uronide material. To determine whether this non-uronide material was contributing to the diffraction pattern, some pure polygalacturonide methyl ester (free of nonuronide material), prepared by the method of Morell, Baur and Link,[23] was deësterified by alkali, acidified, reprecipitated with 50% alcohol to free it of salt, and then titrated to *p*H 7.5 with sodium hydroxide to convert it to the sodium salt. The X-ray powder photograph of this material is identical with that obtained from sodium pectate made from the pectic acid used in this investigation. The diffraction effects observed therefore must arise from sodium pectate alone.

Both this result and the fact that the (003) reflection is very sharp, indicate that the non-uronide material must be attached only infrequently along the galacturonide chain in citrus pectin. There is also one other piece of evidence in agreement with this conclusion. The volumes occupied per three uronide groups in sodium pectate (744 Å.^{3}) and in sodium alginate[24] (727 Å.^{3}) are very nearly the same. The uronic acid analysis on the alginic acid used to make the sodium alginate showed that this material contains not more than 4% (and probably less) non-uronide material.

Acknowledgments.—We are indebted to Mr. H. Lotzkar for making the oriented fiber of sodium pectate used in this investigation. We also wish to express our gratitude to Dr. R. C. Merrill, Dr. Harry Owens and Mr. E. Jansen for many helpful and stimulating discussions regarding pectin chemistry, and to the latter for furnishing us with pure polygalacturonic acid; to Dr. R. M. McCready for furnishing us with the results of his uronic acid analysis on pectic and alginic acids. We also wish to thank Dr. F. T. Jones for his determination of the refractive indices of the fibers and Mr. Jay Allison for taking the photographs of the molecular models.

Summary

The results of an X-ray diffraction investigation of oriented sodium pectate fibers are recorded. The interpretation of these results indicates that the galacturonide chain has the configuration of a three-fold screw axis and that the chains are arranged in closest packing. The structure has pseudo hexagonal symmetry. The identity period in the fiber direction is 13.1 Å. This fiber identity period is somewhat less than the value found for some cellulose derivatives in which the chain has the configuration of a three-fold screw axis. This difference in identity periods has been discussed in terms of molecular models.

On adsorption, sodium pectate in equilibrium with air at a relative humidity of 40% contains 18% water. A considerable portion of this water is located in the crystalline portion of the material.

The non-uronide material (18%) is shown to have no detectable influence on the X-ray pattern.

ALBANY 6, CALIFORNIA RECEIVED JUNE 25, 1945

[23] Morell, Baur and Link, *J. Biol. Chem.*, **105**, 1 (1934).

[24] Palmer and Merrill; to be published soon.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF QUEEN'S UNIVERSITY AND HARVARD UNIVERSITY]

Some Factors Influencing the Ultraviolet Absorption Spectra of Polynuclear Aromatic Compounds. I. A General Survey[1]

BY R. NORMAN JONES

Introduction

Until recently the problem of the relationship between the electronic absorption spectra and the chemical structure of organic compounds could be approached only in a qualitative and empirical manner. An adequate basis for a theoretical treatment of the subject was lacking, and little could be done beyond correlating certain features of the ultraviolet and visible spectra with the specific arrangements of certain groups of atoms in the molecule. Work along these lines led to the establishment of several exceedingly useful empirical rules relating absorption spectra and chemical structure, and these generalizations have proved of considerable practical value in synthetic and analytical organic chemistry.[1a,2,3]

Since the formulation of the resonance theory, progress has been made in the more fundamental explanation of light absorption by polyatomic molecules,[4,5,6] but this purely theoretical approach has not yet progressed sufficiently to provide a satisfactory description of the spectra of the more complex organic molecules. Less rigorous treatments, based on a qualitative application of the principles of quantum mechanics have been developed by several investigators[7,8,9,10,11] and it has become possible to obtain a somewhat clearer concept of the phenomena occurring during electronic activation, even where the complexities of the system preclude a quantitative treatment.

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[1] Presented, in part, before the Organic Division of the American Chemical Society, New York, September, 1944.

[1a] Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 72, 76 (1942).

[2] Jones, *Chem. Rev.*, **32**, 1 (1943).

[3] Jones, *Can. Chem. Process Ind.*, **28**, 497 (1944).

[4] Price, *J. Chem. Soc. Annual Reports*, **36**, 47 (1939).

[5] Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942).

[6] Mulliken, *J. Chem. Phys.*, **7**, 364 (1939), and earlier papers.

[7] Bowen, *J. Chem. Soc. Annual Report*, **40**, 12 (1943).

[8] Förster, *Z. physik. Chem.*, **B41**, 287 (1938).

[9] Pauling, *Fortschr. Chem. organ. Naturstoffe*, **3**, 203 (1939).

[10] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[11] Brooker, *Rev. Mod. Phys.*, **14**, 275 (1942).

During the past three years, data on the ultraviolet absorption spectra of a large variety of polynuclear aromatic compounds have been accumulated in this Laboratory. In making these measurements we have had two objects in view; in the first place if the effects of substituents on the spectra of aromatic hydrocarbons could be predicted, the value of ultraviolet spectrophotometry as a practical aid in the elucidation of the structure of new aromatic compounds would be considerably enhanced. Secondly, such data may provide material for the eventual interpretation of the complex spectra of these hydrocarbons in terms of quantum mechanics.

The Mechanism of Light Absorption by Organic Compounds

Most organic compounds which exhibit light absorption in the visible and nearer ultraviolet region of the spectrum (2000–8000 Å.) contain double bonds, and it is the π-orbital electrons of these bonds which are concerned in the normal processes of light absorption. Two or more electronic structures may be written for these molecules, and resonance among the several structures gives rise to a stable structure of energy content lower than that of any of the contributing structures. In addition, states of higher energy result from the resonance combination, and light absorption is associated with the activation of the molecule from certain lower to certain higher resonance energy states.

The extent of interaction between a molecule and a beam of light would seem to be determined not only by the frequency of the light, but also by the orientation of the molecule with respect to the electric vector of the light wave. Lewis and Calvin[10] have discussed this at some length, and have suggested that, in the general case of a planar molecule with no center of symmetry, such vector effects give rise to two independent absorption bands, or series of bands resulting from two electronic activation processes associated with electric moments oriented normally to each other in the plane of the molecule. Absorption bands resulting from the primary activation process of lower energy (longer wave length) are called *x-bands*, and those of higher energy *y-bands* by these authors. More recently Lewis and Bigeleisen[12] have advanced experimental evidence in support of these concepts, based on the measurement of the spectra of unsymmetrical triphenylmethyl ions suspended in rigid media, using plane polarized light.

The changes in the spectra of carotenoid pigments which have been observed by Zechmeister[13] to accompany *trans* → *cis* isomerism of the conjugated polyene chain have also been explained in terms of vectorization of the electronic activations within the molecule. Zechmeister[13] has shown that for the β-carotene molecule the spectrum is simplest if the *cis–trans* arrangements of the substituents about the ethylenic bonds are such that the molecule is linear and of maximum length. Should *trans* → *cis* isomerization occur at one or more of the ethylenic bonds, so that the molecule acquires a shorter, folded structure, new "*cis*-bands" appear in the spectrum at shorter wave lengths. In the "all *trans*" molecule, only electronic oscillations along the chain are significant, but as a result of the departure from linearity in the *cis*-isomer, an appreciable electric moment may develop in a direction normal to the straight line joining the ends of the conjugated system. The appearance of these *cis*-bands is in accordance with theoretical considerations of Mulliken,[14] and of Zechmeister, Pauling, *et al.*,[15] and provides strong support for the principle of vectorized electronic activation.

The Spectra of Polynuclear Aromatic Hydrocarbons

The compounds with which we are primarily concerned in this paper are alkyl, aryl, carbonyl methoxy, amino and phenolic derivatives of anthracene, phenanthrene, chrysene, 1,2-benzanthracene, 3,4-benzpyrene and 1,2,5,6-dibenzanthracene. The parent hydrocarbons consist of systems of condensed benzenoid rings and may be regarded optically as electron lattices of limited extent, within which there can exist considerable freedom for electron displacements in various directions within the plane of the ring system. It has been shown[16,17] that under normal conditions[18] the electronic activation of such molecules can be induced only by light so oriented that the electric vector lies in the plane of the aromatic ring system. It would seem highly probable that further restrictions on the electronic activation of such two-dimensional lattice molecules would be imposed, such that the activation of different groups of absorption bands in the complex spectra of these hydrocarbons is associated with the specific orientation of the electric vector of the light wave within the plane of the molecule. This may be illustrated by consideration of the spectrum of anthracene (Fig. 1), in which it is reasonable to assume that the short wave group of maxima (A, B) is associated with one process of electronic activation while a second series of maxima C–G form a group of vibrational sub-levels associated with a separate primary activation mechanism. It is highly probable that the electric moments associated with these two series of bands are vectorized in the plane of the molecule, *i. e.*, they

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[12] Lewis and Bigeleisen, This Journal, **65**, 520, 2102, 2107 (1943).

[13] Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

[14] Mulliken, *J. Chem. Phys.*, **7**, 364 (1939).

[15] Zechmeister, LeRosen, Schroeder, Polgár and Pauling, This Journal, **65**, 1940 (1943).

[16] Krishnan and Seshan, *Proc. Indian Acad. Sci.*, **8**, 487 (1938).

[17] Scheibe, Hartwig and Müller, *Z. Elektrochem.*, **49**, 383 (1943).

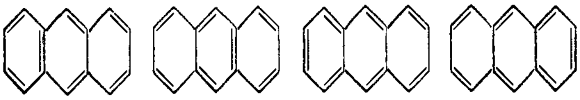
[18] Exceptions are provided by the "s-bands" which are observed only in the spectra of certain molecular aggregates. These are believed to possess a layered structure, caused by the face-to-face association of planar molecules (Scheibe, *Kolloid-Z.*, **82**, 1 (1938)).

are *x*-bands and *y*-bands, using the Lewis nomenclature.

To obtain a clearer picture of the mechanism of light absorption by polynuclear aromatic hydrocarbons, some knowledge of the relative energies of the contributing electromeric structures is required. At present there are no experimental methods by which such relative energies may be determined[19] but in the case of some of the more symmetrical polynuclear hydrocarbons (such as anthracene) it is possible to make tentative conjectures about these.

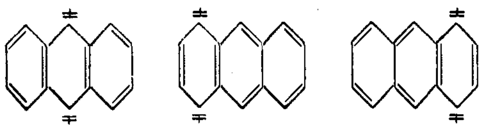
In a first approximation, it may be assumed that the electromeric structures for anthracene in which no separation of charge is involved (Ia–Id) will make the major contributions to the ground state of the molecule, while polarized forms (Ie–Ij) will contribute predominantly to the electronically excited states. The non-polarized contributing structures will differ in energy among themselves,[20] but, for present purposes, this is of secondary importance, as our main concern is with the structures making major contributions to the excited states.

Ground state



Ia Ib Ic Id

Activated state (vertical polarization)



Ie If Ig

Activated state (horizontal polarization)

Ih Ij

The activated states of the anthracene molecule result, *ex hypothesi*, from the resonance combination of the polarized forms. The ten principal polarized contributing structures fall into five groups of two each (Ie–Ij). Of these, Ie, Ih and Ij are probably of predominating importance. Inspection of the ten structures suggests that they fall into two series; the first, consisting of Ie, If and Ig, should make major contributions to an activated state associated with an electric moment oriented vertically in the plane of the molecule, while the structures Ih and Ij contribute mainly to an activated state associated with a horizontally oriented activation mechanism.

If the two band systems in the ultraviolet absorption spectrum of anthracene are associated with vectorized electric moments, it would seem probable that the vectors will be directed vertically and horizontally, and, furthermore, the polarizations in these two planes can be tentatively associated with specific activated structures. Further consequences of these hypotheses with respect to the anthracene molecule will be discussed in a later paper. In the case of other less symmetrical polynuclear aromatic hydrocarbons, the factors influencing the light absorption process must be of an essentially similar nature, although lack of symmetry may make any prediction of the directions of the activating electric moments much more problematical.

The main part of this paper is devoted to a description of the various types of changes which are produced in the spectra of polynuclear aromatic hydrocarbons by the introduction of substituent groups. An attempt is made to provide a partial explanation of these effects in terms of the resonance theory. The mechanism of light absorption outlined in the foregoing paragraphs undoubtedly represents an over-simplification of the true process, but suffices as a basis, in terms of which these substitution effects can be discussed.

Effects of Substituents on the Spectra of Polynuclear Aromatic Hydrocarbons

The changes which are produced in the spectrum of a polynuclear aromatic hydrocarbon by the replacement of one of the aromatic hydrogen atoms with some other atom or group fall into four well differentiated classes. These substituent effects have their counterparts in the spectra of other types of compounds: it will be found convenient to discuss them in separate sections, and to designate them as follows: (a) the bathochromic effect (B-effect), (b) the fine structure effect (Fs-effect), (c) the conjugation effect (C-effect), (d) the steric effect (S-effect).

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(19) It should be kept in mind that the concept of the actual molecular structures being derived from combinations of "classically bonded" electronic structures is, in essence, an attempt at transliteration of a mathematical technique of analysis into more familiar terms. The newer concepts of molecular orbitals (ref. 4, 7) probably provide a closer "picture" of the true nature of the molecule in its ground state and several activated conditions.

