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Infrared Spectra of Polynuclear Aromatic Compounds. I. 1,2-Benzanthracene, the Monomethyl-1,2-benzanthracenes and Some Dimethyl-1,2-benzanthracenes[1]

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The infrared spectra of 1,2-benzanthracene, the complete set of twelve monomethyl-1,2-benzanthrazenes and four dimethyl-1,2-benzanthracenes have been obtained in non-polar solution in the 3300-665 cm.$^{-1}$ region. Where possible, band assignments to methyl and to aromatic CH group vibrations have been made. Spectra–structure correlations are made in several important regions of the spectrum. Certain bands near 1900 cm.$^{-1}$ appear characteristic of the 1,2-benzanthracene nucleus regardless of the number or position of the methyl substituent(s). The wave number of the band at *ca.* 3050 cm.$^{-1}$, assigned to the aromatic CH stretching frequencies, shows more correlation with carcinogenic activity and with indices of electronic structure than does the position of any other infrared band.

Introduction

This Laboratory has recently reported relationships between indices of electronic structure and certain aspects of the infrared spectra of a number of carbonyl compounds[2,3] as well as some compounds containing the NH group.[4] We have also been interested in an extension of this general approach to the field of polycyclic aromatic compounds. The monomethyl-1,2-benzanthracenes appealed to us as an appropriate starting point for aromatic hydrocarbons because of their relatively large number, their range of carcinogenic potency,[5] their availability[6] and because recently a number of their structural indices have been calculated.[7,8] Among previous infrared studies of polynuclear aromatic hydrocarbons two have reported solid state spectra of several methylbenzanthracenes[9,10] but without any comparison with indices of electronic structure. We have been able to obtain the solution spectra of the complete set of monomethyl-1,2-benzanthracene isomers in non-polar solvents. The present paper reports our experimental results and the degree to which they show correlation with calculated indices of electronic structure, with experimentally determined chemical properties and with carcinogenic activity. From this point on the symbol MBA will be used for methyl-1,2-benzanthracene.

Experimental

The solution spectra of 1,2-benzanthracene,[11] the complete set of twelve monoMBAs,[12] and four available diMBAs[13] were obtained in the 3330-665 cm.$^{-1}$ region. All the spectra are shown in Fig. 1.[14] The ordinate, in each case, is intensity, measured in per cent. absorption, the abscissa, wave number, measured in reciprocal centimeters. The 2700–2000 cm.$^{-1}$ region is omitted from Fig. 1 since no absorption bands were observed therein for the sample concentrations and cell thicknesses employed. The "numbered" structure diagram for the parent hydrocarbon, 1,2-benzanthracene, is given in Fig. 2.

Concentrations of 0.05 to 0.10 molar were used for the majority of the spectral regions. For the 1300–665 cm.$^{-1}$ region carbon disulfide was the solvent and a 1 mm. cell thickness was found to be convenient. A 2 mm. cell thickness was used in the 3300–1300 cm.$^{-1}$ region with carbon tetrachloride as the solvent. The 1625–1475 cm.$^{-1}$ region was the only one in which solvent absorption seriously interfered, the carbon tetrachloride being opaque for a 2 mm. cell thickness. Where some spectral indication was obtained, the bands are drawn in with a dotted line in Fig. 1. More concentrated solutions in a 0.3 mm. cell enabled this gap in the spectrum to be bridged for a number of the compounds which were sufficiently soluble and for which there was sufficient sample available.

Relative intensities of band shoulders and of the weaker components of doublets are not easily estimated from the curves of Fig. 1. To obtain a clearer picture of the intensities of such bands, the spectra in certain regions were redrawn using optical density as the ordinate. The overlapping bands were then resolved by an approximate graphical method.[15] The height of the vertical lines in the 3000 cm.$^{-1}$ region of Fig. 1 represents the intensity of these bands, expressed in per cent. absorption.

Most of the spectra in the 3330–1300 cm.$^{-1}$ region were obtained with a Perkin-Elmer No. 21 double beam spectrophotometer equipped with a calcium fluoride prism.[16] A few spectra within this spectral interval were made on a Perkin-Elmer No. 12C single beam spectrometer with calcium fluoride prism[17] or on the Fisk University single beam spectrometer[18] using a lithium fluoride prism.[4] The 1300–665 cm.$^{-1}$ region spectra were obtained at Fisk University

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(1) This paper has been reported in part at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June, 1954, the Sixth International Cancer Congress, Sao Paulo, Brazil, July, 1954, and the European Molecular Spectroscopy Group Conference, Oxford University, Oxford, England, July, 1955.

(2) M.-L. Josien and N. Fuson, *Bull. soc. chim. France*, **19**, 389 (1952).

(3) M. L. Josien, N. Fuson, J. M. Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).

(4) N. Fuson, M.-L. Josien, R. L. Powell and E. Utterback, *ibid.*, **20**, 145 (1952).

(5) J. L. Hartwell, "Survey of Compounds Which Have Been Tested for Carcinogenic Activity," Federal Security Agency, National Cancer Institute, Bethesda, Maryland, 1940, pp. 74–78.

(6) M. S. Newman and R. Gaertner, THIS JOURNAL, **72**, 264 (1950).

(7) B. Pullman and A. Pullman, "Les Theories Electronique de la Chimie Organique," Masson et Cie., Paris, 1952, p. 588.

(8) A. Pullman and B. Pullman, "Cancerisation par les Substances Chimiques et Structure Moleculaire," Masson et Cie., Paris, 1955, chap. 5.

(9) S. F. D. Orr and H. W. Thompson, *J. Chem. Soc.*, 218 (1950).

(10) C. G. Cannon and G. B. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951).

(11) Commercial sample, Eastman Kodak Co.

(12) These were made available to us by Dr. M. S. Newman, Ohio State University, Columbus, Ohio.

(13) 9,10-diMBA and 3,10-diMBA were given to us by Dr. Newman. 3',6-diMBA and 3,7-diMBA were supplied us by Dr. E. Boyland, Chester Beatty Research Institute, Royal Cancer Hospital, London, England.

(14) Tables of frequencies and intensities for all spectra reported in this paper, together with details of the conditions under which the spectra were obtained, have been deposited as Document number 4790 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm, in advance by check or money order payable to Chief, Photoduplication Service, Library of Congress.

(15) *Cf.* J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (*London*), **A167**, 257 (1938).

(16) This instrument was made available to us by Dr. J. R. Lawson, Tennessee A. and I. State University, Nashville, Tennessee.

(17) This instrument was made available to us by Dean G. Brus, Faculty of Science, University of Bordeaux, France.

(18) M.-L. Josien, N. Fuson and A. S. Cary, THIS JOURNAL, **73**, 4445 (1951).

