

THE ULTRAVIOLET ABSORPTION SPECTRA OF ANTHRACENE DERIVATIVES^{1, 2}

R. NORMAN JONES

The Division of Chemistry, The National Research Council of Canada, Ottawa, Canada

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The effects of various substituents on the ultraviolet absorption spectrum of anthracene are considered. The band shifts observed are correlated with the type and position of the substituent group. It is suggested that the substituent may modify the energies of both the ground and the excited states of the molecule and that the effect on the excited state is probably influenced by the position of the substituent relative to certain axes in the molecule.

I. INTRODUCTION

In an endeavor to interpret the effect of substituents on the spectra of triphenylmethyl ions and other dyes, G. N. Lewis and coworkers (6, 7) took account of the orientation of the molecule in the electric field and designated the absorption bands as *x*-bands or *y*-bands on the assumption that they were associated with electric moments directed along mutually perpendicular axes in the main plane of the molecule. A similar hypothesis had been applied previously by Scheibe (13, 14) to account for the abnormal spectra of certain molecular aggregates.

The importance of such directed excitation in connection with the absorption spectra of hydrocarbons has been recognized by Pauling and Zechmeister (16, 17) and by Mulliken (8), who have described the spectrographic changes which accompany *trans*→*cis* isomerism of carotenoids in terms of the effect of the isomerization on the linear extension of the molecule.

The ultraviolet absorption spectra of hydrocarbons such as anthracene, pyrene, and chrysene (2), which contain several condensed aromatic rings, usually exhibit much more structure than do the spectra of the triphenylmethyl ions or the carotenoids. The introduction of substituents into these complex aromatic hydrocarbons at different positions on the ring systems modifies the spectra in a complex manner. In an earlier publication from this Laboratory (3) four distinct types of substitution effects have been recognized and designated by the symbols C (conjugation), Fs (fine-structure), B (bathochromic), and S (steric).

At the present time, a rigorous treatment of the electronic spectra of such complicated molecules by the methods of quantum mechanics is impractical, and it is therefore of interest to examine whether the concept of an oriented ex-

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citation mechanism can be applied to account for some of the substitution effects observed in these polynuclear aromatic hydrocarbons. Furthermore, from a comparative study of such substitution effects some insight might be gained into the process of light absorption by the parent hydrocarbon molecule.

II. THE ELECTRONIC STRUCTURE OF ANTHRACENE

For the purposes of such a study, anthracene has been selected for special consideration since it possesses several advantageous features. Its ultraviolet absorption spectrum can be divided into two clearly distinguishable parts, associated with two groups of maxima, designated A-B and C-H in figure 1. It seems reasonable to assume that these two regions of the spectrum are related

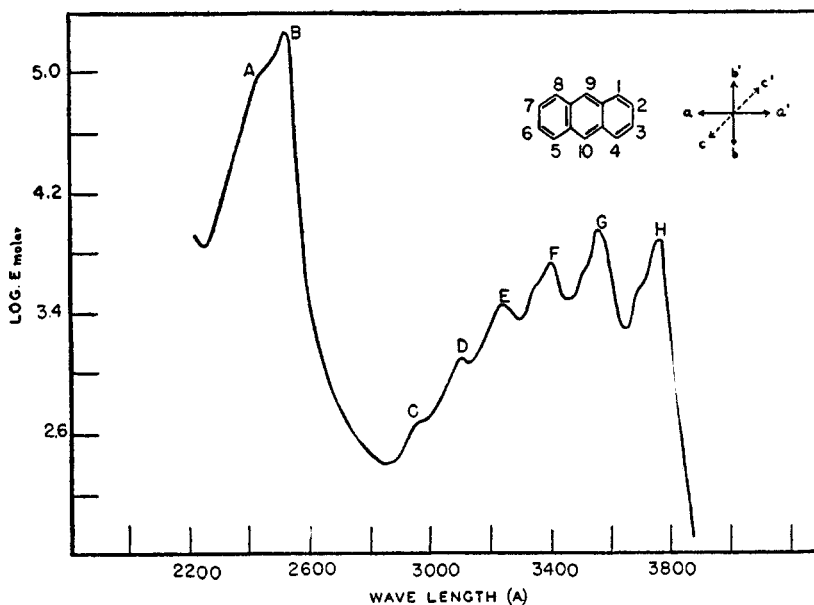
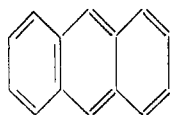


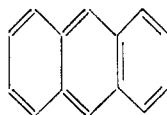
FIG. 1. Ultraviolet absorption spectrum of anthracene (solvent ethanol)

to separate states of electronic excitation. The several maxima in the C-H band group are almost certainly vibrational sub-levels; their frequency differences (table 1) are constant and probably related to the —C—H bending vibration which occurs in the infrared spectrum near 1450 cm.^{-1} . The shape of the anthracene molecule is also favorable for such a study, since the linear extension along each of the three principal axes is appreciably different; at the same time the molecule retains considerable symmetry so that it is reasonable to postulate that if the electric moments associated with the various absorption bands are directed along specific axes, those axes in all probability will correspond with the axes aa' , bb' , and cc' on figure 1.

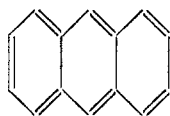
The process of electronic excitation may be visualized in a highly simplified form in the following terms. The four uncharged structures Ia-Id will make



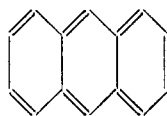
Ia



Ib



Ic



Id

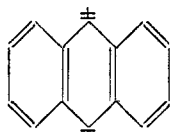
TABLE 1

Position of absorption maxima in ultraviolet absorption spectrum of anthracene

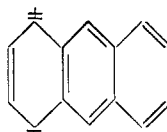
MAXIMUM*	FREQUENCY	FREQUENCY DIFFERENCE
a. Solvent ethanol		
	<i>cm.⁻¹</i>	<i>cm.⁻¹</i>
B.....	39,720 ± 40	
D.....	32,260 ± 30	1370
E.....	30,890 ± 25	1420
F.....	29,470 ± 20	1410
G.....	28,060 ± 20	1420
H.....	26,640 ± 15	
b. Solvent <i>n</i> -heptane		
B.....	39,680 ± 40	
D.....	32,360 ± 30	1350
E.....	31,010 ± 25	1470
F.....	29,540 ± 25	1410
G.....	28,130 ± 20	1460
H.....	26,670 ± 15	

* The maxima A and C are too flat to permit of an accurate determination of the position.