(20) The bond positions in the conventional structural formulas for polynuclear aromatic hydrocarbons are based on the Fries rule (Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935)). According to this rule each aromatic ring of a polynuclear aromatic compound strives to assume a bond structure which most closely approaches the condition of an isolated benzene ring: the structure in which the maximum number of rings contains three double bonds will have the lowest energy content. As annunciated by the authors, this rule was conceived in terms of classical organic chemical theory and applied to the *actual* ground state of the molecule. Its extension as a basis for the comparison of the relative energies of the several non-polarized structures contributing to the ground state of the molecule can be questioned on theoretical grounds, but in the absence of positive evidence to the contrary it may be convenient to hypothesize that the structures Ia and Ib, both of which contain two benzenoid and one quinonoid ring systems, will be of lower energy than the structures Ic and Id, which contain one benzenoid and two quinonoid rings, and that, to a first approximation, the ground state of the anthracene molecule may be represented by the lower of the two energy states which result from the resonance combination of Ia and Ib.

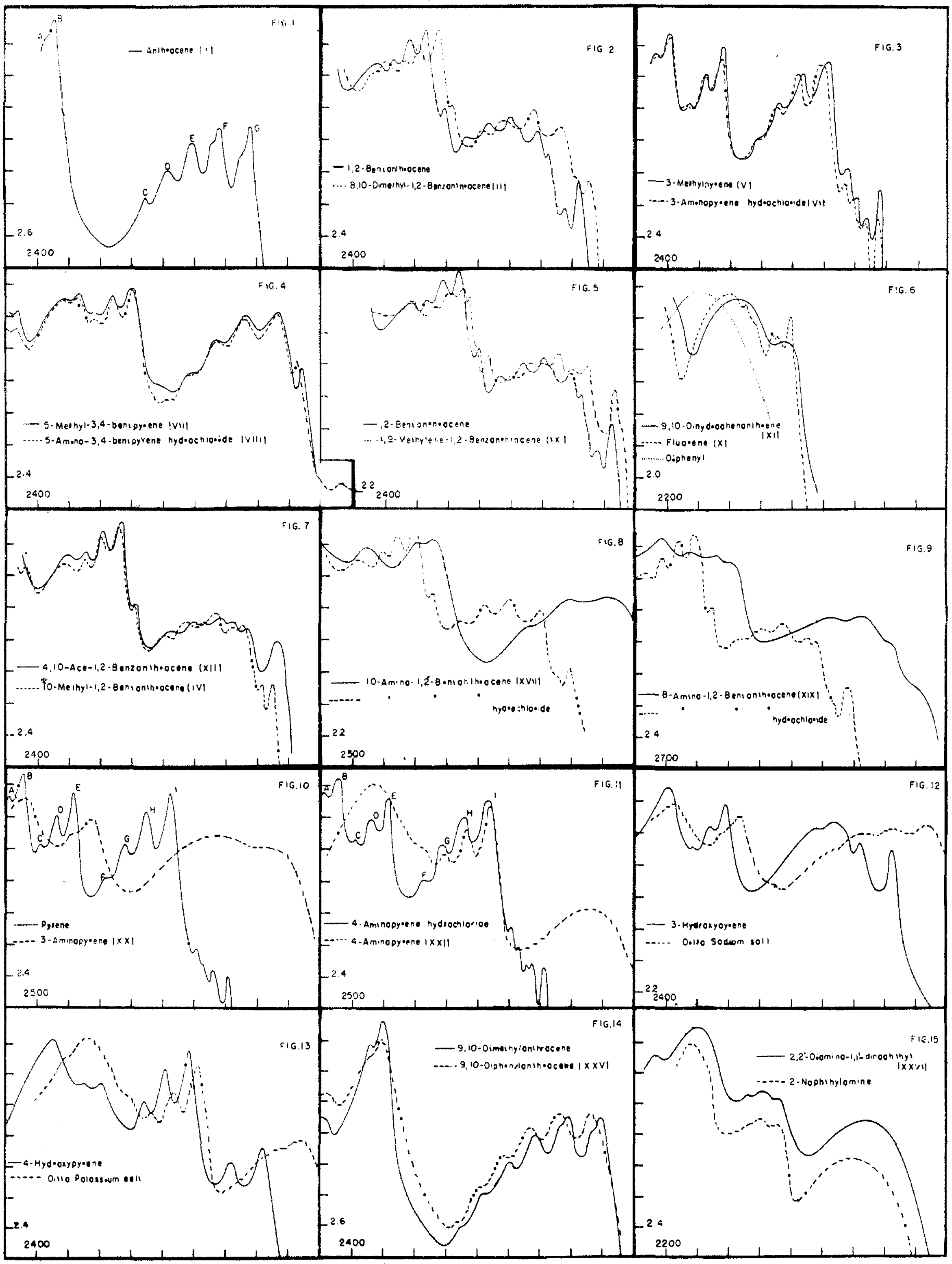
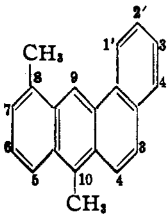


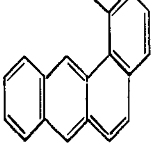
Plate I.—Figures 1–15.—The wave lengths along the abscissa axes are marked at intervals of 200 Å. The ordinate marks indicate the logarithm of the molecular extinction coefficient at intervals of 0.40 unit.

The Bathochromic Effect

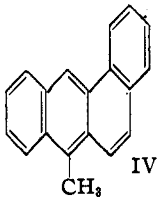
The B-effect is observed most characteristically in the spectra of alkyl derivatives of polynuclear aromatic hydrocarbons; a typical example is provided in Fig. 2 where the spectrum of 8,10-dimethyl-1,2-benzanthracene (II) is compared with the spectrum of 1,2-benzanthracene. The spectra of compounds which exhibit this effect are similar in general shape and intensity to the spectrum of the unsubstituted hydrocarbon, but the whole curve is shifted to longer wave lengths. The magnitude of the shift depends on the position of the substituent in the ring system. In the 1,2-benzanthracene series, eight of the twelve isomeric mono-methyl derivatives have been examined, and it is observed[2] that substitution of the 1′-position (III) causes only a slight displacement of the curve whereas the bathochromic shift is maximal for a methyl group at the 10-position (IV).



II



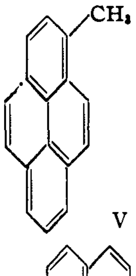
III



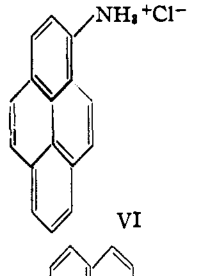
IV

The B-effect commonly occurs when a hydrogen atom attached to any chromophore is replaced by an alkyl group. Shift of the spectrum to longer wave lengths implies a decrease in the energy level differences between the ground and activated states; this may result either from a lowering of the levels of the activated states, a raising of the level of the ground state, or a combination of the two. The reasons for these energy changes are by no means clear; the introduction of the alkyl substituent cannot give rise to any new resonance structures of normal type, but Mulliken,[21] and co-workers have suggested that a small increase in the resonance stabilization energy of the molecule of the alkyl derivatives may result from "hyperconjugation," *i. e.*, coupling between the σ-electrons of the C—H bonds of the methyl group and the bonding electrons of the C—CH$_3$ linkage. These authors have calculated that the increase in resonance stabilization energy from this source is of the correct order of magnitude to account for the observed spectral shifts.

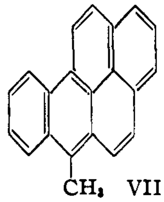
It has been observed[2] that the amine cation substitutent (—NH$_3^+$) gives rise to a B-effect similar to that of the methyl group, the magnitude of the bathochromic shifts produced by the two substituents being closely comparable for substitution at the same position in a polynuclear aromatic hydrocarbon molecule. This is illustrated in Figs. 3–4, where the absorption curves of 3-methylpyrene and of 5-methyl-3,4-benzpyrene are compared with the curves of 3-aminopyrene hydrochloride and 5-amino-3,4-benzpyrene hydrochloride, respectively (V–VIII).



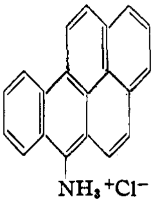
V



VI



VII



VIII

It would be anticipated that any bathochromic shift of the absorption maxima of these compounds attributable directly to the dipole effects of the substituent group would be much more pronounced for the —NH$_3^+$ than for the —CH$_3$ group. The similar quantitative behavior of these two substituents serves to emphasize the fact that the presence or absence of a net charge on a substituent has, *per se*, no significant influence on the ultraviolet absorption spectrum. Other evidence of this is seen in the close similarity which is frequently exhibited between the spectra of carboethoxy derivatives of polynuclear aromatic hydrocarbons, and of the related carboxylate ions, also between derivatives containing the —NH$_2$ and the —O$^-$ substituents which are discussed on page 2136.

In addition to the alkyl and amine cation groups, B-effects are also observed in the spectra of certain derivatives of polynuclear aromatic hydrocarbons in which the substituents contain double and triple bonds in apparent conjugation with the ring system; the cyano, thiocyano, isocyanate and certain halogen derivatives produce effects of this kind (see page 2142).

The Fine Structure Effect

Occasionally the introduction of a saturated methylene or dimethylene bridge across part of a polynuclear aromatic hydrocarbon molecule causes a pronounced sharpening of the resolution of the fine structure bands of the hydrocarbon spectrum, and an actual change in the number and relative intensity of these bands may sometimes occur. Such Fs-effects are comparatively uncommon. An example is provided in Fig. 5 where the spectra of 1′-9-methylene-1,2-benz-

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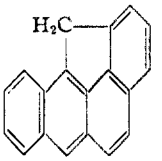
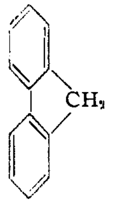
[21] Mulliken, Rieke and Brown, THIS JOURNAL, 63, 41 (1941); Mulliken and Rieke, *ibid.*, 63, 1770 (1941).

anthracene (IX) and 1,2-benzanthracene are compared. In the bridged derivative changes are observed in the fine structure between 2700 and 3000 Å. and also between 3200 and 3700 Å.

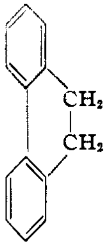


IX

The methylene bridge in fluorene (X) is associated with the production of very prominent fine structure and in Fig. 6 the spectra of fluorene, diphenyl and 9,10-dihydrophenanthrene (XI) are compared. It may be relevant to note that considerable steric strain is incurred in the closure of the five-membered ring in fluorene whereas the 9,10-dihydrophenanthrene molecule is practically strainless in a planar form. The Fs-effect is seen also in the spectrum of 10-methyl-1′,9-methylene-1,2-benzanthracene, accompanied by a B-effect due to the additional methyl substituent.[22] In 4,10-ace-1,2-benzanthracene (XII) an Fs-effect is observed in the 3000–3800 Å. region while the shorter wave length region is normal (Fig. 7).

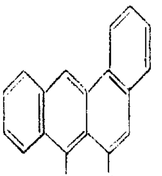


X

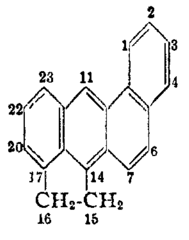


XI

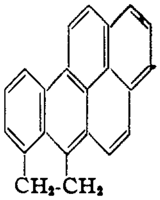
The presence of a methylene or dimethylene bridge linkage is not necessarily associated with increase in fine structure resolution. In cholanthrene (XIII) and the several mono- and dimethyl-cholanthrenes which have been examined,[22–26] the 14-17-dimethylene bridge produces no Fs-effect, neither does the dimethylene bridge in 4′,5-ace-3,4-benzpyrene[27] (XIV). In 4,5-methylenechrysene,[28] 4,5-methylenephenanthrene (XV) and 1′,9-methylene-1,2,5,6-dibenzanthracene (XVI) the methylene bridge linkage produces a normal B-effect.



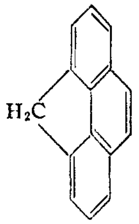
XII



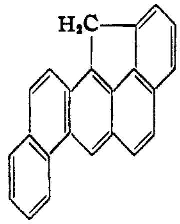
XIII



XIV



XV



XVI

The Fs-effect primarily involves the resolution of fine structure which is attributed to vibrational activations of the molecule. According to Lewis and Calvin,[10] the *loss* of fine structure resolution, frequently observed when chromophoric groups are loaded with saturated substituents, results from the facilitation of a rapid dissipation of the energy of the electronically activated system among the several vibrationally activated states. These authors liken this to the effect produced by loose bolts in the moving parts of a machine. It would seem reasonable to suppose that a strained bridge linkage, such as occurs in fluorene and 1′,9-methylene-1,2-benzanthracene may increase the rigidity of the structure and hinder the dissipation of the energy of the electronically activated molecule, *i. e.*, carrying over the mechanical analogy of Lewis and Calvin such a bridge linkage may act by tightening up the bolts.

The Conjugation Effect

This effect is produced by unsaturated substituents in which the unsaturated linkage is in a position of conjugation with the aromatic system. It is frequently, but not invariably, observed on the introduction of ethylenic and carbonyl groups and also on the introduction of such groups as $-NH_2$, $-OH$ and $-O^-$ which possess donatable electron pairs on the atom attached directly to the aromatic ring system. These substituents may bring about very great changes in the hydrocarbon spectrum, whole groups of bands may be eliminated or may be moved to longer wave lengths by several hundred Ångström units. The groups which produce C-effects have long been recognized as auxochromes in dyestuff chemistry, and there can be little doubt that they act by lowering the energy of certain of the polarized structures which contribute to the resonance states of the activated molecule.