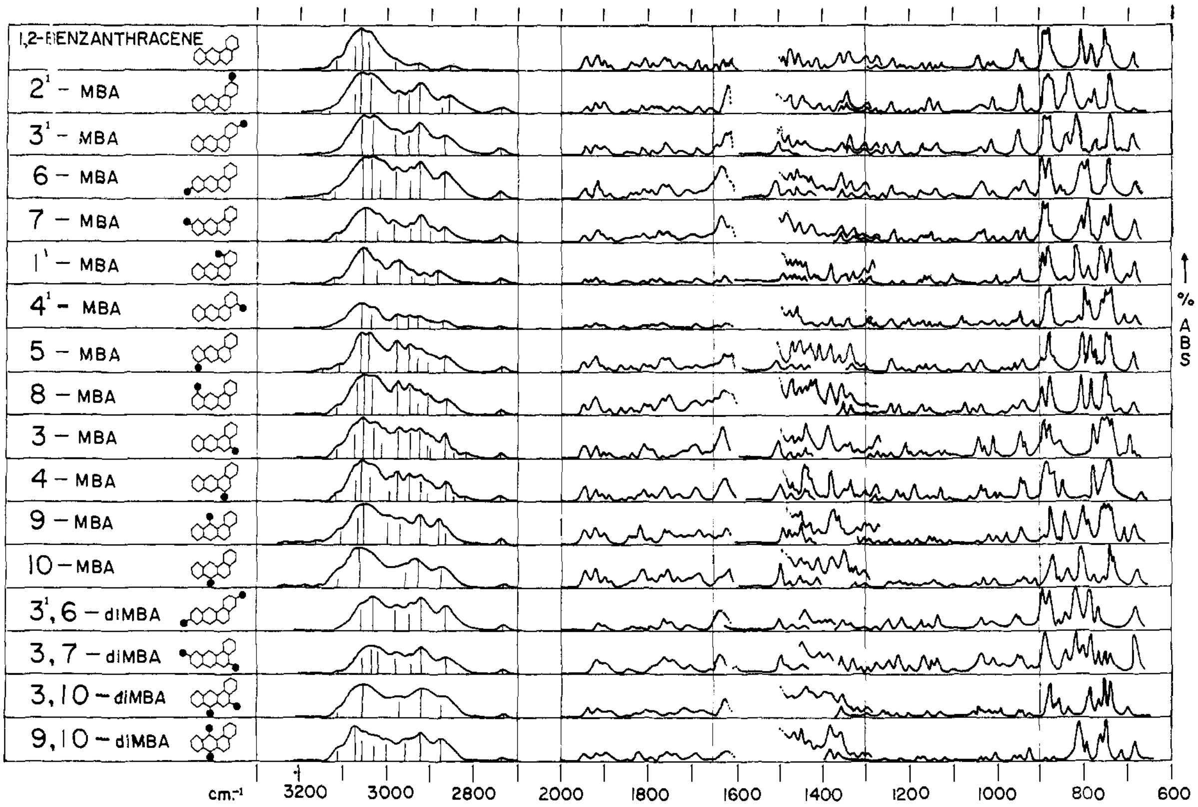

Fig. 1.—0.1 molar CCl_4 and CS_2 solution spectra of 1,2-benzanthracene, the twelve monomethyl-1,2-benzanthracenes and four dimethyl-1,2-benzanthracenes. Solvent interference obscured the sample spectra in the 1625–1475 cm.$^{-1}$ region for some of the compounds. The vertical lines in the 3000 cm.$^{-1}$ region indicate the position and "graphically resolved intensities" of the absorption bands.

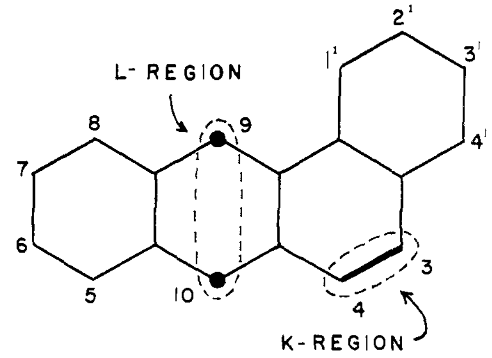

Fig. 2.—Structure diagram and carbon numbering scheme for 1,2-benzanthracene, showing location of the K-region and the L-region.

with a Perkin-Elmer No. 112 single beam, double pass, sodium chloride prism spectrometer, with the exception of a few run off on the Bordeaux University single beam instrument equipped with a sodium chloride prism.[17]

Individual sharp bands were reproducible on the same instrument to within ±2 cm.$^{-1}$ in the 3400–1000 cm.$^{-1}$ region and ±1 cm.$^{-1}$ in the 1000–665 cm.$^{-1}$ region. Errors of the same magnitude could arise from variations in absolute calibration of the different instruments used. In all cases, the spectral slit widths employed were approximately 15 cm.$^{-1}$ at 3000 cm.$^{-1}$, 3 cm.$^{-1}$ at 1700 cm.$^{-1}$, 5 cm.$^{-1}$ at 1200 cm.$^{-1}$ and 2 cm.$^{-1}$ at 700 cm.$^{-1}$.

Analysis of Spectra and Assignments of Bands

We have chosen to discuss first the spectral regions which are associated mainly with skeletal vibrations and CH wagging and rocking vibrations (900–665 cm.$^{-1}$, 1300–900 cm.$^{-1}$ and 2000–1650 cm.$^{-1}$), then the CC stretching and CH deformation frequency region (1650–1300 cm.$^{-1}$) and finally the CH valence vibration region (3300–2700 cm.$^{-1}$). For ease of comparison the mono-MBA spectra in Fig. 1 have been arranged in "substitution groups" or groups of compounds each having the same set of four substituted benzene rings. For example 3-MBA and 4-MBA, both of which have two 1,2-disubstituted benzene rings, one 1,2,4,5-tetrasubstituted ring and one 1,2,3,4,5-pentasubstituted ring, are in the same "substitution group." For convenience in cross reference, Tables II, III and IV, which contain wave numbers of bands in certain regions, are ordered by rows in the same compound order as that of the spectra in Fig. 1.

The 900-665 Cm.$^{-1}$ Region.—In this region lie bands in benzene derivatives which are well known to be associated with out-of-plane bending vibrations of the aromatic ring CH groups.[19] Dannenberg, Schiedt and Steidle,[20] after a careful survey of the spectra of substituted *cyclo*pentenophenanthrenes in this region, conclude that their spectra may be interpreted as the sum of the spectra of the

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(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, chap. 5 (see also Fig. 3 in the present paper).

(20) H. Dannenberg, U. Schiedt and W. Steidle, *Z. Naturforschg.*, **8b**, 269 (1953).

three variously substituted benzene rings contained in the phenanthrene nucleus. Orr and Thompson's[9] study of polynuclear hydrocarbons, including the spectra of 1,2-benzanthracene and ten of its derivatives in the solid state, leads them to draw more limited conclusions. They assign the strong bands at 750 cm.$^{-1}$ to *ortho*-substituted benzene rings contained in the polycyclic nucleus and suggest that the strong bands at 890 cm.$^{-1}$ be associated with 1,2,4,5-tetra-substitution and the strong 805 cm.$^{-1}$ bands with 1,2,3,4-substitution. Cannon and Sutherland[10] are in agreement with the conclusion of Orr and Thompson in this region on the basis of their study of the spectra of aromatic compounds including 1,2-benzanthracene and nine of its derivatives.

Our spectroscopic data in this region can be analyzed in terms of four bands or band regions. The first band at 682 ± 2 cm.$^{-1}$ is of medium intensity in the spectra of all the compounds in Fig. 1 but three (being weak in 2'-MBA and absent in 3-MBA, 4-MBA and 3,10-diMBA). Its presence in 3,7-diMBA rules out its identification with 1,2,3,4-substitution, so it seems to be characteristic of the four-ring skeleton rather than of any particular type of substituted ring. A second band, often complex, at 742 ± 4 cm.$^{-1}$, is of medium intensity in the 3,7-dimethyl isomer and strong in all the rest with the exception of 3',6-diMBA, for which it is absent. Since the latter is the only derivative studied which lacks an *ortho*-substituted benzene ring (see Fig. 2), this 742 cm.$^{-1}$ band is taken to be characteristic of *ortho*-substitution. The third region, 830–790 cm.$^{-1}$, contains at least one strong band for all compounds but 3-MBA, 4-MBA and 3,10-diMBA. Since these are the only three compounds without an isolated pair of adjacent aromatic hydrogen atoms, this region seems characteristic of 1,2,4- and/or 1,2,3,4-substituted benzene rings. The fourth region, 900–870 cm.$^{-1}$, contains a strong band for all spectra shown in Fig. 1 except 9,10-diMBA. The band, where simple, is generally close to 880 cm.$^{-1}$; often, however, the absorption is complex, being a strong doublet with a separation of as much as 15 cm.$^{-1}$. Absorption in this region appears to be a characteristic of isolated aromatic hydrogens (1,2,4,5- and/or 1,2,3,4,5-substitution) since this is the only configuration absent in 9,10-diMBA but common to *all* the other compounds studied.