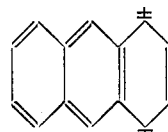
the major contributions to the resonance in the ground state of the molecule, and it will be assumed that other structures such as Ie–Ii, which involve a separation of charge, will be of sufficiently higher energy to render their contributions to the resonance of the ground state of negligible importance. In the electronic-



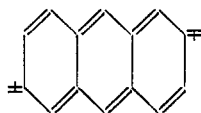
Ie



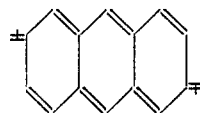
If



Ig



Ih



Ii

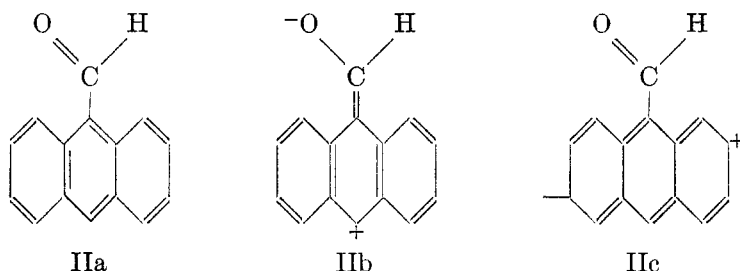
ally excited states, the contributions of such structures may well be significant. These polar structures can be divided into two groups: Ie-Ig, in which the polarization is directed along the bb' -axis; and Ih-Ii, in which the polarization is directed somewhat diagonally but closer to the aa' -axis. If these structures participate in the resonance of the excited states, it is to be anticipated that the electric moments associated with the process of excitation will be directed along axes simply related to the directions of these polarizations.

III. SPECTRA OF ANTHRACENE DERIVATIVES

A. Substituents exhibiting conjugation effects

The direct demonstration of such oriented excitation in the unsubstituted hydrocarbon offers considerable experimental difficulty, since it requires the alignment of the absorbing molecule with respect to the electric vector of the exciting radiation, but a simpler indirect approach to the problem can be made through a study of suitably chosen substituted compounds, particularly those which exhibit a predominant C-effect (3).

In 9-anthraldehyde (IIa) the conjugation in the direction of the bb' -axis is so altered that in the excited state corresponding to one of the Ie structures the negative charge is transferred from a carbon to an oxygen atom and the resultant structure (IIb) should be more stable. On the other hand, the energies of IIc and the corresponding Ih structure will differ much less, since the charge remains on the carbon atoms in both. We may therefore expect that the introduction of the aldehyde group at the 9-position would cause a larger displacement of an



absorption band associated with excitation along the bb' -axis than of an absorption band associated with an electric moment oriented in some other direction. The spectra of anthracene and 9-anthraldehyde in ethanol solution are compared in figure 2. Both the A-B and the C-H groups of bands are displaced bathochromically on introduction of the aldehyde group, but the effect is much greater on the C-H group. In column 6 of table 2 the frequency shifts of the absorption maxima resulting from these substitutions are listed; while the B maximum is shifted by 1550 cm^{-1} , the displacements of the E, F, G, and H maxima are 2650, 2590, 2930, and 2890 cm^{-1} , respectively.

In table 2 and figures 3 and 4 similar data are given for 9-cyanoanthracene and 9-nitroanthracene. These are in agreement with the observations on the 9-aldehyde in demonstrating that the introduction of these substituents at the 9-position displaces the C-H group of maxima much more than the A-B.

In figure 5 the spectrum of 2-aminoanthracene (IIIa) is compared with that of the corresponding aminium ion (IV). The spectrum of the ion resembles that of the unsubstituted hydrocarbon, but the spectrum of the free base exhibits several points of difference, the most significant of which, for the purpose of the present study, being the large bathochromic displacement of the A-B band group. The development of the broad absorption band at the extreme long-wavelength end of the spectrum is a feature common to aromatic amines of this general type. A superficial inspection of the curves in figure 5 suggests further that in 2-aminoanthracene the C-H bands may actually be shifted hypsochromically with respect to those of the ion, or of anthracene itself; however, an analysis of

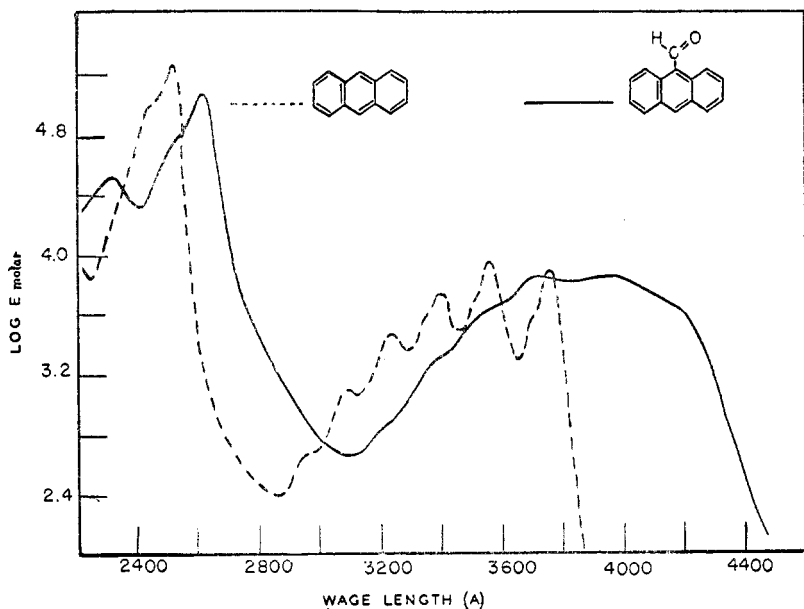


FIG. 2. Ultraviolet absorption spectra of anthracene and 9-anthraldehyde (solvent ethanol).

the frequency shifts must be treated with some reserve in this case, since some doubt exists as to which of the maxima in the ion spectrum corresponds with a given maximum in the spectrum of the free base. The spectra of anthracene and 2-acetoanthracene shown in figure 6 exhibit similar features, and comparison of the curves of figures 5 and 6 with those of figures 2-4 shows clearly that the substituent at position 9 exerts its main effects on the C-H band group, while the substituent at position 2 principally influences the A-B group.