In the discussion of the C-effect which follows, most examples have been drawn from amino and phenolic derivatives, since the small size of these

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(22) Jones, This Journal, **63**, 151 (1941).

(23) Fieser and Hershberg, *ibid.*, **60**, 940 (1938).

(24) Mayneord and Roe, *Proc. Roy. Soc.* (London), **A158**, 634 (1937).

(25) Fieser and Bowen, This Journal, **62**, 2103 (1940).

(26) Mayneord and Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935).

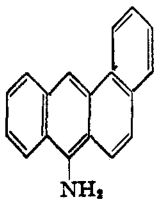
(27) Bachmann and Carmack, This Journal, **63**, 1685 (1941).

(28) Jones, *ibid.*, **63**, 313 (1941).

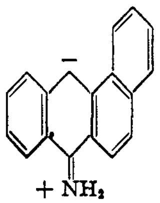
substituent groups reduces the possible secondary effects caused by steric inhibition of resonance.

The Amino Group.—The replacement of hydrogen attached directly to the aromatic ring system by an amino group has produced an effect of this kind in all the amino compounds we have examined, and typical examples are shown in Figs. 8 and 31.

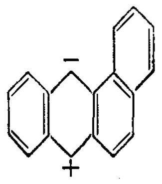
In 10-amino-1,2-benzanthracene (XVII), Fig. 8, the polarized structure XVIIa with the positive charge located on the amino group should be more stable than the analogous polarized structure of the unsubstituted hydrocarbon (XVIIb). The effect of the 10-amino substituent on the polarized structure XVIIc, on the other hand, should be very much less, and structures XVIIc and XVIId should not differ greatly in energy.



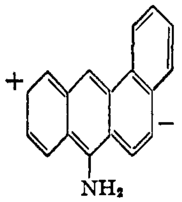
XVII



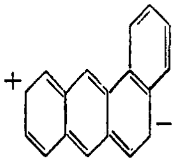
XVIIa



XVIIb



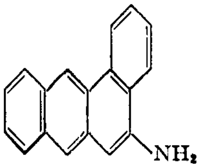
XVIIc



XVIId

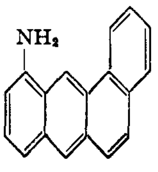
If, in the spectrum of 1,2-benzanthracene, there are groups of absorption bands associated with electric moments oriented in specific directions in the plane of the molecule, it would be anticipated that the C-effect produced by an amino group or other substituent will vary considerably with the position at which it is introduced into the molecule. Should the vectors be directed approximately horizontally and vertically, an amino substituent at the 10-position should bring about a considerable lowering of the energy level associated with a vertical polarization and have much less effect on the horizontal polarization. An analysis of the C-effects of suitably placed substituents might in this manner provide an experimental method for the determination of the significance and orientation of such vectorized electric moments in the molecule.

The spectrum of 10-amino-1,2-benzanthracene may be compared with the spectrum of 3-amino-1,2-benzanthracene (XVIII) (Fig. 31). The group of maxima which lie between 3200 and 3700 Å. in the spectra of the hydrochlorides of both these compounds are shifted to 3800–4200 Å. in the spectrum of the 10-amino derivative, with considerable loss of fine structure, whereas the corresponding series of bands in the spectrum of 3-amino-1,2-benzanthracene is comparatively unaffected. On the basis of the above arguments it may be suggested that the group of absorption maxima which lie between 3200 and 3700 Å. in the spectrum of 1,2-benzanthracene is associated with an electric moment oriented approximately in a vertical direction.

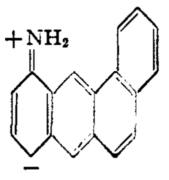


XVIII

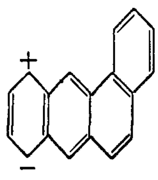
In Fig. 9 the spectrum of 8-amino-1,2-benzanthracene (XIX) is shown. In this compound the substituent would have a major effect in lowering the energy of the polarized structure (XIXb) and, like the 10-amino derivative, should exert a maximum effect on electronic activations associated with a vertically directed polarization. The considerable bathochromic shift of the 3200–3700 Å. group of bands in the spectrum of this compound is consistent with these arguments.



XIX

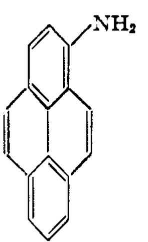


XIXa

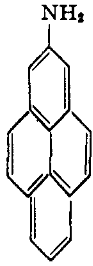


XIXb

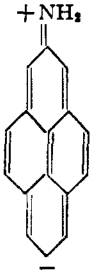
A somewhat more striking example of the selective influence of the position of substitution on the C-effect is provided by the spectra of 3-aminopyrene and 4-aminopyrene (XX, XXI) shown in Figs. 10 and 11.



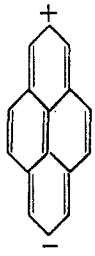
XX



XXI



XXIa



XXIb

In the spectrum of pyrene (Fig. 10) the absorption maxima appear to fall into three groups, max. A-B (2300–2500 Å.), max. C-E (2500–2800 Å.) and max. F-I (2800–3400 Å.) with subsidiary fine structure at still longer wave lengths. In the

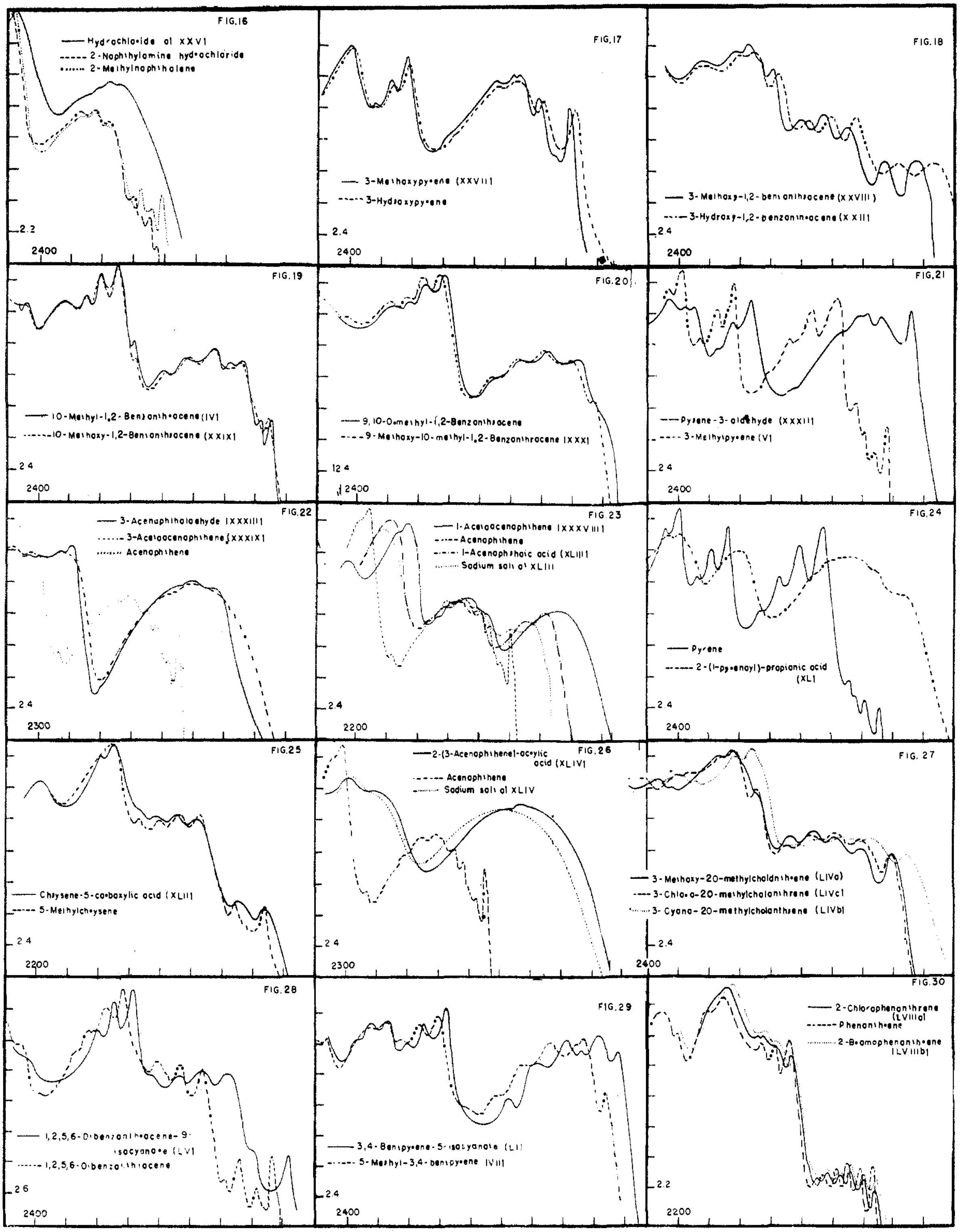


Plate II.—Figures 16–30—(see legend to Plate I).

spectrum of 3-aminopyrene the A-B and the C-E groups of maxima persist, with some broadening and diminution in intensity. The F-I group, however, is modified into one very broad band, extending from about 3200 to 4200 Å. In 4-amino-pyrene the A-B and the C-E groups of maxima have lost their identity, being replaced by a single broad band extending from 2400 to

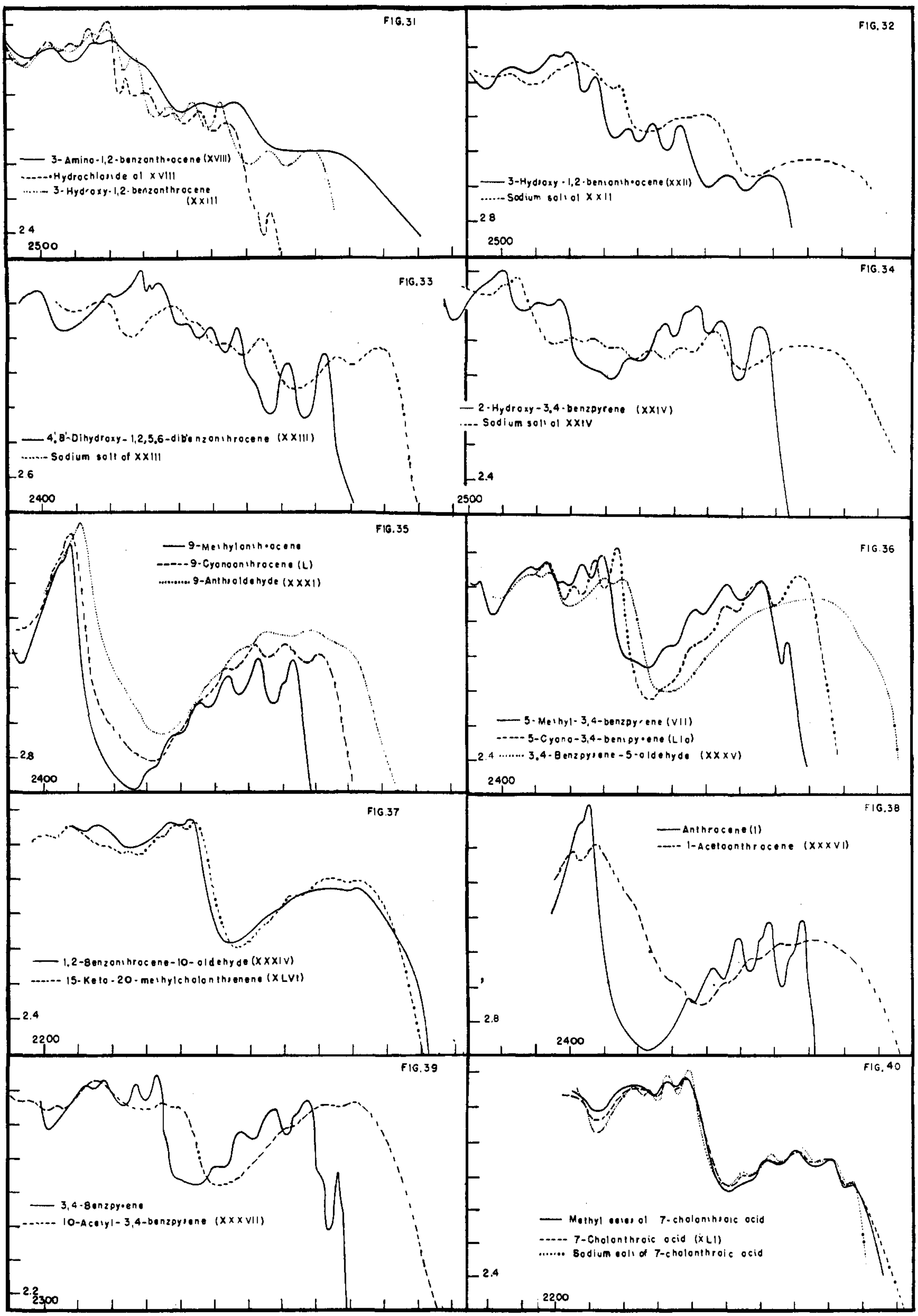
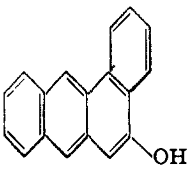


Plate III.—Figures 31–40—(see legend to Plate I).

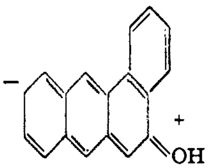
2900 Å., while the F-I group is hardly affected by the introduction of the substituent. A new low intensity band appears with a maximum near 4000 Å.