Bands in the three intervening regions of this part of the spectrum are less easy to categorize and no correlation with ring substitution was found for them. The 730–690 cm.$^{-1}$ region is sparsely populated, only about half the MBAs having a band of medium, or, more generally, weak intensity within this range. The 790–750 cm.$^{-1}$ region is much more crowded, containing at least one band (usually intense, although weak in a few cases) in the spectrum of each compound studied. The 870–830 cm.$^{-1}$ region includes a medium or weak band for about two-thirds of the MBAs.

It should be noted that there is no band present between 879 and 805 cm.$^{-1}$ in the spectrum of 1,2-benzanthracene itself. On the other hand, all the MBAs except the 8-methyl isomer have a band of weak to medium intensity in this region. We suggest that a rocking or wagging frequency of the CH_3 group may possibly be responsible for these bands; deuterization experiments are needed to make a clearcut decision.

We have made no assignment of spectral bands to 1,2,3-trisubstituted benzene rings even though four of the MBAs (the 1'-, the 4'-, the 5- and the 8-) contain this configuration. While bands in the 800–750 cm.$^{-1}$ region are generally assigned to this category for simpler aromatic compounds,[19,20] we could discover no 1,2,3-substitution correlation with the 1,2-benzanthracene spectral bands in this region or in any other. Previously published work on the MBAs[9,10] omits *any* mention of 1,2,3-substitution assignments, and our study of their published spectra does not resolve the matter.

Our attempt by infrared means to differentiate either between 1,2,4-tri- and 1,2,3,4-tetra-substituted rings or between 1,2,4,5-tetra- and 1,2,3,4,5-penta-substituted rings in 1,2-benzanthracene derivatives has not been fruitful. For this reason our results and conclusions for the 900–670 cm.$^{-1}$ region, which extend (but do not contradict) those of previous workers on the same type of compounds, as can be seen from Fig. 3, can best be summarized in terms of the number of adjacent hydrogen atoms remaining around the benzene ring.[21] This summary is given in Table I.

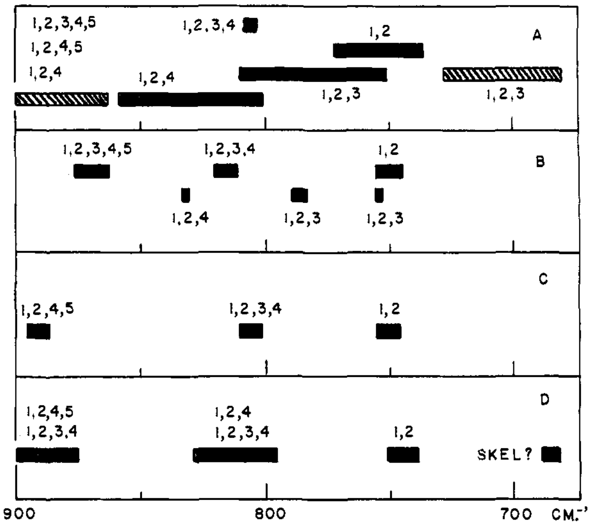

Fig. 3.—Ranges of absorption bands in the 900–670 cm.$^{-1}$ region characteristic of certain types of benzene ring substitution for the following aromatic compounds in CS_2 solution: (A) substituted benzenes[19] (characteristic bands not always present in the two cross-hatched ranges); (B) substituted cyclopentenophenanthrenes[20]; (C) substituted 1,2-benzanthracenes (other work)[9,10]; (D) substituted 1,2-benzanthracenes (present work).

TABLE I

RANGES FOR BANDS ASSIGNED TO SUBSTITUTED BENZENE RINGS IN THE SPECTRA OF 1,2-BENZANTHRACENE AND ITS MONOMETHYL AND DIMETHYL DERIVATIVES

Band position (cm.$^{-1}$)	No. of adjacent hydrogen atoms on a ring	Type of ring substitution
900–870	1	1,2,4,5- and 1,2,3,4,5-
830–790	2	1,2,4- and 1,2,3,4-
?	3	1,2,3-
746–738	4	1,2-

The 1300–900 cm.$^{-1}$ Region.—Bellamy[19] reviews the literature for assignments which have been made for weak bands in substituted aromatic compounds in the 1300–900 cm.$^{-1}$ region, pointing out that they should be used only as confirmatory evidence. In all the spectra in Fig. 1, absorption occurs at *ca.* 950 cm.$^{-1}$ after a transparent stretch just

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(21) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 396 (1950).

above the strong 900–880 cm.$^{-1}$ band region. For the 1′-, the 2′-, the 3′- and the 4′-methyl derivatives, a single sharp peak is dominant; in the others a doublet is observed with a separation ranging up to 10 cm.$^{-1}$. The next general region of absorption, between 1050 and 1000 cm.$^{-1}$, contains from one to four bands in the spectrum of each compound. The 1125–1050 cm.$^{-1}$ region has the sparsest band population of any region below 1500 cm.$^{-1}$, being empty (except for an occasional very weak band at 1105 cm.$^{-1}$) for all but the 1′-, 4′- and 8-MBA derivatives. Finally the 1300–1125 cm.$^{-1}$ spectral region contains, for each compound, a series of roughly equally spaced weak bands of rather uniform intensity, in appearance somewhat like an eroded, coarse-toothed comb.

Our analysis of this region revealed no positive correlation with Bellamy's[19] ranges for 1,2-, 1,2,4- and 1,2,3-substituted aromatic compounds. Perhaps the only positive evidence of structure–spectra correlation in this region is that between 1125 and 900 cm.$^{-1}$ the spectra of the following "substitution group" pairs bear a considerable resemblance to each other: 2′-MBA with 3′-MBA; 6-MBA with 7-MBA; 5-MBA with 8-MBA and 3-MBA with 4-MBA.[22] The spectrum of 1′-MBA does not correspond to that of 4′-MBA, however, even though they also are structural twins from the benzene ring substitution point of view. The same is true for 9-MBA and 10-MBA. In these two cases the spectral differences may well be accounted for by steric hindrance in the 1′- and the 9-methyl isomers, respectively.[23]

The 2000–1650 Cm.$^{-1}$ Region.—Young, Duvall and Wright[24] found that the number and arrangement of substituents on a benzene ring could be determined by a study of the rock salt prism spectra in the 2000–1650 cm.$^{-1}$ region. The solution spectra of 1,2-benzanthracene and its methyl derivatives in this region are crowded and complex when studied with calcium fluoride prism dispersion. At 0.1 molar concentration in a 2 mm. cell the bands are not intense, ranging generally between 10 and 40% absorption, but many of them are very sharp and clearcut. The over-all band pattern varies widely for the different isomers.