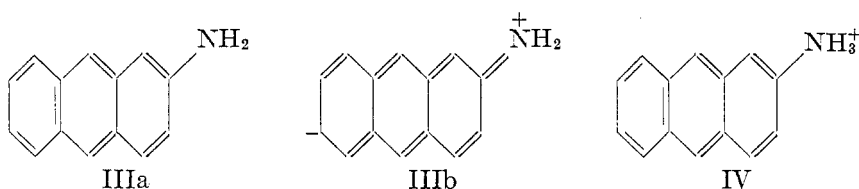


TABLE 2

Frequency shifts of anthracene absorption maxima on introduction of conjugatable substituents

COMPOUND	SOURCE*	SOLVENT	MAXIMUM†	FREQUENCY‡ <i>cm.</i> ⁻¹	SHIFT FROM ANTHRACENE <i>cm.</i> ⁻¹
9-Anthraldehyde.....	a	Ethanol	B	38,170	1550
			E	28,170	2720
			F	26,840	2630
			G	25,130	2930
			H	23,750	2890
9-Cyanoanthracene.....	a	Ethanol	B	39,060	650
			E	28,900	1990
			F	27,510	1960
			G	26,180	1880
			H	24,810	1830
9-Nitroanthracene.....	i	Ethanol	B	39,680	40
			E	30,210	680
			F	28,820	650
			G	27,550	510
			H	26,180	460
2-Aminoanthracene.....	d	Ethanol		38,170	
				31,300	
				29,800	
				28,290	
				24,390	
2-Acetoanthracene.....	g	Ethanol		38,460	
				37,040	
				30,670	
				29,330	
				27,860	
				26,250	
2,3,9,10-Tetraphenylanthracene.....	b	Ethanol	B	34,480	5240
			E	28,900	1990
			F	27,470	2000
			G	26,110	1950
			H	24,700	1940

* See footnote to table 3.

† See figure 1.

‡ The estimated experimental error in the determination of the frequencies of the maxima varies between 40 *cm.*⁻¹ at the high frequencies and 15 *cm.*⁻¹ at the low frequencies, as shown in table 1.

In 2-aminoanthracene the main effect of the amino group will be to lower the energy of one of the I_h structures, yielding instead III_b. In view of the closely knit structure of these molecules, it is hardly to be anticipated that they will

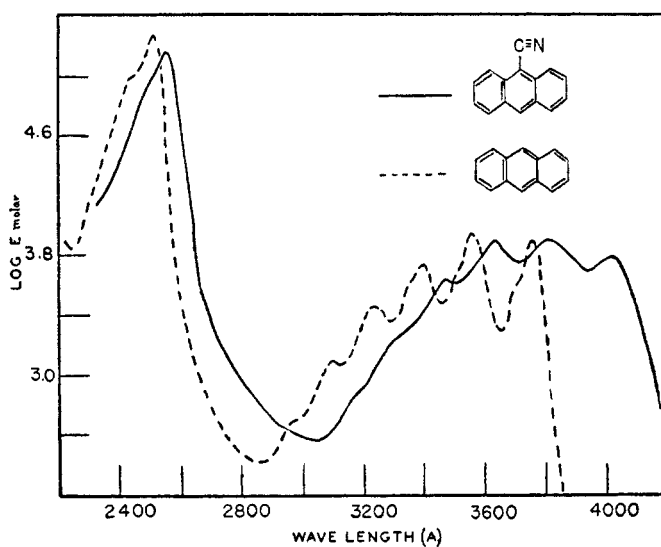


FIG. 3. Ultraviolet absorption spectra of anthracene and 9-cyanoanthracene (solvent ethanol).

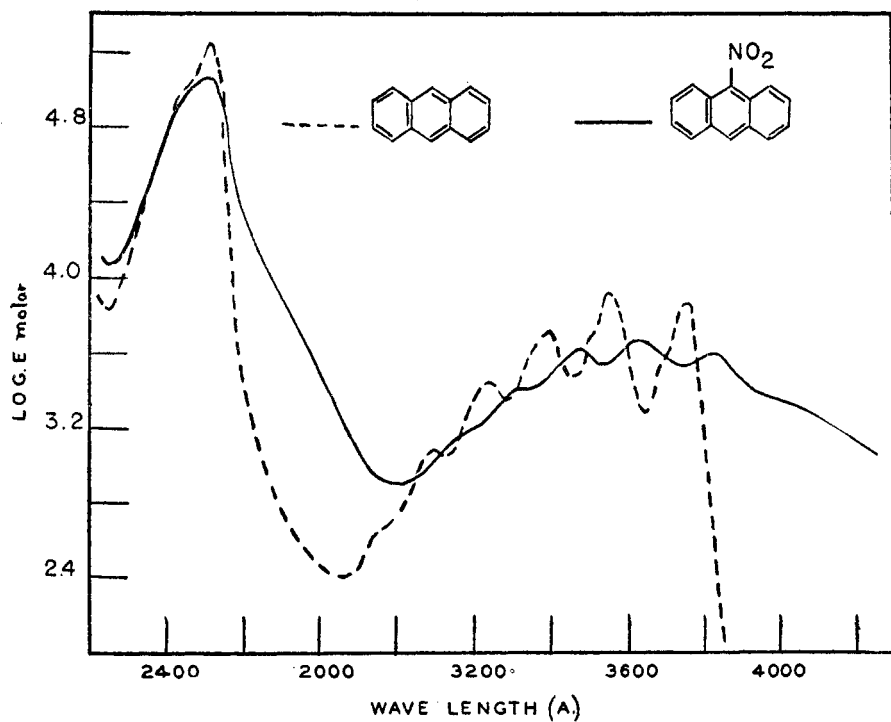


FIG. 4. Ultraviolet absorption spectra of anthracene and 9-nitroanthracene (solvent ethanol).

exhibit such clearly distinctive x -bands and y -bands as do molecules such as carotenoid pigments and triphenylmethyl ions, in which the conjugated systems are more clearly directed along specified axes. Nevertheless, the positional effects of the substituents described above suggest that in anthracene the A-B maxima are associated primarily with excitation directed along the aa' -axis and the C-H maxima with an excitation process directed along the bb' -axis.