In 4-aminopyrene, symmetry factors would suggest that the amino group exerts its main effect in modifying the pyrene spectrum through the lowered energy of the polarized structure (XXIa) in comparison with the energy of XXIb, and from this it may be inferred that the A-B and C-E groups of maxima are associated with activation due to electric moments oriented in or near the vertical plane.

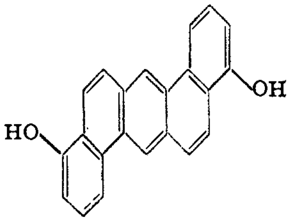
The Hydroxyl Group.—Like the amino group, the hydroxyl group is small, and the C-effects to which it gives rise are unlikely to be disturbed by secondary steric effects. In neutral, or faintly acidic, solvents the introduction of a hydroxyl group disturbs the spectrum of a polynuclear aromatic hydrocarbon much less than does an amino group at the same position. Usually some changes take place in the relative intensities of the several groups of absorption bands, and large bathochromic shifts may occur. Frequently two sharp bands appear at the long wave length end of the spectrum; these may be new bands, or may arise out of the subsidiary fine structure bands commonly observed at the long wave length end of the spectra of polynuclear aromatic hydrocarbons. Typical examples of the C-effect of hydroxyl groups are given in Figs. 32 and 33 where the spectra of 3-hydroxy-1,2-benzanthracene (XXII) and of 4'8'-dihydroxy-1,2,5,6-dibenzanthracene (XXIII) are recorded. In the spectrum of 2-hydroxy-3,4-benzpyrene (XXIV), Fig. 34, only one long wave "hydroxyl band" is present.



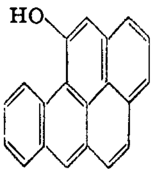
XXII



XXIIa



XXIII



XXIV

The effect of the hydroxyl group on the stabilization of the polarized structures contributing to the activated resonance states of the hydrocarbon molecule is similar in type to, but less in magnitude than, that of the amino group. In 3-hydroxy-1,2-benzanthracene its main influence is probably effected through the lowered energy of the polarized structure XXIIa. The spectra of 3-amino-1,2-benzanthracene hydrochloride, 3-hydroxy-1,2-benzanthracene and 3-amino-1,2-benzanthracene form an interesting series (Fig. 31) in which the phenolic compound lies between the other two. This is in agreement with the well-recognized comparative auxochromic effects of these groups in many classes of dyes.

In the pyrene series the hydroxyl group at 3 greatly changes the structure in the F-I group of maxima and has little effect on the A-B, C-E groups, while in 4-hydroxypyrene the reverse is the case (Figs. 12, 13; compare with curve for pyrene in Fig. 10).

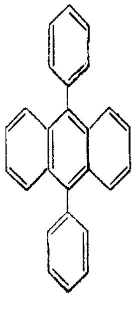
If the spectra of these hydroxy derivatives are determined in strong sodium hydroxide solution, so that the phenolic group is ionized, the spectra are altered considerably, and resemble closely those of the corresponding non-ionized amino compounds. In the examples shown in Figs. 32, 12 and 13, the absorption maxima of the phenolic anions lie at somewhat longer wave lengths than the maxima in the spectra of the amino derivatives.

A discussion of the C-effects produced by carbonyl, methoxy and other types of unsaturated substituents will be deferred until the complications which may be caused by steric inhibition of resonance have been discussed in the following section.

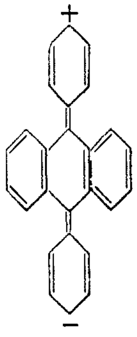
The Steric Effect

It is not uncommon to find that the spectra of certain derivatives of polynuclear aromatic hydrocarbons, in which the substituents are unsaturated, and apparently in conjugation with the aromatic ring system, fail to exhibit the anticipated C-effects; only the B-effect normal to a saturated substituent is observed.

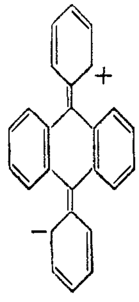
If the spectrum of 9,10-diphenylanthracene (XXV) is compared with that of 9,10-dimethylanthracene (Fig. 14) the similarity is apparent. In the absence of secondary complicating factors, it would be anticipated that the addition of the meso-phenyl groups should greatly reduce the activation energy levels associated with vertical polarization in the plane of the molecule, since, instead of the two structures Ie of anthracene it is now possible to write no less than eighteen electromeric structures, placing positive and negative charges on the ortho and para positions of the meso-phenyl groups. (Two of these structures are shown in XXVa and XXVb, and the remain-



XXV



XXVa

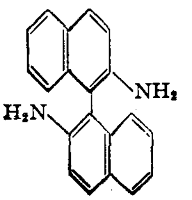


XXVb

ing sixteen are readily derived from these.) Because of the participation of these structures, a great increase in the resonance stabilization of the vertically polarized excited state would be anticipated, and the absorption bands associated with this activation should be shifted to longer wave lengths. The failure to observe such changes must mean that negligible resonance coupling actually occurs between the electronic systems of the meso-phenyl substituents and the anthracene ring system. The co-annular bonds at the 9 and 10 position must be essentially aliphatic.

In the polarized states the co-annular bonds are ethylenic, and in the general case of the ethylenic compound $R_1R_2C{=}CR_3R_4$, the electron orbits in the bond are so directed that the groups R_1, R_2, R_3, and R_4 are co-planar. If the molecule of 9,10-diphenylanthracene is constructed from Stuart, or Fisher–Hirschfelder atom models, it is apparent that the meso-phenyl groups cannot be accommodated in such a planar form without considerable steric interference between the 2′ and 6′ carbon atoms of the phenyl groups and the hydrogen atoms at the 1,4,5 and 8 positions on the anthracene ring (Fig. 44). The meso-phenyl groups are therefore acted upon by opposing forces; the additional resonance energy of the eighteen polarized structures acts to rotate the phenyl groups into the plane of the anthracene ring system, but is opposed by repulsive forces between the non-bonded atoms. Calculations of the magnitude of these opposing forces as a function of the angle between the plane of the phenyl groups and the plane of the anthracene ring would be of considerable interest. The experimental observations described above show, quite definitely, that, in this case, the steric repulsion is dominant, and such conjugation as there might be across the co-annular bonds is insufficient to affect the spectrum. Indeed, methyl groups at the 9 and 10 positions actually produce larger spectral shifts than do the phenyl substituents at the same position (Fig. 14).

Another example of this S-effect is shown in Fig. 15 where the spectrum of 2,2′-diamino-1,1′-dinaphthyl (XXVI) is compared with that of 2-naphthylamine. The close similarity of the curves indicates that coupling between the two naphthalene ring systems across the co-annular bond is very slight. In acid solution the spectrum of the cation from XXVI resembles that of 2-naphthylamine hydrochloride and 2-methylnaphthalene (Fig. 16). Atom models indicate that a planar structure for this compound is not possible, and independent evidence of a non-planar structure for 1,1′-dinaphthyl derivatives is provided.by the optical resolution of 1,1′-dinaphthyl-2,2′-dicarboxylic acid.[29]



XXVI

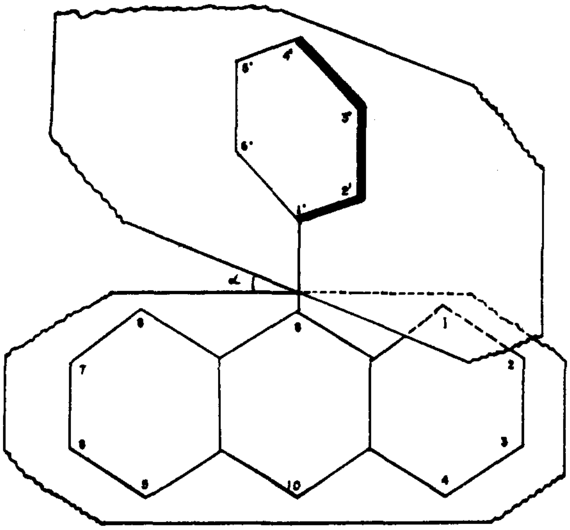
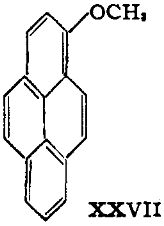


Fig. 44.—Steric hindrance in 9-phenylanthracene; diagram to illustrate the angle α (see Table II). The carbon atoms at 2′ and 6′ on the meso-phenyl group "touch" the hydrogen atoms at the 1 and 8 positions of the anthracene ring system when α = 57°.

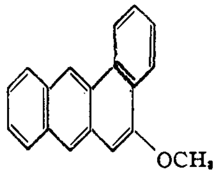
In the above examples, the large size of the groups leaves no room for doubt as to the non-planar form of the molecule. In many molecules containing substituent groups of smaller size and greater flexibility, it is unwise to reason *a priori* from atom models whether or not effects on the spectra, attributable to steric interference with resonance, will occur.

The Methoxy Group.—We have not observed any compound containing only amino or hydroxy groups to exhibit an S-effect. This is no doubt attributable to the small size of these substituents, and the simplest group to provide a clear example of steric interference with resonance is methoxyl.

In Figs. 17, 18, the spectra of 3-methoxypyrene (XXVII) and 3-methoxy-1,2-benzanthracene (XXVIII) are compared with the spectra of the corresponding hydroxy compounds in neutral solution. In both cases the agreement between the curves of the two hydrocarbon derivatives is quite close, and the methoxy groups are clearly



XXVII



XXVIII

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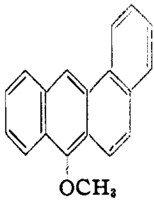
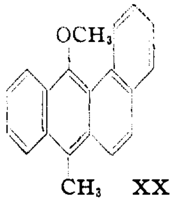
[29] Kuhn and Albrecht, *Ann.*, **465**, 282 (1928).

exhibiting C-effects, attributed to electronic interactions involving one of the two lone pairs of electrons on the oxygen atom with the electrons of the ring system.

In the spectra of 10-methoxy-1,2-benzanthracene (XXIX) and 9-methoxy-10-methyl-1,2-benzanthracene (XXX) (Figs. 19, 20) the methoxy groups produce no C-effect and the curves resemble closely those of 10-methyl-1,2-benzanthracene and 9,10-dimethyl-1,2-benzanthracene,[30] *i. e.*, these methoxy derivatives exhibit S-effects.

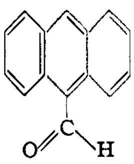


XXIX

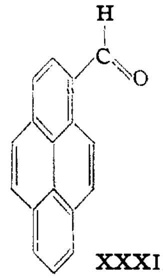


XXX

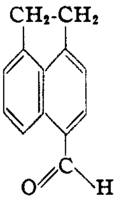
The Carbonyl Group.—Compounds containing carbonyl substituents provide interesting examples of both C- and S-effects. The spectra of five aldehydes (XXXI–XXXV) we have examined are shown in Figs. 21–22 and 35–37. All the curves show large C-effects.[31]



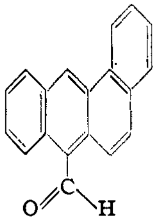
XXXI



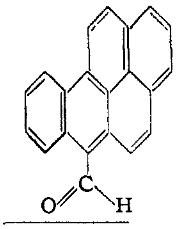
XXXII



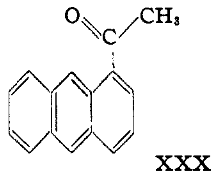
XXXIII



XXXIV

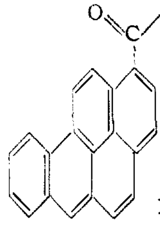


XXXV

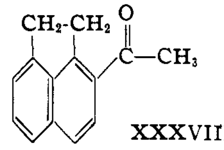


XXXVI

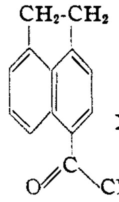
The replacement of the hydrogen atom of an aldehyde group by methyl increases the size of the substituent considerably, and accordingly the potentialities for steric interference with resonance increase also. Nevertheless, in none of the acetyl compounds which we have examined has an S-effect been noted. The spectra of 1-acetoanthracene, 10-acetyl-3,4-benzpyrene, 1-acetoacenaphthene, 3-acetoacenaphthene and 2-(1-pyrenoyl)-propionic acid (XXXVI–XL) are compared with the relevant saturated hydrocarbons or methyl derivatives in Figs. 22–24 and 38–39. In all of these cases the introduction of the conjugated carbonyl group leads to a broadening of the absorption and loss of fine structure, behavior strictly comparable with that of the aldehydes described above.



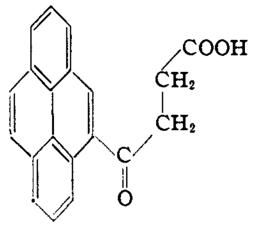
XXXVII



XXXVIII

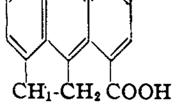


XXXIX

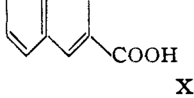


XL

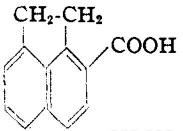
In two compounds containing the carboxylic acid group, 7-cholanthroic acid (XLI), and chrysene-5-carboxylic acid (XLII) (Figs. 40, 25), the substituents are in highly hindered positions and the compounds exhibit S-effects; the spectra of the methyl ester and of the sodium salt of 7-cholanthroic acid are similar to the curve of the free acid, except for somewhat sharper structural resolution in the spectrum of the salt. The carboxylic acid group in 1-acenaphthoic acid



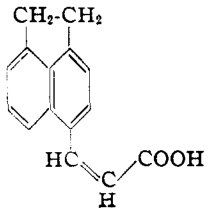
XLI



XLII



XLIII



XLIV

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[30] In comparing the C- and S-effects of groups in this manner, it is preferable to use the corresponding methyl derivative of the hydrocarbon as a saturated comparison substance, rather than the unsubstituted hydrocarbon. In this way an approximate correction can be made for the B-effect of the substituent.