We analyzed these spectra to see if two isomers in the same "substitution group" would have the same spectral pattern. The results are intriguing! 6-MBA and 7-MBA (same substitution group) have essentially the same spectrum between 2000 and 1650 cm.$^{-1}$. The same is true of 1′- and 4′-MBA, of 5- and 8-MBA and of 9- and 10-MBA. But the spectra of 3- and 4-MBA differ sharply at one point in this region, and those of 2′- and 3′-MBA differ markedly at two. None of these differences can be explained as due to the presence of overtones or combination bands since the 3- and 4-isomers' spectra are essentially identical in the 800–950 cm.$^{-1}$ region, the same being true for the 2′- and 3′-pair. Nor is steric hindrance involved in either of these two cases. Furthermore while 6- and 7-MBA are in the same "substitution group" as 2′- and 3′-MBA, their spectra differ from the latter two at five points and at three points, respectively. Similarly while 1′- and 4′-MBA are in the same "group" at the 5- and 8-MBA isomers, the spectra of these two pairs differ from each other at six points in this region.

Depaigne-Delay and Lecomte[25] have shown that in this region fall fundamental vibrations of the benzene ring skeleton. We suggest that the more complicated four-ring system has correspondingly more fundamentals in this region and that the movement of the methyl group from point to point over the periphery of the 1,2-benzanthracene nucleus in the different isomers sometimes affects the position of these fundamentals even though the "substitution group" is unchanged.

While this region is, then, not very dependable as a guide to the points of substitution for polycyclic aromatic compounds, certain regularities in the spectra between 2000 and 1650 cm.$^{-1}$ occur which are of interest. 1,2-Benzanthracene, its twelve monomethyl isomers and its 3,10- and 9,10-dimethyl isomers[26] all have a band at 1811 ± 5 cm.$^{-1}$ and a pair of bands at 1945 ± 3 cm.$^{-1}$ and 1918 ± 3 cm.$^{-1}$. In addition, one or both of two additional bands at 1900 ± 4 cm.$^{-1}$ and at 1887 ± 1 cm.$^{-1}$ may be present. The 1887 cm.$^{-1}$ band is always weak. The relative intensities of the other three bands in the 1900 cm.$^{-1}$ region are variable in the spectra of the different isomers, each taking a turn several times at being the strongest. We suggest that these persistent bands result from 1,2-benzanthracene skeletal fundamental vibrations whose frequencies are unaffected or only slightly affected by the position(s) of the methyl group substituent(s).

We obtained the carbon tetrachloride solution spectra of naphthalene and its 1-methyl, its 2-methyl and its 1-chloro derivatives in this 1900 cm.$^{-1}$ region with calcium fluoride prism dispersion. Bands at 1944, 1930, 1915, 1903 and 1736 cm.$^{-1}$ (all ±4 cm.$^{-1}$) persist with varying intensities in the spectra of all four naphthalene compounds. Additional substituted naphthalenes need to be surveyed before this tentative naphthalene characterization is as well established as the one just described for the 1,2-benzanthracenes.

The ranges for characteristic bands of 1,2-benzanthracenes and of naphthalenes are summarized in Fig. 4. It would be of interest to see whether substituents other than the methyl group leave these particular spectral band frequencies unchanged for the benzanthracenes. We are continuing studies of this kind on other aromatic compounds to see whether the 2000–1700 cm.$^{-1}$ region may be useful as a means of identifying the skeleton of polycyclic aromatic compounds regardless of the number or type of substituent or the point of substitution.

The 1650–1300 Cm.$^{-1}$ Region.—Certain bands in the 1650–1300 cm.$^{-1}$ region have been assigned in the literature to skeletal vibrations, others to aromatic CH and to methyl group deformation vibrations. Nolin and Jones[27] put the symmetric

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(22) However while 2′-MBA and 3′-MBA are also in the same "substitution group" as 6-MBA and 7-MBA, the spectra of the former pair in this region are quite different from the latter pair.

(23) M. Orchin, *J. Org. Chem.*, **16**, 1165 (1951). In a private communication, dated June 21, 1955, Dr. Orchin states that lines 4–6, page 1167, of his paper should read, ". . . the melting point of the picrate of each of the twelve monomethyl-1,2-benzanthracenes is, with two exceptions, higher than the melting point of picric acid or the melting point of the hydrocarbon, whichever is lower."

(24) C. W. Young, R. B. Duvall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

(25) A. Depaigne-Delay and J. Lecomte, *J. phys. radium*, **7**, 38 (1946).

(26) 3′,6- and 3,7-diMBA were not available for study at the time this comparison was made on a double beam spectrophotometer with CaF_2 prism. Their spectra in this region, recently obtained on a single beam CaF_2 prism spectrometer (see Fig. 1), appear not to fit the range of Fig. 4 as well as did the others.

(27) B. Nolin and R. N. Jones, THIS JOURNAL, **75**, 5626 (1953).

and antisymmetric CH_3 deformation vibrations of aliphatic $-C-CH_3$ at 1379 and 1461 cm.$^{-1}$ (with a shoulder at 1454 cm.$^{-1}$), respectively. Pitzer and Scott's[28] toluene analysis assigns the same two vibrations of aromatic $Ar-CH_3$ to 1380 and 1450 cm.$^{-1}$, respectively. Depaigne-Delay and Lecomte[25] in a study of *ortho*-disubstituted benzene rings make the following general correlations: aromatic CH in-plane bending vibrations (out-of-phase) at 1300–1250 cm.$^{-1}$ and (in-phase) at 1400–1350 cm.$^{-1}$; skeletal vibrations at 1620–1550 cm.$^{-1}$, 1500–1470 cm.$^{-1}$ and 1460–1440 cm.$^{-1}$. Josien and Lebas'[29] findings for monosubstituted benzenes are in accord with Depaigne-Delay and Lecomte.[25]

In the solution spectra of 1,2-benzanthracene and its sixteen methyl derivatives (see Fig. 1), the 1650–1510 cm.$^{-1}$ region contains only one band, of widely varying intensity, at 1629 ± 11 cm.$^{-1}$ (with a satellite at *ca.* 1613 cm.$^{-1}$ in five cases). In sharp contrast stands the 1510–1300 cm.$^{-1}$ region which is richly endowed with bands. A relatively intense band at 1500 ± 8 cm.$^{-1}$, as well as a band at 1476 ± 10 cm.$^{-1}$, persists in all seventeen compounds.[30] A band at 1382 ± 3 cm.$^{-1}$, of varying intensity, is present in all but 1,2-benzanthracene itself. Two bands at 1355 ± 7 cm.$^{-1}$ and 1335 ± 10 cm.$^{-1}$ appear in the spectra of all the compounds, the intensity varying considerably. These bands are tabulated in Table II. In each of the MBAs a number of absorption bands are found in this spectral region which do not fit into clearcut sequences, and these have been omitted from Table II (see for example footnote *a*).