B. Substituents exhibiting steric effects

Several investigators (1, 2, 3, 9, 10) have drawn attention to the effects of steric hindrance on the spectra of aromatic compounds. Where the introduction of a

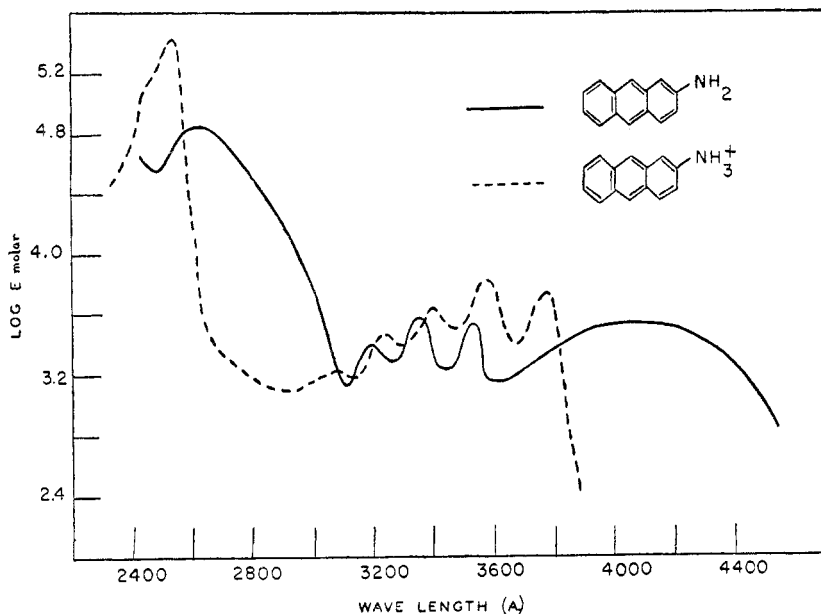


FIG. 5. Ultraviolet absorption spectra of 2-aminoanthracene (solvent ethanol) and 2-aminoanthracene hydrochloride (solvent 2 *N* hydrochloric acid in 50 per cent aqueous ethanol).

substituent increases the energy barriers opposing the establishment of a planar conjugated system, such steric effects become of major importance.

The spectra of certain 9,10-diarylanthracenes are of particular interest in this connection. The introduction of phenyl groups at positions 9 and 10 causes very little change in the anthracene spectrum (3); it is indeed somewhat surprising to observe that the introduction of methyl groups actually produces a greater displacement (*vide infra*). In figure 7 are shown the spectra of 9,10-diphenylanthracene and 2,3,9,10-tetraphenylanthracene (V). Comparison of the data in table 2 indicates that the introduction of the additional phenyl substituents at positions 2 and 3 displaces the C-H maxima by only 800 cm^{-1} , while the B maximum is shifted by 4000 cm^{-1} . Whereas the phenyl groups at

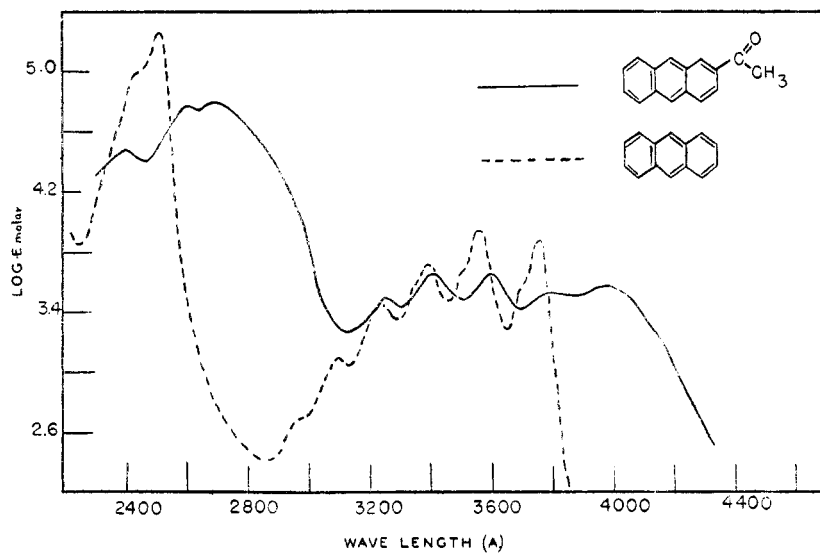


FIG. 6. Ultraviolet absorption spectra of anthracene and 2-acetoanthracene (solvent ethanol).