[31] In determining the spectra of aldehydes in ethanolic solution the possibility of reversible hemi-acetal formation must not be overlooked. In an attempted determination of the spectrum of pyrene-3-aldehyde in solution in ethanol, serious deviations from Beer's Law were observed and were attributed to this cause. The curve recorded in Fig. 21 for pyrene-3-aldehyde was made with a solution in *n*-heptane.

TABLE I

TYPE OF EFFECT PRODUCED BY VARIOUS SUBSTITUENTS ON THE SPECTRA OF HYDROCARBON DERIVATIVES

Conjugation effect	Conjugation effect	Steric effect
3-Amino-1,2-benzanthracene	9-Anthraldehyde	9,10-Diphenylanthracene
8-Amino-1.2-benzanthracene	Pyrene-3-aldehyde	2,2′-Diamino-1.1′-dinaphthyl
10-Amino-1,2-benzanthracene	3-Acenaphthaldehyde	10-Methoxy-1.2-benzanthracene
3-Aminopyrene	1,2-Benzanthracene-10-aldehyde	9-Methoxy-10-methyl-1,2-benzanthracene
4-Aminopyrene	3,4-Benzpyrene-5-aldehyde	7-Cholanthroic acid
3-Hydroxy-1.2-benzanthracene	1-Acetoanthracene	Chrysene-5-carboxylic acid
2-Hydroxy-3,4-benzpyrene	10-Acetyl-3,4-benzpyrene	
4′,8′-Dihydroxy-1.2,5.6-dibenzanthracene	1-Acetoacenaphthene	
3-Hydroxypyrene	3-Acetoacenaphthene	
4-Hydroxypyrene	2-(1-Pyrenoyl)-propionic acid	
3-Methoxypyrene	1-Acenaphthoic acid	
3-Methoxy-1,2-benzanthracene	2-(3-Acenaphthene)-acrylic acid	

(XLIII) shows a normal C-effect[32] as also does the conjugated side chain group in XLIV (Figs. 23 and 26).

Correlation of the S-Effect with Steric Hindrance as Determined Geometrically

In Table I, the compounds discussed in the foregoing section are classified into two groups, according to whether C- or S-effects are observed. It is of interest to compare these experimental observations with the predictions of steric interference with resonance which would be inferred from purely geometrical considerations of the molecules.

In Table II the minimum angle of approach between the plane of the substituent group and the plane of the main aromatic ring system has been calculated for a number of these compounds.[33] This angle (α) is illustrated in Fig. 44 in the typical example of 9-phenylanthracene. The values taken for the various atomic constants employed in these calculations are summarized in Table III. Of these, most uncertainty is attached to the values for the minimum distance of approach between non-bonded atoms. In the calculations it has been assumed that the axial bond joining the substituent to the aromatic ring system is completely aliphatic. Shortening of this bond through resonance would result in an increase in the values of α.

TABLE II

MINIMUM ANGLE OF APPROACH (α) BETWEEN THE PLANE OF THE SUBSTITUENT GROUP AND THE PLANE OF THE MAIN AROMATIC RING SYSTEM

Compound	Angle α, deg.
Compounds exhibiting S-effects	
Chrysene-5-carboxylic acid	Strained at 90
9-Methoxy-10-methyl-1,2-benzanthracene	Strained at 90
7-Cholanthroic acid	90 (approx.)[a]
10-Methoxy-1,2-benzanthracene	90
9.10-Diphenylanthracene	57[b,c]
Compounds exhibiting C-effects	
3-Methoxypyrene	68
3-Methoxy-1,2-benzanthracene	68
1-Acetoanthracene	51
10-Acetyl-3,4-benzpyrene	51
3-Acetoacenaphthene	51
2-(1-Pyrenoyl)-propionic acid	51
3,4-Benzpyrene-5-aldehyde	45[b]
1,2-Benzanthracene-10-aldehyde	45[b]
9-Anthraldehyde	45[b]
Benzophenone	30
10-Amino-1,2-benzanthracene	29[b]
Pyrene-3-aldehyde	18
3-Acetoacenaphthene	18
2-(3-Acenaphthene)-acrylic acid	18
3-Hydroxy-1,2-benzanthracene	0
3-Hydroxypyrene	0

[a] It is assumed that the space occupied by the dimethylene bridge near carbon atom 14 is equivalent to that of a methyl group at the same position. [b] Symmetry factors impose this barrier twice in a complete rotation of the substituent about the axial bond. [c] Further interference occurs at $\alpha = 42°$.

Considering first the compounds in Table I which are observed to exhibit appreciable steric interference with resonance, it is seen from Table II that in 9-methoxy-1,2-benzanthracene and chrysene-5-carboxylic acid the structures are strained, even when the substituents are oriented

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[32] Comparison of the spectra of acenaphthene, 1-acenaphthoic acid and 1-acetoacenaphthene provides some interesting points. In all three compounds the absorption in the region between 2600 and 3000 Å. is similar, but in the carbonyl derivatives the short wave length maximum suffers a considerable bathochromic shift, and new structure appears between 3200 and 4000 Å. The modification of the hydrocarbon spectrum is least for the carboxylate ion, and greatest for the acetyl group.

[33] In a first approach to this problem, an attempt was made to measure these angles directly, using Stuart and Fisher–Hirschfelder models. This was found to be unsatisfactory, as both types of model lack the necessary mechanical precision. The angles observed using the Fisher–Hirschfelder models agreed better with the calculated values than those obtained with Stuart models (manufactured by E. Leybold's Nachfolger, Köln-Bayental). The latter models always gave smaller angles. This was traced to the fact that the covalent bond length of the Stuart $C_{aromatic}$ atom model is 1.65 cm., corresponding to a length of 0.825 Å. for the bond length in the atom, since the scale of the models is 2×10^8. This makes the distance between the centers of two adjacent carbon atoms in the benzene ring 1.65 Å. compared with the accepted experimental value of 1.39 Å. The reduction in the Stuart hydrogen atom of the covalent bond length to 0.15 Å. from the accepted experimental value of 0.30 Å. only partially compensates for the longer carbon bond.

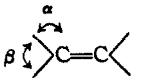
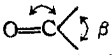
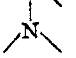
TABLE III

BOND LENGTHS, ANGLES AND ATOMIC INTERFERENCE DISTANCES EMPLOYED IN CALCULATION OF ANGLES GIVEN IN TABLE II

Covalent Bond Radii[a]

Hydrogen	0.30 Å.
$C_{aliphatic}$	0.77
$C_{ethylenic}$	0.67
$C_{aromatic}$	0.70
$O_{ethereal}$	0.66
$O_{ketonic}$	0.55
N_{amino}	0.70

Bond angles[b]

	$\alpha = 122°$	$\beta = 116°$
	$\alpha = 120°$	$\beta = 116°$
Aromatic ring	120°	
	108°	
	108°	

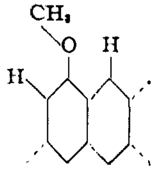
Interference Radii[c]

H (bound to carbon)	0.90 Å. (assumed also for H bound to oxygen).
C	1.45
O	1.22
Methyl group	2.00
N	1.35

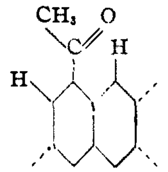
[a] Pauling "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, chap. V. [b] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, chap. V. [c] Stuart, *Z. physik. Chem.*, **B27**, 350 (1934). These are values reported by Stuart for the "Wirkungsradius" of the atom. For the methyl group the van der Waals radius of 2.0 A. (see Pauling, ref. *a* above, p. 189) is employed.

in the position of minimum interference, with the plane of the substituent group normal to the plane of the aromatic ring system. In 7-cholanthroic acid a precise calculation of the angle is not possible, as the space occupied by the strained 5,10-dimethylene bridge cannot be accurately evaluated. If it is assumed, however, that this group occupies space in the neighborhood of the 10-position comparable with that of a 10-methyl group, the molecule is free of strain only if the carboxylic acid group is normal to the plane of the main ring system. In 10-methoxy-1,2-benzanthracene the calculations show that the methoxy group must lie in a perpendicular plane. In 9,10-diphenylanthracene an approach to within 57° of a planar structure is permitted.

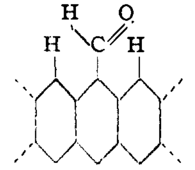
In very few of the compounds in Table II which do show conjugation effects does the geometry of the molecule permit of a truly planar form. In the compounds containing methoxy, acetyl and aldehyde groups with the structural arrangements XLVa, XLVb and XLVc the interference angle is quite large. In aldehydes with the partial structure XLVd it is less (18°).



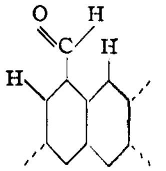
XLVa



XLVb



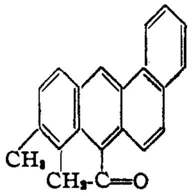
XLVc



XLVd

As the effect of a given substituent on the spectrum of a hydrocarbon is influenced both by the nature of the substituent and its angle of orientation, it is only in a few special cases that constructive inferences can be drawn from these data. It might reasonably be assumed that the C-effect of the hydroxyl and the methoxyl groups would be comparable if not disturbed by steric effects or hydrogen bonding. For 3-hydroxypyrene and 3-methoxypyrene the calculated minimum angles between planes are 0 and 68°, respectively, yet the comparison of the spectra in Fig. 17 does not indicate that this large angular difference produces such a profound effect on the spectrum as might be anticipated.

It is also instructive to compare the spectra of 1,2-benzanthracene-10-aldehyde (XXXIV) and 15-keto-20-methylcholanthrene (XLVI) shown in Fig. 37. The curves of these two compounds differ only in that the curve of the cholanthrene compound is shifted slightly to longer wave lengths. In 1,2-benzanthracene-10-aldehyde the minimum angle between planes is 45°, whereas in compound XLVI the incorporation of the carbonyl group in a cyclopentanone ring system tends to hold it close to the main plane of the molecule. Part, at least, of the bathochromic displacement of the curve of the ketocholanthrene compound must be attributed to the B-effect of the methyl group at the 20-position and, if allowance is made for this, it would seem that the conjugation effect of the carbonyl group is closely the same in both compounds.

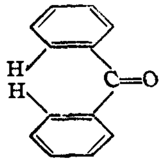


XLVI

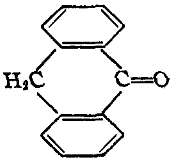
These results suggest that an absence of coupling between two parts of a chromophoric system can be predicted only where the geometrical considerations indicate that part of the chromophoric system must be in a plane normal to that of the remainder; even under these conditions an exception is provided by 9,10-diphenylanthracene. It is most probable that the lack of correlation between the predictions based on spectroscopy and those based on molecular geometry is to be attributed to uncertainties in the atomic dimensions, particularly the interference radii. It must be noted in this connection that such atomic constants have been evaluated for molecules in the ground state while we are concerned here with electronically activated molecules.

Steric Factors and Resonance in the Spectra of Benzophenone, Anthrone and Fluorenone

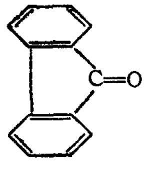
In an attempt to gain more information concerning resonance coupling between non-planar conjugated systems, the spectra of benzophenone, anthrone and fluorenone (XLVII-XLIX) have been compared. In the benzophenone molecule the two phenyl groups cannot be accommodated in the same plane because of interference between the hydrogen atoms at the 2 and 2′ positions. Calculations assuming an angle of 130° between the 1,4-axes of the phenyl groups[34] indicate that the minimum angle between the planes of the benzene rings is about 30°. In the anthrone molecule the conditions for resonance should be identical with those in benzophenone, except that the mutually interfering hydrogen atoms are replaced by a methylene bridge linkage which holds the molecule in a planar form.[35]



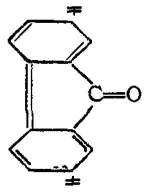
XLVII



XLVIII



LXIX



XLIXa

The spectra of benzophenone and anthrone are compared in Fig. 41. The benzophenone curve shows two maxima (2580 and 3380 Å.). The longer wave length maximum is a typical "carbonyl band" and can be associated with the presence of the ketone group. Between these two maxima there is a suggestion of an inflection near 2800 Å. The introduction of the methylene bridge produces some shift of the high intensity part of the curve to longer wave lengths, most noticeable in the region of the inflection near 3080, but the carbonyl absorption is not affected by the act of ring closure. The development of structure in the anthrone spectrum, not noted in the benzophenone spectrum is probably associated with an Fs-effect of the methylene group. The shift of the high intensity section of the curve, however, must be attributed to changes in the activation energy levels as a result of the increased resonance in the planar structure.