TABLE II

SEQUENCES OF ABSORPTION BANDS IN THE 1650-1300 CM.$^{-1}$ REGION FOR 1,2-BENZANTHRACENE AND ITS METHYL DERIVATIVES[a]

Compound	Band sequences (cm.$^{-1}$) at approximately 1629	1613	1500[b]	1476	1382	1355	1335
1,2-Benzanthracene	1627	1615[c]	(1497)	1476		1360	1339
2'-MBA	1618		(1500)	1476	1380	1354	1343
3'-MBA	1623	1614	1501	1478	1384[c]	1355	1339
6-MBA	1634	1612	1507	1474	1380	1357	1337
7-MBA	1635	1613	(1497)	1485	1380	1357	1329
1'-MBA	1630		1492	1476	1382	1358	1345
4'-MBA	1621		(1495)	1478	1382	1356	1344
5 MBA	1624	1611	1498[c]	1469	1381	1363	1334
8 MBA	1625	1610	(1501)	1470	1381	1354	1337
3-MBA	1633		1505	1475	1388[c]	1351	1343
4-MBA	1627		1500	1475	1383	1356	1340
9-MBA	1625		1497	1468	1379	1360[c]	1326
10-MBA	1621		1503	1480	1381	1357	1340
3',6-MBA	1637		1502	1472	1382	1355	1340
3,7-MBA	1640		1498	1486	1382	1358	1332
3,10-MBA	1626		(1500)	1473	1384	1359	1324
9,10-MBA	1626		(1498)	1466	1383	1359	1331

[a] The bands in the crowded region 1465 to 1385 cm.$^{-1}$ are omitted from this table, since they could not be grouped in unambiguous sequences. [b] The 1605–1490 cm.$^{-1}$ region was *not* explored in CCl_4 solution in a 0.3 mm. cell for seven compounds. The values enclosed within parentheses in this column, which were obtained from samples in a 2.0 mm cell, are probably a little too low. [c] Average wave number of doublet.

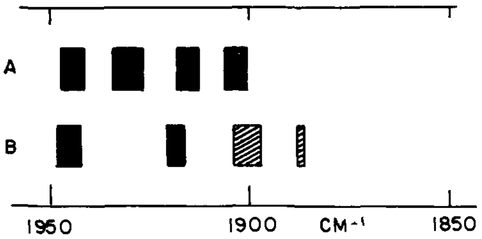

Fig. 4.—Ranges of absorption bands in the 1900 cm.$^{-1}$ region (CCl_4 solution) characteristic of the following polycyclic ring systems regardless of substitution: (A) naphthalene (a fifth characteristic band range at 1736 ± 3 cm.$^{-1}$ is not shown); and (B) 1,2-benzanthracene (one or the other of the two cross-hatched bands may be absent, but not both; fifth characteristic band, at 1811 ± 5 cm.$^{-1}$, not shown).

While Orr and Thompson[9] make no specific comments on the absorption bands in this 1650–1300 cm.$^{-1}$ region, Cannon and Sutherland[10] point out a weak band at 1620 ± 10 cm.$^{-1}$ in the solid spectra of all the benzanthracenes they studied. They also mention weak bands present in some cases at 1550 cm.$^{-1}$ and/or at 1500 cm.$^{-1}$. To the extent that solid and solution spectra can be compared, we find our solution results on the MBAs in this region to agree with Orr and Thompson's[9] solid (film) spectra considerably better than with Cannon and Sutherland's[10] solid (Nujol mull) spectra.

In line with the assignments previously cited,[25,27–29] the 1629 and 1500 cm.$^{-1}$ bands may be associated with two skeletal vibrations of the benzanthracene nucleus. Bands in the 1360–1250 cm.$^{-1}$ region can be thought of as largely due to aromatic CH in-plane bending vibrations. The 1382 cm.$^{-1}$ band, absent only in the unsubstituted hydrocarbon, is clearly the symmetric methyl group deformation vibration. Assignment of the asymmetric methyl vibration is ambiguous. The 1490–1400 cm.$^{-1}$ region is very crowded and complex as a result of the superposition of perhaps several skeletal vibrations as well as this methyl vibration. While we suggest that the 1476 cm.$^{-1}$ band is due to a skeletal vibration and that one or more bands in the 1460–1440 cm.$^{-1}$ region results from the asymmetric methyl group deformation vibration, a deuteration experiment is needed to confirm these assignments.

The 3300–2700 Cm.$^{-1}$ Region.—It is well known that the aromatic CH valence vibrations occur just above 3000 cm.$^{-1}$ [19] while the methyl group CH stretching vibrations are found just below 3000 cm.$^{-1}$.[31] We will consider first the 3000–2700 cm.$^{-1}$ region.

Fox and Martin[32] state that in non-polar solution spectra the asymmetric and symmetric stretching vibrations of the methyl group in alkanes are located at 2962 ± 10 cm.$^{-1}$ and 2872 ± 10 cm.$^{-1}$, respectively, additional bands due to the methyl group occurring occasionally at 2934 and 2912 cm.$^{-1}$. Posefsky and Coggeshall[33] report that for

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[28] K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943).

[29] M.-L. Josien and J.-M Lebas, *Bull. soc. chim. France*, 53, 57, 62 (1956).

[30] For a number of these spectra, only an indication of this band is present because no thin (0.3 mm.) cell CCl_4 solution spectra could be obtained.

[31] Reference 19, chapter 2.

[32] J. J. Fox and A. E. Martin, *Proc. Roy. Soc.*, (*London*), **A175**, 208, 234 (1940).

[33] A. Posefsky and N. D. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

TABLE III

ABSORPTION BANDS IN THE 3100–2700 CM.$^{-1}$ REGION FOR TOLUENE, THE TWO METHYLNAPHTHALENES AND THE TWELVE MONOMETHYL- AND FOUR DIMETHYL-1,2-BENZANTHRACENES[a]

Spectral regions (ν in cm.$^{-1}$; I in % absorption)[b]

Point of substitution	3055 ± 20[c]		2975 ± 5		2945 ± 5		2923 ± 5		2900 ± 6		2866 ± 5		2821 ± 5		2734 ± 5	
	ν	I	ν	I	ν	I	ν	I	ν	I	ν	I	ν	I	ν	I
Methylbenzene (toluene)																
1	3035	90	2979	35	2953*	60	2922	80			2871	60			2732	13
Methylnaphthalene																
1	3053	90	2970	65	2946	65	2925	65			2861	60			2732	15
2	3055	95	2971	40	2945	30	2922	50			2862	30			2732	7
Methyl-1,2-benzanthracenes																
2′	3044	85	2970	35	2945	35	2922	65			2861	35			2737	7
3′	3042	85	2976	45	2945	40	2921	70			2863	45			2736	10
6	3042	90	2975	60	2942	40	2920	80			2864	60			2737	15
7	3043	80	2980	40	2942	30	2921	60	2900	20	2867	35			2737	10
1′	3051	85	2966*	55	2940	15	2910*	15			2881*	30			2739	8
4′	3054	60	2973	30	2949	20	2927	25	2899	5	2869	18	2818	5	2737	5
5	3049	90	2974	65	2946	55	2927	30	2903	20	2865	40			2735	5
8	3046	90	2974	70	2944	65	2928	30	2906	45	2861	40			2737	10
3	3052	95	2973	65	2942	60	2921	60	2900	30	2865	55	2817	15	2737	15
4[d]	3054	95	2974	70	2945	65	2919	45	2905	20	2863	50	2818	10	2737	15
9[e]	3050	95	2968*	50			2920	70	2880*	60	2864	20	2826	5	2734	10
10	3060	95	2957*	40			2928	70			2874*	50			2735	7
3′,6	3033	85	2978	45	2946	40	2920	80			2864	60			2733	18
3,7	3033	60	2979	35	2944	20	2920	65			2863	40			2733	10
3,10	3055	85	2970	40			2921	70			2873*	35			2730	5
9,10	3070	85	2957*	45			2923	70			2875*	55			2734	6

[a] Bands marked with an asterisk (*) are included in a column even though they do not fit within the region limits indicated at the top of the column. [b] The band intensities are "graphically resolved intensities" as described in the text. [c] The bands listed in the 3055 cm.$^{-1}$ region are complex, the wave number given being the "center of gravity" wave number as illustrated in Fig. 6. [d] 4-MBA also has a 25% band at 2992 cm.$^{-1}$. [e] 9-MBA also has a 50% band at 2996 cm.$^{-1}$.

oxygenated and sulfurized compounds in which the hetero atom is not attached directly to the methyl group the CH_3 group absorptions for compounds in carbon tetrachloride solution are close to 2960, 2930 and 2870 cm.$^{-1}$. Nolin and Jones,[27] working with deuterated diethyl ketones (CH_3CH_2CO-CH_2CH_3) in carbon tetrachloride solution, state that the methyl group is responsible for absorptions at 2977, 2936 and 2883 cm.$^{-1}$. They go on to assign the 2977 cm.$^{-1}$ band to the CH_3 asymmetrical stretching vibration and suggest that the other two bands may result from a Fermi resonance interaction between the CH_3 symmetrical stretching vibration and the second harmonic of the asymmetrical CH_3 distortion vibration which they locate at 1461 cm.$^{-1}$.