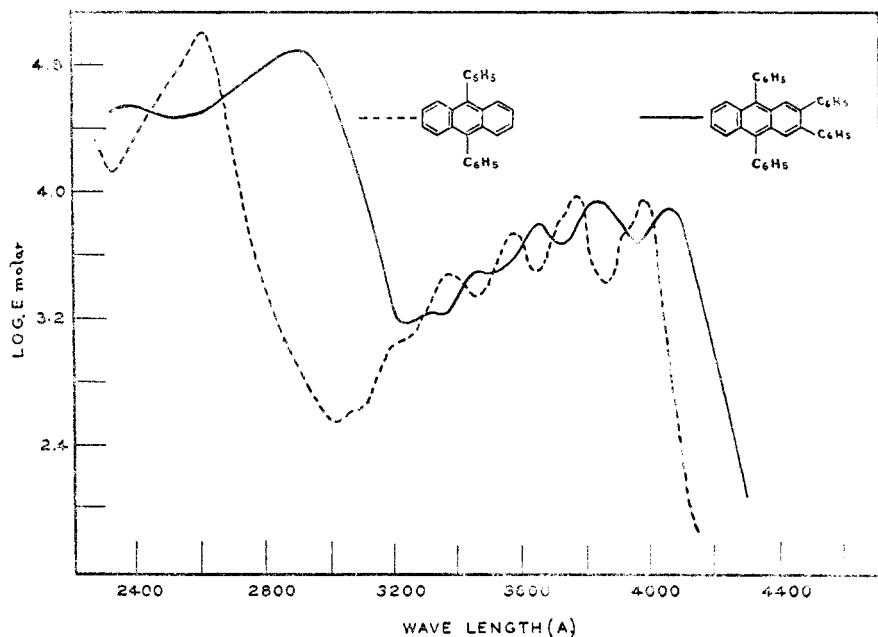
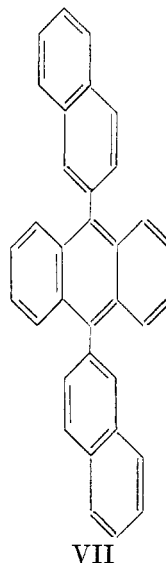
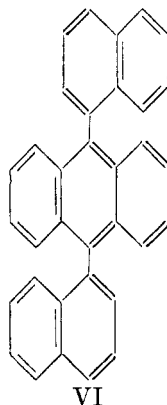
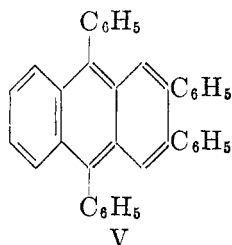


FIG. 7. Ultraviolet absorption spectra of 9,10-diphenylanthracene and 2,3,9,10-tetraphenylanthracene (solvent ethanol).

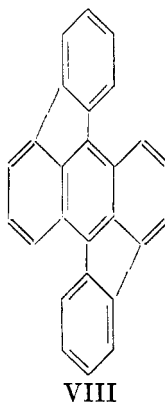
positions 9 and 10 are hindered to such an extent that they probably lie more or less perpendicular to the main plane of the anthracene molecule, the phenyl groups at positions 2 and 3 are less hindered and, like the other 2-substituents

discussed above, exert a major action on the A-B maxima presumed to be associated with an electric moment directed along or near to the *aa'*-axis.

In 9,10-diphenylanthracene, the additive contribution of the meso-phenyl groups to the total absorption of the molecule is too small to be observed, but in 9,10-di(1-naphthyl)anthracene³ (VI) and 9,10-di(2-naphthyl)anthracene³ (VII) the naphthyl chromophores absorb strongly near 3200 Å. in the region of the



anthracene minimum, and in figures 8 and 9 the spectra of these two compounds are shown, together with the computed curves for mixtures of 1 mole of 9,10-dimethylantracene with 2 moles of 1-methyl- or 2-methyl-naphthalene. The additive contributions of the naphthyl chromophores are clearly in evidence. The methyl derivatives are to be preferred to the unsubstituted hydrocarbons as comparison substances, since they allow a rough correction to be made for



³ Compounds supplied by Dr. R. B. Woodward.

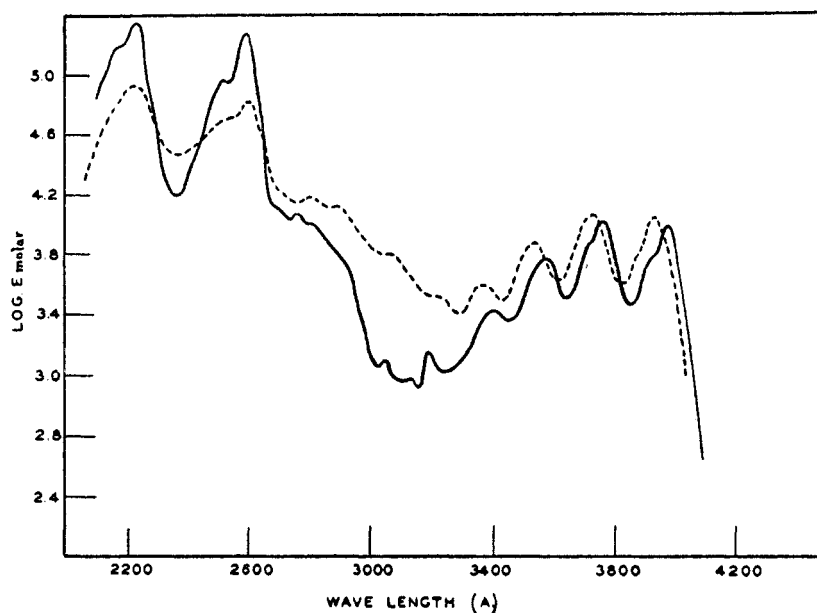


FIG. 8. Ultraviolet absorption spectra: -----, 9,10-di(1-naphthyl)anthracene; ———, computed curve for 1 mole of anthracene and 2 moles of 1-methylnaphthalene (solvent ethanol).

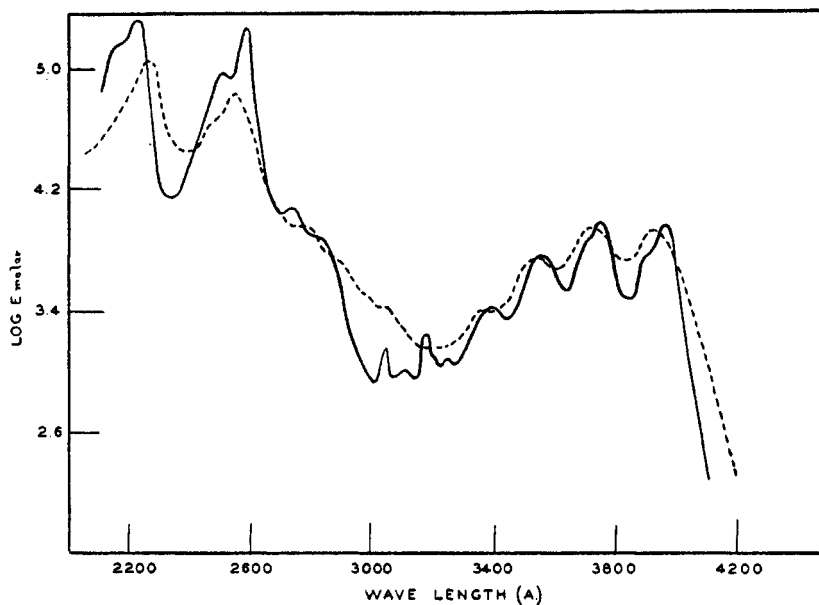


FIG. 9. Ultraviolet absorption spectra: -----, 9,10-di(2-naphthyl)anthracene; ———, computed curve for 1 mole anthracene and 2 moles of 2-methylnaphthalene (solvent ethanol).

the bathochromic effect caused by the replacement of the meso —C—H bond by a pseudo-aliphatic C—C bond.

