>n</i> -butyltolane.....	(58)

diene side chain is conjugated with the aromatic system it produces profound changes in the chromophore, e.g., 1-phenyl-1,3-pentadiene (LXXIV) (197). In the α,ω -diphenylpolyenes (VII), which have been investigated intensively by Hauser, Kuhn, and Seitz (102) and by Rădulescu and Bărbulescu (201), the long polyene chain appears to be the major factor in the light absorption process, since the spectra differ little in type from those of the carotenoid pigments in which the phenyl groups are replaced by aliphatic end groups.

Aromatic hydrocarbons containing alkene chains provide possibilities of *cis-trans* isomerism. The spectra of *cis*- and *trans*-stilbenes have been investigated by Arends (7), by Smakula and Wassermann (239), and, most recently, by Lewis, Magel, and Lipkin (151). Considerable differences are observed between the spectra of the two isomers. Lewis and coworkers have discussed these differences and their bearing on the photoconversion of one isomer into the other (151). Ramart-Lucas (204) examined the spectra of several pair of *cis-trans* isomers outside the hydrocarbon field and concluded that, although the spectra of such isomers frequently exhibit differences, it seems unlikely that the absolute configurations of the two isomers can be deduced from their ultraviolet absorption spectra alone.

References to the spectra of alkene, cycloalkene, and alkyne derivatives of aromatic hydrocarbons are summarized in tables 7 and 8; so few alkyne-substituted aromatic hydrocarbons have been examined that it is not possible to draw any general conclusions concerning the effect of such groups on the spectra.

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