The methyl group vibrations have not been studied as fully for methylated aromatic compounds as for aliphatic compounds. Figure 5 shows that even for benzene and naphthalene, two of the simplest unsubstituted aromatic compounds, the addition of the CH_3 group introduces at least five new bands in the 3000–2700 cm.$^{-1}$ region in place of the two or three which might be expected from a study of aliphatic CH_3 group stretching vibration assignments.[27,32,33] That the same is true of the methyl benzanthracenes[34] can be seen from Fig. 1. Table III, which summarizes the 3100–2700 cm.$^{-1}$ region for all the methylated compounds whose spectra appear in Figs. 1 and 5, shows that a well defined band of medium intensity at 2865 cm.$^{-1}$ is present in *all* and thus may be correlated with the symmetric CH_3 stretching vibration found about 6 cm.$^{-1}$ to higher frequencies in the aliphatics.[27,32,33] But the strongest band in the 3000–2900 cm.$^{-1}$ region for toluene and the methylnaphthalenes is the one at 2923 cm.$^{-1}$ rather than the band at 2975 cm.$^{-1}$. The same is true for half the monomethyl- and for all the four dimethylbenzanthracenes studied. Furthermore all but one (that of 1′-MBA) of the *ca.* 2923 cm.$^{-1}$ MBA bands fall within a 10 cm.$^{-1}$ interval, while four (those for 1′-, 9- and 10-MBA and 9,10-di-MBA) of the *ca.* 2975 cm.$^{-1}$ MBA bands fall outside of the similar 10 cm.$^{-1}$ interval.

The superior strength of the lower frequency band in the 3000–2900 cm.$^{-1}$ spectral interval leaves the assignment of the asymmetrical CH_3 stretching frequency in question. Some conceivable explanations are, (a) the methyl group is not free to rotate, the degeneracy of the asymmetric vibration thereby being removed, thus giving rise to three CH_3 stretching vibration bands, presumably those at 2975, 2923 and 2870 cm.$^{-1}$, the other bands being accounted for by overtones and combinations; (b) the methyl group rotation is hindered in such a way that the potential curve has two unequal minima, *i.e.*, two rotational isomers are present, giving rise to as many as six stretching vibration bands for the CH_3 groups; (c) Fermi resonance splitting, attributed to interaction, in the methyl group, of stretching vibration fundamentals with close-lying first overtones of strong deformation vibration fundamentals in the 1500–1350 cm.$^{-1}$ region, accounts for one or two of the several extra bands; and (d) the 2865 cm.$^{-1}$ band and either the 2975 cm.$^{-1}$ or the 2923 cm.$^{-1}$ band are the symmetric and asymmetric CH_3 vibrations, respectively, the other bands being due to overtones and combinations.

Explanations (a) and (b) are unlikely because of the high degree of interaction required to remove so completely the

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(34) The 10-MBA, 3,10-diMBA and 9,10-diMBA are the only exceptions, as they have only four bands in this region (see Table III).

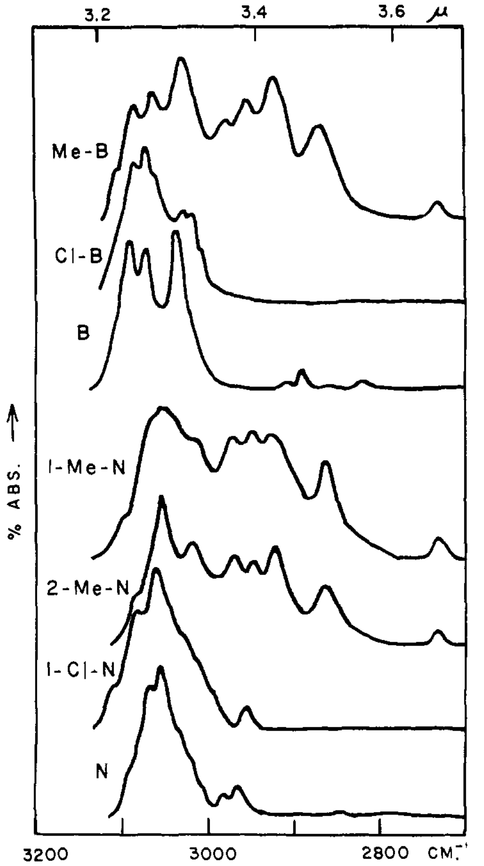

Fig. 5.—CCl_4 solution spectra in the 3000 cm.$^{-1}$ region of methylbenzene (toluene), chlorobenzene, benzene, 1-methylnaphthalene, 2-methylnaphthalene, 1-chloronaphthalene and naphthalene.

degeneracy and to shift the bands so far apart. Explanation (c) parallels the suggestion made by Nolin and Jones[27] for the diethyl ketones. But this hypothesis also seems unlikely in the present instance because, while the set of bands in the CH_3 stretching vibration region for MBAs follow a remarkably similar pattern from isomer to isomer, there are wide variations in the number and positions of the corresponding CH_3 bending region bands frequencies, whose overtones are involved in this explanation.

In order to see whether hypothesis (d) was adequate, we made a study of the possible contributions of overtones and combination bands to the complexity of the 3000-2700 cm.$^{-1}$ region of the 12 monoMBAs. Combination bands of the $\nu_1 + \nu_2$ type, using fundamentals in the 1500-1400 cm.$^{-1}$ region, proved to be so numerous as to almost completely "blanket" the 2800-3000 cm.$^{-1}$ region. First overtones appear to contribute materially to the intensity of three of the six main band sub-regions in the 3000-2800 cm.$^{-1}$ interval (see Table III), namely, those at 2945, 2923 and 2866 cm.$^{-1}$ and may account entirely for the 2945 cm.$^{-1}$ absorption. Although there was no clear correlation between the intensities of these overtones band candidates and those of the corresponding fundamentals, hypothesis (d) appears to be the best that is available with the information at hand. We plan to do deuterization experiments on these compounds to contribute to a solution of this problem.

The region just below 3000 cm.$^{-1}$ should not be left without remarking that the most consistent "identification tag" for the methylated aromatics is the weak but clearcut band at 2734 ± 5 cm.$^{-1}$ (see Table III). This weak band, noted by Fox and Martin[35] in methylnaphthalenes, is absent in chloro derivatives and in the unsubstituted aromatics but is always present in the aromatic methyl derivatives whose spectra we have obtained (see Figs. 1 and 5). We suggest the possibility that this band is the first overtone of the symmetric CH_3 deformation vibration which appears so regularly at *ca.* 1382 cm.$^{-1}$ in all the MBAs (see Table II).