If the steric restrictions on the coplanarity of 9,10-diphenylanthracene could be eliminated, a spectrum very different from that of anthracene might ensue. In rubicene (VIII) this is partly achieved by the introduction of bridge linkages between the phenyl groups and the anthracene ring system. This removes two of the centers of steric interference and replaces them by linkages which force the meso-aryl groups into a condition approaching planarity. The spectra of 9,10-diphenylanthracene and rubicene are shown in figure 10. The curves differ

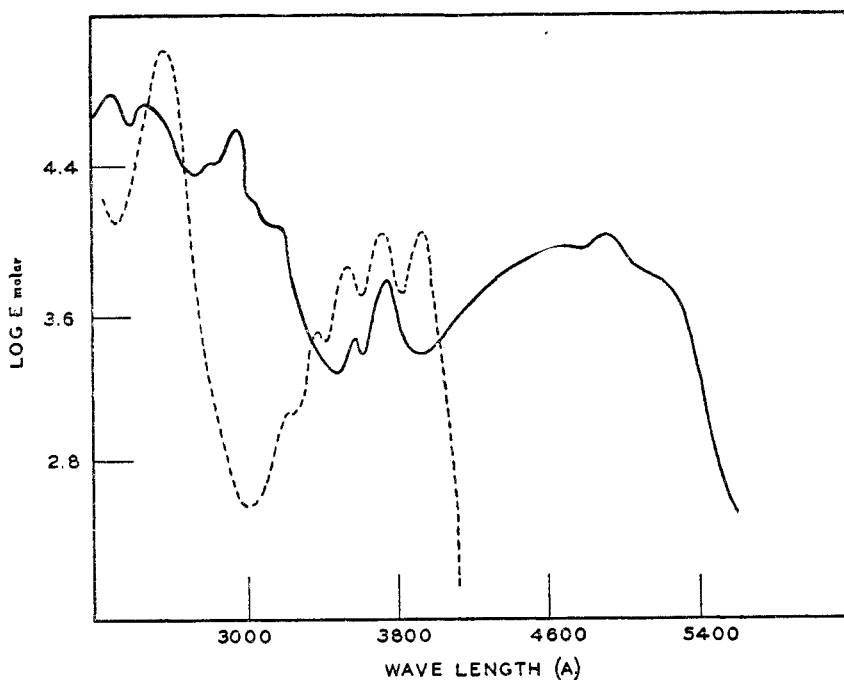


FIG. 10. Ultraviolet absorption spectra: ———, rubicene; -----, 9,10-diphenylanthracene (solvent ethanol).

quite considerably, the rubicene spectrum extending very much further towards longer wave lengths suggestive of a considerable diminution in the levels of certain of the excited states. The introduction of such bridge linkage, however, probably causes changes of a more fundamental character in the electronic structure, since it permits of the participation in the resonance of new types of structures in which the bridge linkage is ethylenic.

C. Substituents exhibiting B-effects

The substituents considered in the above discussions are all of the potentially conjugatable type and, in the absence of steric inhibitions, will facilitate charge transfer in the conjugated systems to which they are attached. This is not so in the case of saturated substituents, such as alkyl groups and aminium ions. It

TABLE 3

Frequency shifts of anthracene absorption maxima on introduction of non-conjugatable substituents

COMPOUND	SOURCE*	SOLVENT	MAXIMUM†	FREQUENCY <i>cm.⁻¹</i>	SHIFT FROM ANTHRACENE <i>cm.⁻¹</i>
9-Methylantracene.....	a	Ethanol	B	39,180	540
			E	30,120	770
			F	28,710	780
			G	27,320	740
			H	25,890	750
		<i>n</i> -Heptane	B	39,060	620
			E	30,170	840
			F	28,780	760
			G	27,360	770
			H	25,940	730
9,10-Dimethylantracene.....	a, c	Ethanol	B	38,460	1260
			E	29,420	1470
			F	27,930	1540
			G	26,530	1530
			H	25,130	1515
		<i>n</i> -Heptane	B	38,460	1220
			E	29,410	1600
			F	28,010	1530
			G	26,560	1570
			H	25,160	1510
9,10-Diphenylantracene.....	a	Ethanol	B	38,610	1110
			E	29,670	1220
			F	28,250	1220
			G	26,880	1180
			H	25,510	1130
9-Methyl-10-ethylanthracene.....	c	<i>n</i> -Heptane	B	38,390	1290
			E	29,410	1600
			F	27,970	1570
			G	26,530	1600
			H	25,130	1540
9-Methyl-10- <i>n</i> -propylantracene.....	c	<i>n</i> -Heptane	B	38,390	1290
			E	29,370	1640
			F	27,970	1570
			G	26,530	1600
			H	25,120	1550
9-Methyl-10- <i>n</i> -butylantracene.....	c	<i>n</i> -Heptane	B	38,390	1290
			E	29,330	1680
			F	27,930	1610
			G	26,490	1640
			H	25,090	1580