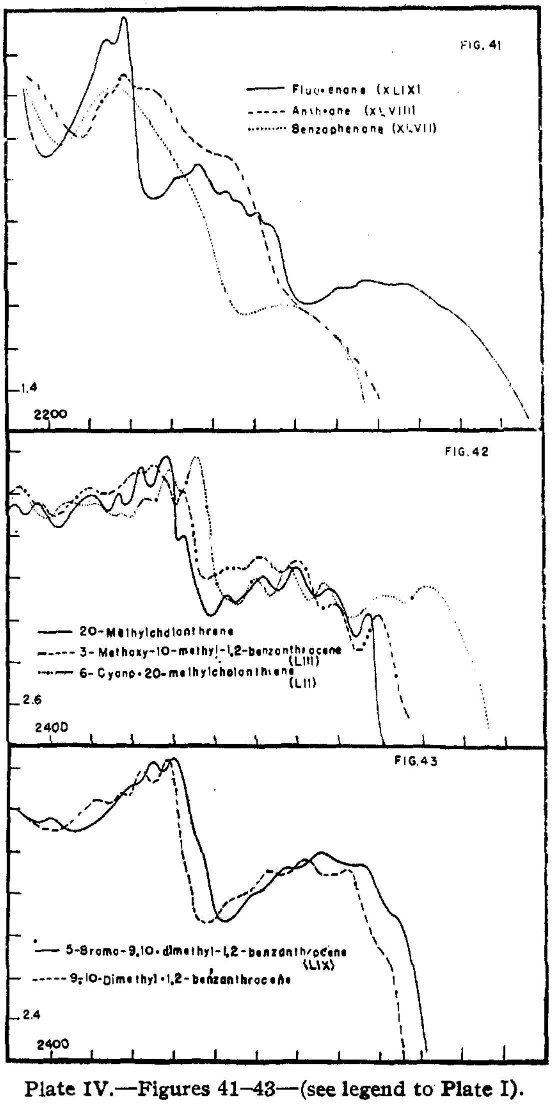


Plate IV.—Figures 41–43—(see legend to Plate I).

In fluorenone the two mutually interfering ortho hydrogen atoms of benzophenone are replaced by a direct linkage between the two rings, and the changes which result in the spectrum are profound. The Fs-effect is very marked indeed, particularly in the region between 2800 and 3300 Å. Also striking is the large bathochromic effect on the carbonyl band. This band is shifted well

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(34) Bergmann, Engel and Meyer, *Ber.*, **65**, 446 (1932). See also Coates and Sutton, *J. Chem. Soc.*, 567 (1942).

(35) Anthrone can isomerize to anthranol, and in determining the spectrum care must be taken that this isomerization is suppressed. At normal temperatures, in neutral solvents the keto-enol equilibrium between anthrone and anthranol lies very much to the anthrone side: the formation of anthranol in the solution is readily detected by its intense blue fluorescence. The solutions used in the determination of the anthrone spectrum (Fig. 41) were prepared by shaking anthrone with cold absolute alcohol and were non-fluorescent.

into the visible region of the spectrum and is responsible for the yellow color of fluorenone. In comparing the spectra of anthrone and fluorenone it should be observed that the prominent changes in fine structure resolution are not accompanied by changes in the positions of the main maxima. In fluorenone additional resonance structures such as XLIXa can be written, and it would seem that the participation of these structures leads to a lowering of the energy levels association with activations centered about the carbonyl group, but do not effect the energy levels associated with absorption at wave lengths less than 3400 Å., except in so far as modification of fine structure resolution is concerned.

These comparisons of the spectra of benzophenone, anthrone and fluorenone agree with other evidence presented in this paper in showing that the effects of substituents and minor structural changes on the spectra of aromatic compounds may be predominantly associated with specific groups of maxima in the spectra, leaving other regions of the spectrum comparatively unaffected. The comparison of the anthrone and benzophenone spectra also illustrate the effect of steric interference with resonance in the latter compound. On the basis of the accepted data for atomic dimensions (Table IV) the angle between the planes of the two benzene rings in benzophenone is 30° and the curves suggest that this amount of rotation definitely reduces the resonance across the ring systems. The comparison between the spectra of 15-keto-20-methylcholanthrene and 1,2-benzanthracene-10-aldehyde discussed on page 35 (where a bond was rotated into a planar form through an angle of 45° by a comparable act of ring closure) led to the contrary conclusion, *i. e.*, that such distortion from a planar form has little effect on the spectrum. It would therefore seem that purely geometrical considerations are of little value in predicting the probability of steric interference with resonance, unless that interference is of such a magnitude that an axial rotation approaching 90° is induced at some position along the chromophoric system.

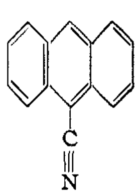
Suppression of Conjugation Effects in the Absence of Steric Hindrance

In the discussion of the effects produced by conjugatable[36] substituents, it has so far been assumed that the energies of the polarized structures which involve the participation of the conjugated side chains are appreciably less than those of the related polarized structures pertaining to the unsubstituted parent hydrocarbon, and the changes in the spectra have been attributed to this cause.

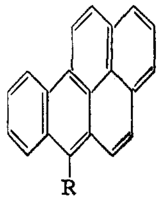
In certain cases it may happen that the energies of the polarized structures involving the participation of conjugatable substituents are comparable with those of the analogous structures of the unsubstituted hydrocarbon, and in such cases the introduction of the conjugatable substituent should produce little change in the shape or position of the absorption spectrum.

Cyano Derivatives

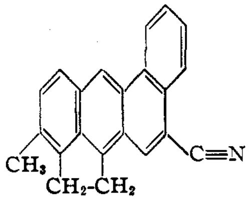
The spectra of 9-cyanoanthracene (L) and 5-cyano-3,4-benzpyrene (LIa) are compared with those of the corresponding methyl derivatives in Figs. 35 and 36. Both of the cyano derivatives exhibit strong bathochromic effects, but the shapes of the absorption curves parallel those of the methyl derivatives very closely, and show only minor broadening of the bands and loss of the fine structure such as is exhibited by the corresponding aldehyde derivatives; the effect of introducing the cyano group is intermediate in type between that produced by a saturated substituent and that of a substituent showing conjugation with the ring. In 6-cyano-20-methylcholanthrene (LII) Fig. 42 the introduction of the cyano group has little effect at wave lengths less than 3900 Å., but two new bands appear with maxima at 4020 and 4250 Å. This curve should be compared also with that of 3-methoxy-10-methyl-1,2-benzanthracene (LIII) in which the substituent is seen to modify the shape of the benzanthracene curve considerably in the region between 2200 and 3200 Å. The curves for 3-methoxy-20-methylcholanthrene (LIVa) and 3-cyano-20-methylcholanthrene are more alike (Fig. 27) and in this case the cyano group appears to exhibit a more normal conjugation effect.



L



LIa R = —C≡N
LIb R = —N=C=O



LII

The isocyanate group (—N=C=O) likewise may produce only a B-effect in certain compounds, as is illustrated in the spectra of 1,2,5,6-dibenzanthracene-9-isocyanate (LV) in Fig. 28 and 3,4-benzpyrene-5-isocyanate in Fig. 29.

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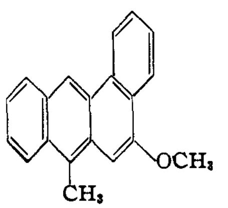
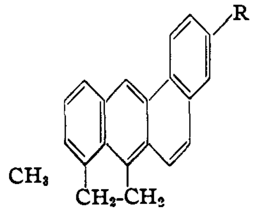
[36] In order to emphasize certain distinctions, the adjective "conjugated" *will henceforth be reserved to describe formal systems of* alternate double and single linkages in which conjugation effects are actually observed. "Conjugatable" will be used to describe systems of alternate double and single bonds, irrespective of whether or not such conjugation effects do, in fact, occur.

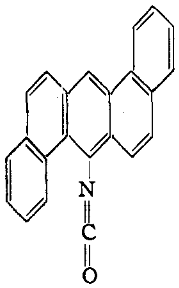
Several examples of compounds containing the thiocyano group (—S—C≡N)[37] and the carbamidoacetic acid group (—NH—CO—NH—CH$_2$-—COOH)[38] have been reported elsewhere, and these also exhibit B-effects only.



LIII



LIVa R = —OCH$_3$
LIVb R = —C≡N
LIVc R = —Cl

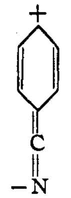


LV

As the cyano, thiocyano and isocyanate groups are linear and relatively small, failure to exhibit marked C-effects cannot be attributed to steric interference with resonance in these cases. Pauling[39] has shown that in the alkyl cyanides the main resonance is between the structures LVIa and LVIb. If this is true also in the aromatic compounds, structures such as LVIc may be presumed to play the major part in modifying the hydrocarbon spectrum.

$R:C:::N:$ LVIa

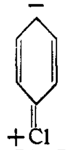
$R:\overset{+}{C}::\overset{-}{N}:$ LVIb



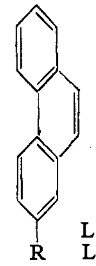
LVIc

Halogen Derivatives

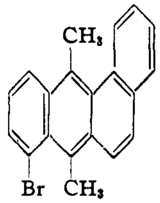
In chloro derivatives of hydrocarbons, the six orbital electrons of the chlorine atom not involved in the covalent chlorine–carbon bond are potentially available for secondary bonding, and the reduction of the C—Cl bond length of 1.76 Å. to a value of 1.69 Å. in chlorobenzene[40] suggests that structures of the type LVII might participate in the activated states of chloro derivatives of aromatic hydrocarbons.



LVII



LVIIIa R = —Cl
LVIIIb R = —Br



In 3-chloro-20-methylcholanthrene (LIVc) the effect of the chlorine atom on the region of the spectrum below 3200 Å. is like that of the cyano and the methoxy group. The spectra of 2-chlorophenanthrene (LVIIIa) and 2-bromophenanthrene (LVIIIb), Fig. 30, resemble the phenanthrene spectrum so closely that in the case of these derivatives structures involving a double bond between the halogen atom and the ring can be making no significant contribution to the activated state. In 5-bromo-9,10-dimethyl-1,2-benzanthracene (LIX) (Fig. 43) the bromine atom likewise produces little change in the spectrum.

Summarizing the evidence presented in this last section, it seems that even in cases where steric hindrance can be discounted, it is still possible to have conjugatable substituents introduced into the polynuclear aromatic hydrocarbon molecule without necessarily modifying the shape of the spectral curve. Such substituents are of a type in which the tendency to conjugate is weakened by resonance stabilization effects centered within the substituent group.

TABLE IV

THE ULTRAVIOLET ABSORPTION SPECTRA OF POLYNUCLEAR AROMATIC COMPOUNDS: WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

Compound[a]	Source[b]	Solvent	Absorption maxima Wave length,[c] Å.	Absorption maxima Intensity, log E_m
	A.	Hydrocarbons		
2-Methylnaphthalene (I)	31	EtOH	3190	2.71
			3120	2.48
			3050	2.74
			2760	3.68
			2240	5.02
Acenaphthene	31	EtOH	3210	3.20
			3140	3.00
			(3110)	3.06
			3060	3.46
			3000	3.62
			2890	3.81
			2790	3.77
			(2660)	3.52
			2430	3.10
			2280	4.94
			(2230)	4.80
9-Methylanthracene	9	EtOH	3860	3.92
			(3810)	3.65
			3660	3.94
			3480	3.75
			3320	3.43

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(37) Jones, THIS JOURNAL, 63, 2528 (1941).
(38) Creech and Jones, *ibid.*, 63, 1661 (1941).
(39) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, page 198.
(40) Brockway and Palmer, THIS JOURNAL, 59, 2181 (1937).

TABLE IV (*Continued*)

			Absorption maxima	
Compound[a]	Source[b]	Solvent	Wave length,[c] Å.	Intensity, log E_m
			(3160)	3.04
			(3000)	2.61
			2560	5.26
			(2490)	5.02
9,10-Dimethylanthracene	19	EtOH	3980	3.99
			(3910)	3.72
			3780	4.00
			(3700)	3.80
			3570	3.77
			3410	3.43
			3260	3.03
			(3100)	2.60
			2600	5.24
			2510	4.93
			2200	4.00
9,10-Diphenylanthracene (XXV)	29	EtOH	3920	4.03
			3720	4.04
			3540	3.85
			3370	3.52
			(3220)	3.10
			2590	5.02
			2260	4.31
9,10-Dihydrophenanthrene (XI)	20	EtOH	See THIS JOURNAL, 63, 1658 (1941)	
4,5-Methylenephenanthrene (XV)	27	EtOH	3450	2.64
			3390	2.31
			3290	2.73
			(3210)	2.45
			3130	2.65
			2990	4.12
			2880	4.04
			2760	3.96
			(2610)	4.30
			2520	4.74
			(2480)	4.70
1,2-Benzanthracene*	32	EtOH	See THIS JOURNAL, 62, 148 (1940)	
10-Methyl-1,2-benzanthracene* (IV)	24	EtOH		
8,10-Dimethyl-1,2-benzanthracene* (II)	20	EtOH		
9,10-Dimethyl-1,2-benzanthracene*	33	EtOH		
4,10-Ace-1,2-benzanthracene* (XII)	25	EtOH	See *ibid.*, 64, 802 (1942)	
1',9-Methylene-1,2-benzanthracene* (IX)	4	EtOH	See *ibid.*, 62, 148 (1940)	
4,5-Methylenechrysene*	5	EtOH	See *ibid.*, 63, 313 (1941)	
Pyrene	31	EtOH	3715	2.40
			3615	2.49
			(3550)	2.56
			3510	2.76
			3340	4.69
			3185	4.46
			3055	4.05
			(2950)	3.64
			2724	4.70
			2617	4.41
			2520	4.05
			2403	4.93
			2315	4.64
3-Methylpyrene* (V)	27	EtOH	See *Chem. Rev.*, 32, 1 (1943)	
3,4-Benzpyrene*	31	EtOH	See *Cancer Research*, 2, 237 (1942)	
5-Methyl-3,4-benzpyrene (VII)	14	EtOH	4090	3.74
			3940	4.45
			3730	4.41
			3540	4.11
			(3390)	3.70
			3000	4.76
			2880	4.65
			2760	4.45
			2670	4.67
			2570	4.61
			2270	4.46
1,2,5,6-Dibenzanthracene*	39	EtOH	See *Cancer Research*, 2, 237 (1942)	
5-Methylchrysene*		EtOH	See THIS JOURNAL, 63, 313 (1941)	
1',9-Methylene-1,2,5,6-dibenzanthracene* (XVI)	10	EtOH	3940	2.58
			(3850)	2.58
			3720	3.15
			3560	4.20
			3400	4.20
			3260	4.19
			3190	4.24
			3000	5.10
			2900	4.96
			2780	4.73
B. Amino Derivatives				
2-Naphthylamine*	31	EtOH	3400	3.28
			2920	3.73
			2805	3.82
			2360	4.78
		2 *N* HCl in 50% aq. EtOH	3150	2.02
			3110	2.38
			(3050)	2.40
			3010	2.66
			2850	3.58
			2765	3.75
			2665	3.72
			2215	5.03
2,2'-Diamino-1,1'-dinaphthyl (XXVI)	28	EtOH	3460	3.75
			(2960)	4.02
			2820	4.14
			2730	4.08
			2410	4.97