We turn now to a consideration of the 3100-3000 cm.$^{-1}$ region. The prominent band in this region, assigned to the aromatic CH stretching vibration, is a triplet for toluene, somewhat similar to that for benzene (see Fig. 5). In the methylnaphthalenes, however, as Fox and Martin[35] already have shown, the appearance of this band is markedly different from that for naphthalene, benzene or toluene. Josien and Lebas[29] have shown this difference to exist also for many monosubstituted benzenes. They discuss the assignment of the absorption band peaks at some length. We have found the $\nu(CH)_{ar}$ band for the MBAs to be complex also, the positions and relative intensities of the partially resolved sub-peaks varying widely for different isomers. Though it is not possible to make sub-peak assignments, we felt it desirable to have, for each isomer, a wave number value which would be representative of this whole aromatic CH vibration band complex. Such a "center-of-gravity" wave number was obtained in the following manner, as shown in Fig. 6. It is given by the average position (dot-dash straight line) of a median line, shown solid and curved, for that portion of the absorption contour that lies in the range 65-95% of maximum absorption. Hereafter, and in Fig. 8, this wave number is denoted by "$\nu(CH)_{ar}$."

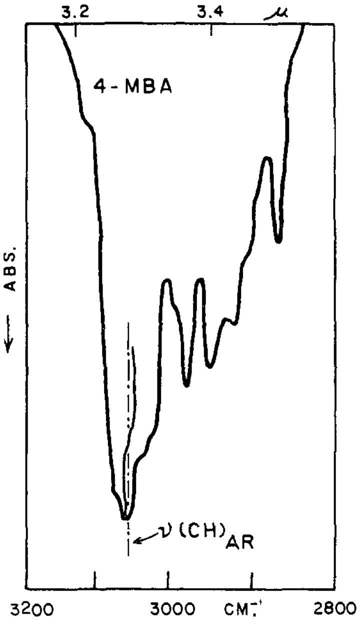

Fig. 6.—CCl_4 solution spectrum of 4-MBA in the 3000 cm.$^{-1}$ region. The vertical dotted line designates the "center of gravity" wave number, *i.e.*, the average position of the median line between 65 and 95% absorption for the complex absorption band assigned to the aromatic CH stretching vibrations.

[35] J. J. Fox and A. E. Martin, *J. Chem. Soc.*, 318 (1939).

It should be noticed that whereas for simpler aromatic compounds the addition of a methyl substituent always lowers the aromatic CH stretching frequency,[2,3,36–38] methyl substitution on 1,2-benzanthracene shows anomalies. A study of Table III shows that (a) 2′-, 3′-, 6-, 7- and 8-methyl and 3′,6- and 3,7-dimethyl substitutions conform to the usual situation of causing a shift to lower wave numbers; (b) 1′-, 4′-, 5-, 3- and 4-methyl and 3,10-dimethyl substitutions cause almost no shift; and (c) 10-methyl and 9,10-dimethyl substitutions cause an appreciable shift to *higher* frequencies.

Correlation of Infrared Spectra with Electronic Structure

We now turn to an analysis of the infrared spectra of the benzanthracenes in the light of certain calculated indices of electronic structure.[39] Attention will be centered on the absorption bands which can be assigned, with reasonable assurance, to specific molecular sub-groups such as CH_3 and CH_{ar}, since their positions and/or intensities may be sensitive enough to changes in the electronic environment to permit their use as specific indicators of electronic structure at various points in the different isomers. Similarly produced shifts, if any, of skeletal bands would inevitably be masked by larger shifts due to differences in the gross structure and symmetry of the different isomers.

The twelve carbon atom sites for possible addition or substitution reactions of the *parent hydrocarbon* 1,2-benzanthracene (see Fig. 2) have been studied theoretically in a number of different ways. The index of free valence of these exposed carbon atoms has been calculated by both the molecular orbital and the valence bond methods.[7,40–43] The conjugating powers and the related self-polarizabilities[44] as well as the localization energies[45] have also been computed. These different indices predict approximately the same sequential order of reactivity of the twelve exposed carbon atoms.

Columns A and B of Table IV give the indices of free valence and the conjugating power of the reactive carbons

TABLE IV: STRUCTURAL INDICES OF 1,2-BENZANTHRACENE, K-REGION ADDED ELECTRON DENSITIES OF THE MBAs AND EXPERIMENTALLY DETERMINED PROPERTIES OF 1,2-BENZANTHRACENE AND THE MBAs[a]

		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
p[b]	ν(CH)ar,[c] cm.⁻¹	V_p	C_p	Q_k	ΔQ_k	ΔQ^*_k	$\Delta\lambda_D$, Å.	$\Delta\lambda_B$, Å(0)	$\Delta\nu PH$, cm.⁻¹	$\Delta\nu FL$, cm.⁻¹	ΔRA	R_K	ΔT, °C.	D, cal./mole	K_1	C.A.[d] (skin)	C.A.[e] (inject)
0	3053			1.283	0.0000	0.000	0	0	0	0	(−)0.3	0.48	20	0.034	1.33	0	0
2′	3044	0.409	0.410		.0055	.036	35	15	140		12.9		58	.059	1.23	0	
3′	3042	.404	.404		.0049	.010	15	25	220		(−)2.4		24	.029	1.34	0	
6	3042	.407	.409	1.294	.0039	.003	15	25	30	200	8.0	.64	30	.022	1.32	+	
7	3043	.408	.410	1.294	.0039	.013	10	(−)5	80	200	2.5		37	.019	1.25	+	+
1′	3051	.440	.429		.0039	.001	5	0	480	250			(−)3	.040		0	
4′	3054	.451	.439		.0065	.024	55	35	170				17	.030		0	
5	3049	.458	.452	1.296	.0043	.009	20	50	150	100	5.4		44	.032	1.41	++	++
8	3046	.456	.449	1.292	.0030	(−).001	30	50	280	250			38	.023	1.34	+	
3	3052	.456	.449	1.298	.0050	(−).164	35	(−)5	310	300	8.4	.50	31	.029	1.27	+	++
4	3054	.455	.441	1.298	.0050	(−).164	15	10	480	100	12.9		28	.013	1.35	+	++
9	3050	.502	.495	1.296	.0043	.003	35	105	(−)240	550	5.6	.96	(−)7	.019	1.64	++	+++
10	3060	.514	.513	1.306	.0073	.039	40	135	(−)130	350	4.0	.91	52	.023	1.66	+++	++++
3′,6	3033	.406			.0088											0	
3,7	3033	.432		1.309	.0089											0	
3,10	3055	.485		1.321	.0123												
9,10	3070	.508		1.319	.0116				(−)1000	1250	11.6	2.70			1.87	++++	++++

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(36) N. Fuson, M.-L. Josien and E. M. Shelton, THIS JOURNAL, **76**, 2526 (1954).

(37) M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948).

(38) R. N. Jones and collaborators, THIS JOURNAL, **70**, 2026 (1948); **71**, 247 (1949); **72**, 956 (1950).

(39) The Pullmans (reference 8, pp. 63 and 152) discuss dynamic indices for reacting molecules as well as structure indices for non-reacting molecules. We limit our discussion to indices of the latter type since our spectra were obtained on compounds which were not undergoing chemical change.

(40) A. Pullman, *Compt. rend.*, **224**, 1354 (1947).

(41) G. Bertier, C. A. Coulson, H. H. Greenwood and A. Pullman, *ibid.*, **226**, 1906 (1948).