TABLE 3—Continued

COMPOUND	SOURCE*	SOLVENT	MAXIMUM†	FREQUENCY	SHIFT FROM ANTHRACENE
				<i>cm.⁻¹</i>	<i>cm.⁻¹</i>
9-Methyl-10-benzylanthracene.	c	<i>n</i> -Heptane	B	38,240	1440
			E	29,410	1600
			F	28,010	1530
			G	26,560	1570
			H	25,090	1580
1,3-Dimethylanthracene.	f	<i>n</i> -Heptane	B	38,990	690
			F	29,160	380
			G	27,780	350
			H	26,280	390
2,9,10-Trimethylanthracene.	f	<i>n</i> -Heptane	B	38,170	1510
			E	29,290	1720
			F	27,890	1650
			G	26,490	1640
			H	25,090	1580
		Ethanol	B	38,240	1480
			E	29,240	1650
			F	27,860	1610
			G	26,460	1600
			H	25,060	1580
2,3,9,10-Tetramethylanthracene.	h	Ethanol	B	37,600	2120
			F	27,400	2070
			G	25,970	2090
			H	24,630	2010
1,9-Dimethyleneanthracene.	g	<i>n</i> -Heptane	B	38,680	1000
			F	28,130	1410
			G	26,740	1390
			H	25,310	1360
	e	Ethanol	B	38,760	960
			F	28,130	1340
			G	26,740	1320
			H	25,320	1320
1,2-Trimethylene-5,10-dimethylene-anthracene.	e	<i>n</i> -Heptane	B	38,020	1660
			E	29,110	1900
			F	27,700	1840
			G	26,250	1880
			H	24,870	1800

TABLE 3—*Concluded*

COMPOUND	SOURCE*	SOLVENT	MAXIMUM†	FREQUENCY <i>cm.</i> ⁻¹	SHIFT FROM ANTHRACENE <i>cm.</i> ⁻¹
1, 2-Trimethylene-5, 10-dimethylene-anthracene— <i>Concluded</i>	e	Ethanol	B	38,020	1690
			E	29,150	1740
			F	27,620	1850
			G	26,180	1880
			H	24,880	1760

* (a) See table IV of reference 3; (b) Dr. C. F. H. Allen, Eastman Kodak Co.; (c) Dr. E. Berliner, Bryn Mawr College; (d) Dr. L. F. Fieser, Harvard University; (e) Dr. L. F. Fieser and Dr. E. B. Hershberg, Harvard University; (f) Dr. L. F. Fieser and Dr. H. Heymann, Harvard University; (g) Dr. L. F. Fieser and Dr. H. M. Irwin, Harvard University; (h) Dr. L. F. Fieser and Dr. T. Webber, Harvard University; (i) compound synthesized in our own laboratories.

† See figure 1.

‡ See footnote to table 2.

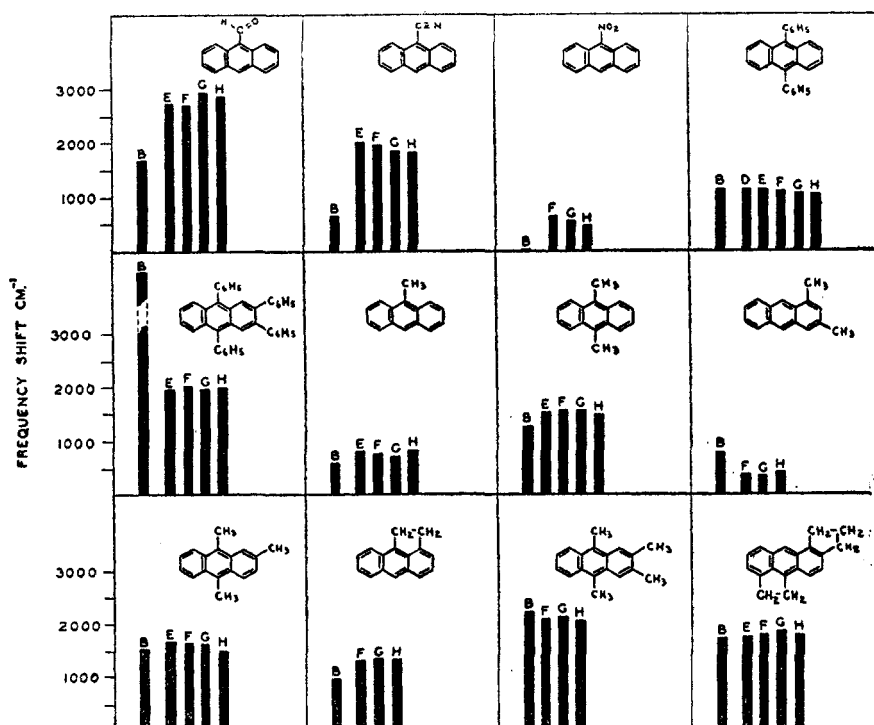


FIG. 11. Diagrammatic representation of frequency displacements of principal anthracene absorption maxima produced by introduction of various substituents.

is well known that the replacement of a hydrogen atom of an aromatic ring system by a methyl group commonly causes a bathochromic displacement of the absorp-

tion curve accompanied by little change in the shape of the absorption envelope except for some loss in the resolution of the vibrational fine structure. The positions of the absorption maxima for a variety of alkylanthracenes are listed in table 3, together with the frequency shifts of the principal maxima relative to those of anthracene.

In both 9-methyl- and 9,10-dimethylantracene the frequency shifts of the A-B maxima differ much less from those of the C-H maxima than is the case for the substituents exhibiting conjugation effects. Thus in the case of 9,10-dimethylantracene the B maximum is displaced by 1250 cm^{-1} and the E, F, G, and H maxima by about 1500 cm^{-1} , while the comparable figures for 9-cyanoanthracene are 650 and 1900 cm^{-1} . This uniformity of the bathochromic shifts produced by alkyl substituents in distinction from the selective effects of the conjugatable substituents is illustrated diagrammatically in figure 11, in which the vertical columns are drawn proportional to the frequency displacements caused by introduction of the substituent, the individual maxima being designated by the letter at the top of each column.

The series of compounds 9,10-dimethylantracene, 9-methyl-10-ethylantracene, 9-methyl-10-*n*-propylantracene, and 9-methyl-10-*n*-butylantracene are included in table 3. The increase in the length of the aliphatic chain of the 10-alkyl group in this series of compounds has an exceedingly small effect on the positions of the maxima, the observed variations being within the limits of experimental error. There is here no indication of any hypsochromic shift on passing from the methyl to a higher alkyl substituent, as has been observed by some investigators (11, 12) in other series of alkylbenzene derivatives.