TABLE IV (*Continued*)

Compound[a]	Source[b]	Solvent	Absorption maxima Wave length,[c] Å.	Intensity, log E_m
		N HCl aqueous	(2930)	4.05
			2850	4.09
			(2760)	4.01
3-Amino-1,2-benzanthracene* (XVIII)	6, 11	EtOH 2 *N* HCl in 50% aq. EtOH	See This Journal, **63**, 151 (1941)	
8-Amino-1,2-benzanthracene* (XIX)	20	EtOH	(4300)	3.00
			(4150)	3.55
			(4070)	3.72
			3950	3.90
			3780	3.88
			(3160)	4.54
			3050	4.66
			2855	4.72
			2670	4.90
		2 *N* HCl in 50% aq. EtOH	3870	3.01
			3665	3.58
			3610	3.62
			3470	3.80
			3320	3.76
			(3170)	3.62
			2995	4.02
			2895	4.95
			2785	4.84
			2690	4.63
			2580	4.45
10-Amino-1,2-benzanthracene* (XVII)	6	EtOH 2 *N* HCl in 50% aq. EtOH	See This Journal, **63**, 151 (1941)	
3-Aminopyrene* (XX)	27	EtOH	(4075)	3.98
			3625	4.17
			2845	4.39
			(2720)	4.16
			2420	4.63
		2 *N* HCl in 50% aq. EtOH	3740	2.65
			3660	2.56
			(3610)	2.59
			3585	2.86
			3540	3.02
			3390	4.56
			3240	4.42
			3100	4.00
			(2970)	3.60
			2740	4.64
			2630	4.38
			2530	4.06
			2415	4.90
			(2340)	4.66
4-Aminopyrene* (XXI)	27	EtOH	4000	3.24
			3385	4.52
			3230	4.24
			3090	3.92
			(2960)	4.00
			2660	4.80
		2 *N* HCl in 50% aq. EtOH	See *Chem. Rev.*, **32**, 1 (1943)	
5-Amino-3,4-benzpyrene (VIII)	2	1.2 *N* HCl in 90% aq. EtOH	4050	3.83
			3930	4.42
			3720	4.37
			3540	4.09
			3400	3.70
			3000	4.74
			2890	4.63
			2770	4.37
			2660	4.63
			2560	4.59
			2260	4.32
			2200	4.34
C. Hydroxy Derivatives				
3-Hydroxy-1,2-benzanthracene* (XXII)	8, 34	EtOH	See This Journal, **63**, 151 (1941)	
		N NaOH in 50% aq. EtOH	4325	3.52
			3685	4.03
			(3520)	4.00
			3170	4.35
			2960	4.63
			(2800)	4.49
			2550	4.48
3-Hydroxypyrene	27	EtOH	3860	3.97
			3660	4.08
			3480	4.34
			3360	4.26
			2780	4.54
			2680	4.28
			2570	4.02
			2410	4.77
		0.5 *N* NaOH in 50% aq. EtOH	4080	4.27
			3860	4.23
			3700	4.18
			(3090)	3.56
			2870	4.39
			(2750)	4.17
			2450	4.56
4-Hydroxypyrene	27	0.01 *N* HCl in 99% EtOH	3840	3.43
			3640	3.24
			3370	4.65
			3210	4.40
			3080	4.01
			2810	4.26
			2700	4.26
			2500	4.84
		N KOH in 50% aq. EtOH	4080	3.52
			3430	4.48
			3280	4.15
			3130	3.87
			(2990)	4.06
			(2880)	4.44
			2720	4.86
			(2610)	4.62
4′,8′-Dihydroxy-1,2,5,6-dibenzanthracene (XXIII)	1	EtOH	See *Cancer Research*, **4**, 209 (1944)	

TABLE IV (*Continued*)

Compound[a]	Source[b]	Solvent	Absorption maxima Wave length,[c] Å.	Intensity, log E_m
		2 N NaOH in 50% aq. EtOH	4365	4.08
			4140	3.98
			3680	4.19
			3485	4.12
			(3310)	4.33
			3155	4.56
			(3010)	4.40
			2750	4.63
2-Hydroxy-3,4-benzpyrene* (XXIV)	18	EtOH	4225	4.23
			3980	4.28
			3840	4.42
			3650	4.21
			3440	3.82
			3015	4.48
			2895	4.46
			2690	4.82
		N NaOH in 50% aq. EtOH	4525	3.97
			3945	4.13
			3730	3.93
			3560	3.91
			(3390)	3.92
			3205	4.02
			3085	4.02
			2760	4.75
			2690	4.63
D. Methoxy Derivatives				
3-Methoxy-1,2-benzanthracene* (XXVIII)	8, 34	EtOH	See THIS JOURNAL, **63**, 151 (1941)	
10-Methoxy-1,2-benzanthracene (XXIX)	12	EtOH	3880	3.08
			3710	3.79
			3530	3.94
			3360	3.85
			3210	3.66
			3020	3.83
			2910	4.99
			2800	4.89
			2700	4.61
			2580	4.58
			(2280)	4.50
9-Methoxy-10-methyl-1,2-benzanthracene (XXX)	13	EtOH	3940	3.31
			3800	3.84
			3610	3.96
			3450	3.84
			3300	3.61
			2930	4.91
			2820	4.86
			2720	4.62
			2620	4.55
			(2330)	4.35
3-Methoxy-20-methylcholanthrene (XIVa)	26	EtOH	4010	3.55
			3800	3.63
			3600	3.76
			3480	3.84
			3320	3.78
			(3120)	4.30
			(3080)	4.40
			2940	4.87
			2850	4.82
			(2550)	4.40
			2460	4.51
3-Methoxypyrene (XXVII)		EtOH	3820	4.00
			(3720)	3.39
			3620	4.11
			3490	4.39
			3460	4.40
			3350	4.34
			2780	4.60
			2660	4.34
			2560	4.05
			2410	4.78
E. Aldehydes				
3-Acenaphthaldehyde (XXXIII)	21	n-Heptane	3420	3.90
			3310	4.00
			(3200)	3.93
			2530	4.46
			2460	4.41
			2260	4.35
9-Anthraldehyde (XXXI)	9	n-Heptane	3980	3.84
			3710	3.84
			(3520)	3.58
			(3350)	3.25
			2620	5.10
1,2-Benzanthracene-10-aldehyde (XXXIV)	9	EtOH	4035	3.91
			3850	3.91
			3030	4.69
			2910	4.65
			2490	4.60
Pyrene-3-aldehyde (XXXII)	35	n-Heptane	3910	4.43
			3720	4.37
			3630	4.41
			3580	4.39
			(3440)	4.16
			2870	4.58
			2750	4.29
			(2650)	3.93
			2490	4.49
			2430	4.49
			2330	4.59
3,4-Benzpyrene-5-aldehyde* (XXXV)	14	EtOH	4240	4.25
			3110	4.47
			3010	4.49
			2682	4.57
			2580	4.55
F. Ketones				
Benzophenone (XLVII)	31	EtOH	3325	2.19
			2530	4.27
Anthrone (XLVIII)		EtOH	(3500)	2.06
			3060	3.62
			(2700)	4.27
			2570	4.39
Fluorenone (XLIX)	30	EtOH	3925	2.40
			3780	2.43
			(3600)	2.34
			(3280)	2.97
			3210	3.07
			3150	3.19

TABLE IV (*Continued*)

Compound[a]	Source[b]	Solvent	Absorption maxima	
			Wave length,[c] Å.	Intensity, log E_m
			3060	3.28
			2930	3.54
			(2830)	3.40
			2570	5.00
			2480	4.79
1-Acetoacenaphthene (XXXVIII)	17, 23	EtOH	3520	3.66
			(3080)	3.56
			2930	3.82
			(2860)	3.76
			2530	4.76
			(2470)	4.64
			2140	4.27
3-Acetoacenaphthene (XXXIX)	15	EtOH	3300	3.95
			(3200)	3.89
			2450	4.37
			2240	4.36
			2120	4.45
1-Acetoanthracene (XXXVI)		EtOH	3850	3.73
			3660	3.71
			(3460)	3.53
			(3300)	3.24
			(3040)	3.19
			(2780)	4.12
			2540	4.84
			2410	4.76
15-Keto-20-methylcholanthrene (XLVI)	14	EtOH	4030	4.01
			3860	4.04
			(3650)	3.83
			3080	4.69
			2960	4.66
			(2850)	4.50
			2680	4.35
			(2560)	4.39
			2340	4.62
			2180	4.52
2-(1-Pyrenoyl)-propionic acid (XL)	36	EtOH	(3850)	3.85
			(3680)	4.19
			3520	4.34
			2810	4.40
			2420	4.62
			2330	4.60
10-Acetyl-3,4-benzpyrene (XXXVII)	36	EtOH	4120	4.40
			3960	4.39
			(3700)	4.08
			(3580)	3.84
			(3120)	4.37
			3000	4.42
			2600	4.74
			2380	4.40
			(2200)	4.46
G. Carboxylic Acids and Esters				
1-Acenaphthoic Acid (XLIII)	15	EtOH	3420	3.63
			3300	3.52
			3000	3.66
			2880	3.78
			2780	3.71
			2420	4.82
		N NaOH in 50% aq. EtOH	3360	3.52
			3230	3.43
			(3020)	3.67
			2870	3.77
			2360	4.68
2-(3-Acenaphthene)-acrylic Acid (XLIV)	35	EtOH	3440	4.19
			3340	4.14
			(2490)	4.36
			2320	4.51
		0.2 *N* NaOH in 50% aq. EtOH	3300	4.15
			(2500)	4.30
			2330	4.56
7-Cholanthroic Acid (XLI)	23	0.01 *N* HCl in 95% EtOH	3940	3.48
			3790	3.78
			3620	3.89
			3450	3.79
			3300	3.60
			2960	4.73
			2870	4.69
			2710	4.61
			2640	4.61
		0.5 *N* NaOH in 50% aq. EtOH	3940	3.51
			3820	3.80
			3630	3.94
			3460	3.84
			3300	3.63
			2980	4.82
			2860	4.75
			2740	4.56
			2660	4.62
Methyl ester of 7-Cholanthroic Acid*	23	Hexane	See THIS JOURNAL, **62**, 1354 (1940)	
Chrysene-5-carboxylic Acid (XLII)	22	0.05 *N* HCl in 95% EtOH	3670	2.86
			3500	2.95
			3240	4.01
			3110	4.05
			2980	4.03
			2700	4.96
			2620	4.80
			2200	4.47
H. Cyano Derivatives				
9-Cyanoanthracene (L)	9	EtOH	4020	3.79
			3820	3.90
			3640	3.90
			3460	3.62
			(3290)	3.20
			(3160)	2.74
			2560	5.17
3-Cyano-20-methylcholanthrene (LIVb)	26	EtOH	4100	3.54
			3860	3.74
			3680	3.76
			3500	3.75
			3080	4.91
			2960	4.80
			2720	4.46
			2620	4.57
			2420	4.51

TABLE IV (*Concluded*)

Compound[a]	Source[b]	Solvent	Absorption maxima Wave length,[c] Å.	Intensity, log E_m
6-Cyano-20-methylcholanthrene (LII)	7	EtOH	4250	4.74
			4020	3.65
			3740	3.77
			3560	3.90
			3410	3.80
			3105	4.95
			2980	4.83
			2870	4.56
			2740	4.40
			2620	4.51
			2490	4.53
5-Cyano-3,4-benzpyrene* (LIa)	16	Dioxane	4160	4.51
			3935	4.46
			3734	4.15
			(3500)	3.68
			3085	4.85
			2955	4.70
			2830	4.40
			2680	4.69
I. Isocyanate Derivatives				
1,2,5,6-Dibenzanthracene-9-isocyanate* (LV)	3	Hexane	4040	3.08
			(3830)	3.10
			3665	4.15
			3480	4.19
			3335	4.12
			(3150)	4.12
			3035	5.23
			2915	5.10
			2805	4.72
3,4-Benzpyrene-5-isocyanate* (LIb)	2	Hexane	4165	4.27
			4045	4.51
			3920	4.30
			3830	4.45
			3645	4.14
			3445	3.68
			3045	4.83
			2905	4.64
			2800	4.40
			2680	4.70
			2560	4.67
			(2440)	4.43
J. Halogen Derivatives				
2-Chlorophenanthrene (LVIIIa)	37	EtOH	3490	2.16
			3420	2.29
			3330	2.42
			3260	2.36
			3170	2.39
			3110	2.31
			2950	3.93
			(2850)	4.06
			2770	4.21
			2730	4.20
			2540	4.84
2-Bromophenanthrene (LVIIIb)	37	EtOH	3490	2.32
			3420	2.38
			3330	2.50
			3260	2.43
			3180	2.47
			2950	3.92
			2840	4.13
			2770	4.26
			2730	4.26
			2550	4.89
5-Bromo-9,10-dimethyl-1,2-benzanthracene (LIX)	38	EtOH	(4090)	3.35
			(3900)	3.86
			3720	3.98
			3560	3.85
			(3290)	3.40
			3000	4.89
			2890	4.86
			(2780)	4.61
			2400	4.32
3-Chloro-20-methylcholanthrene (LIVc)	26	EtOH	3980	3.55
			3760	3.74
			3620	3.83
			3450	3.80
			3300	3.66
			3100	4.38
			2960	4.87
			(2890)	4.80
			2660	4.59
			2580	4.58
			2380	4.52

NOTES ON TABLE IV

[a] The spectra of compounds marked (*) were determined photographically by a technique already described (see Jones, THIS JOURNAL, **62**, 148 (1940)). The remainder were measured on a Beckman spectrophotometer (see page 2149). [b] Source references: (1) Cason and Fieser, THIS JOURNAL. **62**, 2681 (1940). (2) Creech, *ibid.*, **63**, 576 (1941). (3) Creech and Franks, *ibid.*, **60**, 127 (1938). (4) Fieser and Cason, *ibid.*, **61**, 1740 (1939). (5) Fieser and Cason, *ibid.*. **62**, 1293 (1940). (6) Fieser and Creech, *ibid.*, **61**, 3502 (1939). (7) Fieser and Desreux, *ibid.*, **60**, 2255 (1938). (8) Fieser and Dietz, *ibid.*, **51**, 3141 (1929). (9) Fieser and Hartwell. *ibid.*, **60**, 2555 (1938). (10) Fieser and Hershberg, *ibid.*, **57**, 1681 (1935). (11) Fieser, Hershberg, Long and Newman, *ibid.*. **59**, 475 (1937). (12) Fieser and Hershberg, *ibid.*, **59**, 1028 (1937). (13) Fieser and Hershberg, *ibid.*, **60**, 1893 (1938). (14) Fieser and Hershberg. *ibid.*, **60**, 2542 (1938). (15) Fieser and Hershberg, *ibid.*, **61**, 1272 (1939). (16) Fieser and Hershberg, *ibid.*. **61**, 1565 (1939). (17) Fieser and Hershberg, *ibid.*, **62**, 49 (1940). (18) Fieser and Heymann, *ibid.*, **63**, 2333 (1941). (19) Fieser and Heymann, *ibid.*, **64**, 376 (1942). (20) Fieser and Johnson, *ibid.*, **61**, 1647 (1939). (21) Fieser and Jones. *ibid.*. **64**, 1666 (1942). (22) Fieser and Joshel. *ibid.*, **62**, 1211 (1940). (23) Fieser and Kilmer. *ibid.*, **62**, 1354 (1940). (24) Fieser and Newman, *ibid.*. **58**, 2376 (1936). (25) Fieser and Novello. *ibid.*. **64**, 802 (1942). (26) Fieser and Riegel, *ibid.*, **59**, 2561 (1937). (27) Sample supplied to Professor Fieser by the Gesellschaft für Teerverwertung m. b. H. (28) Synthesized by Dr. E. Berliner. (29) Supplied by Dr. R. B. Woodward. (30) Synthesized by Dr. R. N. Jones. (31) Commercial sample, recrystallized to constant melting point. (32) Synthesized by Dr. H. J. Creech by method due to Dr. W. E. Bachmann (*J. Org. Chem.*, **1**, 347 (1936)). (33) Synthesized by Dr. T. G. Webber. (34) Synthesized by Dr. Creech by method due to Fieser and Dietz (see ref. 8 above). (35) Synthesized by Dr. J. E. Jones. (36) Synthesized by Dr. E. B. Hershberg. (37) Synthesized by Dr. C. C. Price. (38) Synthesized by Dr. J. L. Wood. (39) Synthesized by Dr. C. C. Price. [c] The wave lengths in parentheses refer to prominent points of inflection.

Experimental

The wave lengths of the absorption maxima and the extinction coefficients at the maxima of the several compounds discussed in this paper are summarized in Table IV. The spectra of the compounds marked with an asterisk were determined by a photographic method which has been described in an earlier publication.[41] The spectra of the remainder of the compounds were measured on a Beckman ultraviolet spectrophotometer. A constant band width of 10 Å. was employed.

The majority of the compounds were made available through the kindness of Professor L. F. Fieser. They were prepared in connection with a program of research on the synthesis of carcinogenic hydrocarbons carried out by Professor Fieser and collaborators. The methods of synthesis and proofs of structure of all but a few of these compounds have been described in the literature, and references to the relevant publications are included in the footnote to Table IV.

Conclusions

It would be reasonable to expect that the effects of substituent groups in these compounds should parallel the observed behavior of the same groups attached to other chromophores; the weak bathochromic shifts produced by alkyl substituents and the more pronounced effects of amino, carbonyl and phenolic groups accordingly call for no special comment.

The two observations of most interest which emerge from the analyses of the data presented here are, in the first place, the indication that, in the complex spectra of these hydrocarbons certain groups of absorption maxima may be associated with electronic activations centered about specific carbon atoms in the molecule. This is most notable in the spectra of 3-aminopyrene and 4-aminopyrene on page 2133. Such effects are not always observed and in most cases the substituent modified the whole spectrum. It would seem reasonable to conclude that where such localized substitution effects do occur, the substituent group must lie along an axis of electronic oscillation in the molecule. In the more general case where the polarizable substituent does not lie along such an axis, its influence on the hydrocarbon spectrum will depend upon the vectorized components of its polarizability in the directions of the electronic oscillations in the molecule. This would suggest that a careful analysis of the spectra of a complete series of hydroxy or amino derivatives of a polynuclear aromatic hydrocarbon may provide a means by which the directions of such axes in the molecule may be located.

The second observation from these data is the failure to achieve a satisfactory correlation between the evidence of steric hindrance with resonance as observed experimentally in the ultraviolet absorption spectra, and the prediction of its occurrence from considerations of molecular geometry. This failure is probably attributable to the somewhat naive picture of the molecule presented by the conventional atom models, according to which the "surface" of an atom is presented as a non-penetrable sphere. A satisfactory quantitative treatment of the factors determining the extent of steric interference with resonance is lacking and would clear up several outstanding problems relevant to the theory of absorption spectra and related phenomena.

In the spectra of amino, phenolic and carbonyl derivatives where the normal "auxochromic" shifts are observed, the vibrational fine structure characteristic of the spectra of polynuclear aromatic hydrocarbons is to a large extent eliminated, and in the classification of spectra we have regarded such loss of fine structure as a necessary attribute of a "C-effect." This may not be fully justified; the spectra of the cyano derivatives discussed on page 2142 provide cause for special mention in this connection. We have chosen to treat these compounds separately from the compounds exhibiting C-effects, since, although the bathochromic effects produced by the introduction of a cyano group may be quite large, the vibrational fine structure is to a large extent retained. The same is true also of the isocyanates and thiocyano derivatives. These are the only groups of compounds which we are unable to accommodate in the system of classification of spectra developed in this paper. The system of classification into B-, Fs-, C- and S-effects was suggested largely by practical considerations, as affording a basis in terms of which a somewhat heterogeneous mass of data might be organized into a form suitable for discussion. It is not a matter of serious concern if small groups of compounds are found which are not readily assimilated into it; rather such cases provide a stimulus for further investigation.

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Summary

A comparative study has been made of the ultraviolet absorption spectra of some eighty polynuclear aromatic compounds, the majority of which are alkyl, aryl, carbonyl, methoxy, amino and phenolic derivatives of anthracene, phenanthrene, chrysene, 1,2-benzanthracene, 3,4-benzpyrene and 1,2,5,6-dibenzanthracene.

From these data it is possible to make generalizations concerning the changes produced by such substituents in the spectra of the parent hydrocarbons. For the purpose of discussion, the effects so produced are divided into four classes

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[41] Jones, THIS JOURNAL, 62, 148 (1940).

referred to as the B (bathochromic) effect, the Fs (fine structure), C (conjugation) and S (steric) effects.

Alkyl and most alicyclic substituents produce only B-effects, *i. e.*, a shift of the whole absorption curve to longer wave lengths occurs, with little change of shape. A few alicyclic derivatives exhibit an increase in the fine structure resolution (Fs-effect). In many derivatives in which there is an unsaturated substituent with the double bond in a position to conjugate with the main aromatic ring system, a more profound change in the spectrum occurs (C-effect); such groups as $-NH_2$, $-OH$ and $-O^-$, in which there are donatable pairs of electrons on the atom attached directly to the aromatic ring system also show C-effects. In the fourth class (S-effect) are included the spectra of compounds containing formally conjugated systems which fail to exhibit such changes, and in which it is presumed that the failure is caused by steric interference with resonance.

It is noted that in the spectra of certain compounds which exhibit C-effects, the modification of the hydrocarbon spectrum is mainly associated with specific groups of maxima, other groups of maxima being relatively unchanged. An attempt is made to explain such localized influences by the assumption that the several absorption bands in the complex spectra of these aromatic compounds are associated with processes of electronic excitation vectorized in the plane of the aromatic ring system.

In cases where C- or S-effects are observed, calculations have been made of the minimum angle of approach between the plane of the aromatic ring system, and the main plane of the substituent group, in an attempt to determine whether steric interference with resonance can be predicted from purely geometrical considerations of molecular structure. In many cases such predictions do not agree with the spectrographic observations.

Certain compounds, notably those containing conjugated cyano and isocyanate groups, fail to exhibit normal C-effects, although the linear shape of these substituents eliminates the possibility of steric inhibition of resonance being responsible. Compounds containing these substituents tend to show quite large bathochromic shifts of the hydrocarbon spectrum, but do not show the accompanying loss of fine structure resolution usually seen in the spectra of amino, carbonyl and conjugated alkene substituents.

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[Contribution from the Sugar Research Foundation Laboratory and from the Department of Chemistry, No. 306 in Organic Chemistry, Massachusetts Institute of Technology]

New Aliphatic Borates[1]

By Allen Scattergood, Warren H. Miller[2] and Julian Gammon, Jr.[2]

Over a dozen aliphatic borates have been mentioned in the literature, but the constants and analyses of several of these are missing, including two which are sold commercially. Several of the known borates have therefore been prepared under more carefully controlled conditions and the missing data collected. In addition, ten new borates have been prepared in order to study their properties and possible applications, especially in sugar chemistry. Three of the new borates are crystalline.

Experimental

Most of the alcohols from which the borates were prepared are commercial products. They were fractionated through a 115-cm. electrically heated, helix-packed column with total condensation and a variable take-off. The H.E.T.P. of the column was 2.5 cm. Interchangeable ground glass joint equipment and Glas-col heating mantles were used throughout this research.

The new borates were prepared by the method of Bannister.[3] Quantities proportional to one mole of boric acid and three moles of the purified alcohol were employed. An excess of alcohol sufficient to remove three moles of water as the azeotrope was used. To ensure complete reaction, a 10% over-all excess of alcohol was generally taken. The mixture was distilled through the column described. During the distillation of the water-alcohol azeotrope, it was found that proper adjustment of the take-off returned the alcohol layer to the column so that an excess of alcohol may not be necessary. After the unreacted alcohol had been distilled off, the borate was fractionated through the column at atmospheric pressure unless it decomposed or boiled above 275°, in which case the column was operated at reduced pressure. Several borates which had been reported unstable in the literature were distilled successfully at atmospheric pressure.

A high boiling residue often was left after the distillation of the trialkyl borates. In the case of tri-*s*-butyl borate, an attempt to distil this residue at atmospheric pressure resulted in decomposition to a vapor which spontaneously ignited and burned with a green flame.

The Bannister method was applied successfully to all primary and secondary alcohols studied, but was unsuccessful in the case of the three tertiary alcohols tried. This suggests that primary and secondary alcohols contaminated with tertiary alcohols may be purified through their borates.

The data as to the preparation and properties of these borates are contained in Table I.

Hydrolysis of Borates

There is little information in the chemical literature concerning the rate of hydrolysis of alkyl borates, but the rates which are mentioned are stated to be very rapid. The

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[1] The material in this paper is taken in part from theses submitted to the Massachusetts Institute of Technology by Warren H. Miller and Julian Gammon, Jr., in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

[2] U. S. Navy, V-12 program.

[3] W. J. Bannister, U. S. Patent 1,668,797 [*C. A.*, **22**, 2172 (1928)]; J. R. Johnson and S. W. Tompkins, "Organic Syntheses," **13**, 16 (1933).