To account for the effects of these saturated substituents some modification of the argument developed above is needed. In the consideration of the conjugatable substituents, it was tacitly assumed that the whole effect of the substituent was to reduce the energy of the excited state, and that with this action there was associated a selective factor dependent on the alignment of the substituent with respect to certain axes in the molecule. The absorption maxima would also be displaced bathochromically by any change in the molecular structure which would raise the energy of the ground state to a greater extent than it raised the energy of the excited state, and a change of this type, acting primarily on the ground state, would produce a non-selective effect displacing all the maxima by the same amount.

To a first approximation, it would appear that the conjugatable substituents exert their principal action on the spectra by lowering the energy of the excited states, while the alkyl and other non-conjugatable substituents modify the spectra by bringing about an increase in the energy of the ground state. More probably effects of both types are simultaneously active for both types of substituents.⁴ Although the 9-alkyl substituents cause displacements of the maxima which are more equal than those of the 9-cyano-, 9-nitro-, and 9-aldehyde groups, there still remains some difference in excess of the experimental error, and this differ-

⁴ Views similar to these have been expressed independently by Price (11).

ence is in the same sense as the difference noted for the conjugatable substituents. In 1,3-dimethylantracene the displacement of the B maximum exceeds by about 300 cm^{-1} that of the C-H maxima. This difference might be ascribed to some stabilization of the excited states through a hyperconjugation effect, and the magnitude of the difference may be of significance as a rough measure of the extent of such hyperconjugation.

In the case of the conjugatable substituents which exhibit C-effects, the introduction of the substituents will undoubtedly change the energy of the ground

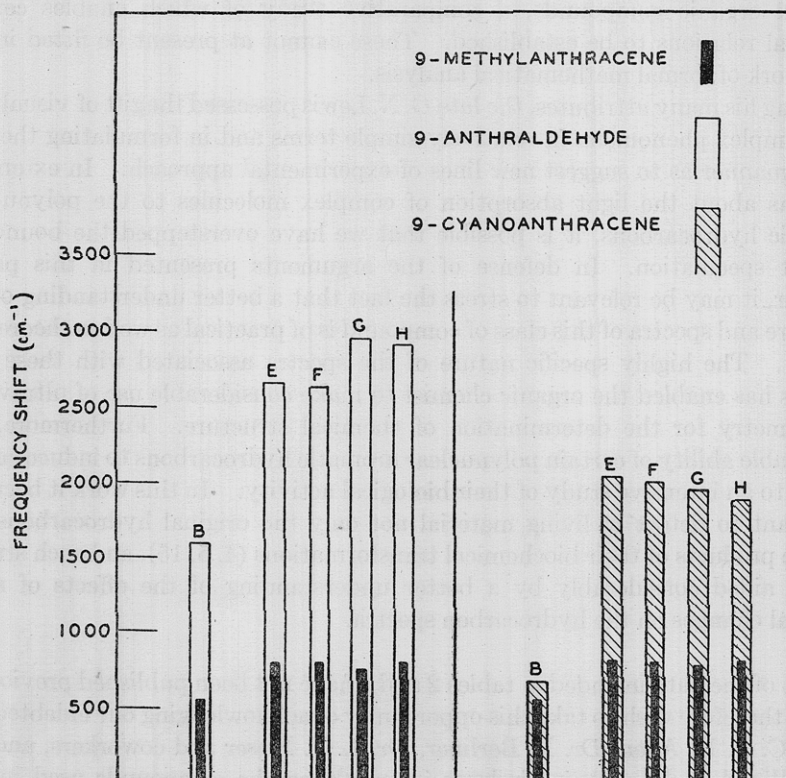


FIG. 12. Frequency displacements of anthracene produced by 9-aldehyde and 9-cyano groups with 9-methyl shifts superimposed.

state to some extent, and if this could be determined and allowed for, the directional specificity of the residual effect on the excited state would appear more pronounced. If the effect of the 9-aldehyde group on the ground state be assumed to be about the same as that of the 9-methyl substituent, and if the hyperconjugation effect of the methyl group be neglected, some idea of the influence of the aldehyde group on the excited state can be derived by subtracting the frequency shifts of the 9-methyl group on each band from that of the 9-aldehyde group. This is shown diagrammatically in figure 12. A similar analysis of 9-cyanoanthracene, also shown in figure 12, would suggest that practically the

whole of the displacement of the B maximum in this case might be related to the raising of the energy of the ground state.

IV. CONCLUSIONS

In the semiempirical projection of a theoretical principle beyond the limits of strict or approximate mathematical treatment, it is difficult to decide at what point reasoned argument degenerates into uncritical speculation. In the present instance we are confronted with a considerable body of data on the spectra of complex organic compounds, a comparative study of which enables certain empirical relations to be established. These cannot at present be fitted into a framework of formal mathematical analysis.

Among his many attributes, the late G. N. Lewis possessed the gift of visualizing such complex phenomena in relatively simple terms and in formulating them in such a manner as to suggest new lines of experimental approach. In extending his ideas about the light absorption of complex molecules to the polynuclear aromatic hydrocarbons, it is possible that we have overstepped the bounds of prudent speculation. In defense of the arguments presented in this paper, however, it may be relevant to stress the fact that a better understanding of the structure and spectra of this class of compound is of practical as well as theoretical interest. The highly specific nature of the spectra associated with these ring systems has enabled the organic chemist to make considerable use of ultraviolet spectrometry for the determination of chemical structure. Furthermore, the remarkable ability of certain polynuclear aromatic hydrocarbons to induce cancer has led to an intensive study of their biological activity. In this work it becomes important to detect in living material not only the original hydrocarbons but also the products of their biochemical transformations (4, 5, 15), and such studies will be aided considerably by a better understanding of the effects of small chemical changes on the hydrocarbon spectra.

Most of the data included in tables 2 and 3 have not been published previously, and we therefore wish to take this opportunity of acknowledging our indebtedness to Dr. C. F. H. Allen, Dr. E. Berliner, Dr. L. F. Fieser and coworkers, and Dr. R. B. Woodward for their kindness in supplying the compounds used in this investigation. Thanks are also due to Mrs. G. D. Thorn, Mr. A. Cahn, and Miss Kathleen McLean for technical assistance. Part of the work, carried out at Queen's University, Kingston, Ontario, was aided by a grant from The Penrose Fund of The American Philosophical Society.

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