(42) R. Daudel, *Bull. Cancer*, **35**, 110 (1948).

(43) N. P. Buu-Hoi, R. Daudel and C. Vroelant, *Bull. soc. chim. France*, **16**, 211 (1949).

(44) G. M. Badger, R. S. Pearce and R. Pettit, *J. Chem. Soc.*, 1112 (1952).

(45) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

[a] Refer to the legend under Fig. 8 for detailed explanation of the columns headed A through N. [b] Point(s) of substitution of the methyl group(s) on the carbon atom(s) of the 1,2-benzanthracene nucleus. [c] Center-of-gravity band wave number of the aromatic CH groups' stretching frequencies. [d] Carcinogenic activity when rubbed on the skin (reference 8, Chap. 1). [e] Carcinogenic activity when injected (ref. 8, Chap. 1). "++++" = very potent carcinogen; "+" = activity just noticeable; and "0" = no activity at all.

in 1,2-benzanthracene, these two having been selected by us as sufficiently representative of the various calculated values available. The first row in Table IV, p = 0, is for unsubstituted 1,2-benzanthracene as a whole and there are, accordingly, no entries in this row in columns A and B. The next four rows represent the benzanthracene carbon atoms (p = 2′, 3′, 6 and 7) which are the least reactive from the point of view of theoretical calculations. The next six rows (p = 1′, 4′, 5, 8, 3 and 4) are the benzanthracene carbons with medium free valence index and, thus, average reactivity. The next two rows (p = 9 and 10) have the highest free valence index. Column A entries for the final four rows (p = 3′, 6-, 3,7-, 3,10- and 9,10-) are the averages of the two free valence indices at the corresponding two reactive points.

No correlation was found between the free valence index of a carbon atom on the benzanthracene nucleus and the spectrum of the corresponding MBA below 2000 cm.$^{-1}$. However the spectrum in the 3000 cm.$^{-1}$ region does show correlation in several different ways. The over-all appearance of the 3000 cm.$^{-1}$ region for the four MBAs in which the methyl groups are attached to low free valence index carbons are similar, as can be seen from Fig. 7A. The low index spectra differ markedly from the spectra of the high index isomers (particularly that of 10-MBA, that of 9-MBA being altered by steric hindrance) as shown in Fig. 7B. The intermediate index spectra (see Fig. 7C) show much variety among themselves. Methyl substitution on the positions of highest index (10- and 9,10-) causes the wave number of the symmetric methyl stretching vibration at 2865 cm.$^{-1}$ to increase by 10 cm.$^{-1}$ and results in the 2975 and 2945 cm.$^{-1}$ bands fusing together into an unresolved doublet. Neither the 2734 cm.$^{-1}$ nor the 2923 cm.$^{-1}$ bands show any displacement trends with free valence index.

The most striking indicator turns out to be the position of the massive absorption band assigned to the aromatic CH stretching vibrations. The values of $\nu(\text{CH})_{\text{ar}}$ have been repeated in the second column of Table IV for easy reference. Figure 8A′ shows the trend of $\nu(\text{CH})_{\text{ar}}$ with free valence index for the dimethyl derivatives, Fig. 8A for the monomethyl derivatives. Figure 8B graphs the corresponding trend as a function of conjugative power of the point of substitution. The graph points for the isomers in which the methyl group is substituted on the reactive carbons with the lowest free valence index (V_{p}) or conjugative power (C_{p}) form a close group at the lower left in each case. The highest V_{p} and C_{p} points are at the upper right, while the intermediate index points tend to fan out in the middle of the graphs. The point for 9-MBA stands out as an exception to this trend.

An extension of the free valence index calculations for the reactive points of *substituted benzanthracenes* such as the methylbenzanthracene isomers has *not* been made because of the difficulties of computation.[46] Instead, attention for the methyl derivatives has been largely centered on what is termed the K-region,[47] this being the region containing atoms C_3 and C_4 and the C_3C_4 aromatic bond (see Fig. 2). A. Pullman, using the valence bond method, has evaluated the "total charge" of the K-region[40] and the charge *added* to the K-region as a result of methyl substitution at each of the twelve reactive carbon atoms.[48] Daudel[42] has calculated free valence indices for C_3 and C_4, "excess charge" on C_3 and C_4 and the C_3C_4 bond order for a number of derivatives. Greenwood[49] has computed, by means of molecular orbitals, the charge added to the K-region by methyl substitution at various points. The dependence of these various theoretical indices of K-region activity on the position of the methyl group is, with some reasonable exceptions,[8] very similar, and we have chosen the K-region total charge (Q_{K}),[40] and the added charge as found both by resonance (ΔQ_{K})[48] and by molecular orbital ($\Delta Q_{\text{K}}'$)[49] methods, as being representative. Columns C, D and E of Table IV contain these indices for unsubstituted 1,2-benzanthracene (top row) and its monomethyl and dimethyl derivatives, the value in each row corresponding to the derivative substituted at the carbon atom whose number is given in the first column headed "p."

Again, as in the case of V_{p} and C_{p}, no correlation of Q_{k} or ΔQ_{k} with CC stretching or CH bending frequencies was observed in the spectral region below 2000 cm.$^{-1}$, but interesting relationships appear with the CH stretching frequencies in the 3000 cm.$^{-1}$ region. If one considers the mono-MBAs alone, the 2865 cm.$^{-1}$ band ($\nu(\text{CH}_3)_{\text{sym}}$) increases in frequency with increase in Q_{k}, the 2975 and 2945 cm.$^{-1}$ bands fuse, the other CH_3 group bands show no consistent trends, and the frequency of the 3050 cm.$^{-1}$ band ($\nu(\text{CH})_{\text{ar}}$) is a roughly increasing function of Q_{k} and ΔQ_{k}. In this last case, illustrated graphically in Figs. 8C and 8D, the point for the 9-methyl derivative fits into the general trend, in contrast to the case for V_{p} and C_{p} (Figs. 8A and 8B). The $\nu(\text{CH})_{\text{ar}}$ of the dimethyl derivative series considered separately is also an increasing function of Q_{k}. But, with the exception of 9,10-diMBA, neither the diMBAs nor 1,2-benzanthracene itself fit into the trend of the monomethyl derivatives. Figure 8E illustrates the lack of any simple relationship between $\nu(\text{CH})_{\text{ar}}$ and the added charge, $\Delta Q'_{\text{k}}$, calculated by the molecular orbital method,[49] in contrast to the trend noticed with ΔQ_{k} calculated by the valence bond method (Figs. 8C and 8D).

Correlation of Infrared Spectra with Results of Other Chemical and Spectroscopic Investigations of the Methyl Benzanthracenes

In addition to calculations of electronic structure indices, a number of experimental studies of the MBAs have been made, such as the ultraviolet absorption spectra,[44,50,51] phosphorescence spectra,[52]

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(46) Reference 8, chapter 2.

(47) A. Pullman, *Ann. Chim.*, **2**, 5 (1947).

(48) A. Pullman, *Bull. soc. chim. France*, **21**, 595 (1954).

(49) H. H. Greenwood, *Brit. J. Cancer*, **5**, 441 (1951).

(50) R. N. Jones, This Journal, **67**, 2127 (1945); *Chem. Revs.*, **32**, 1 (1943); **41**, 353 (1947).

(51) G. M. Badger and R. S. Pearce, *J. Chem. Soc.*, 3072 (1950).

(52) M. M. Moodie and C. Reid, *J. Chem. Phys.*, **22**, 252 (1954).

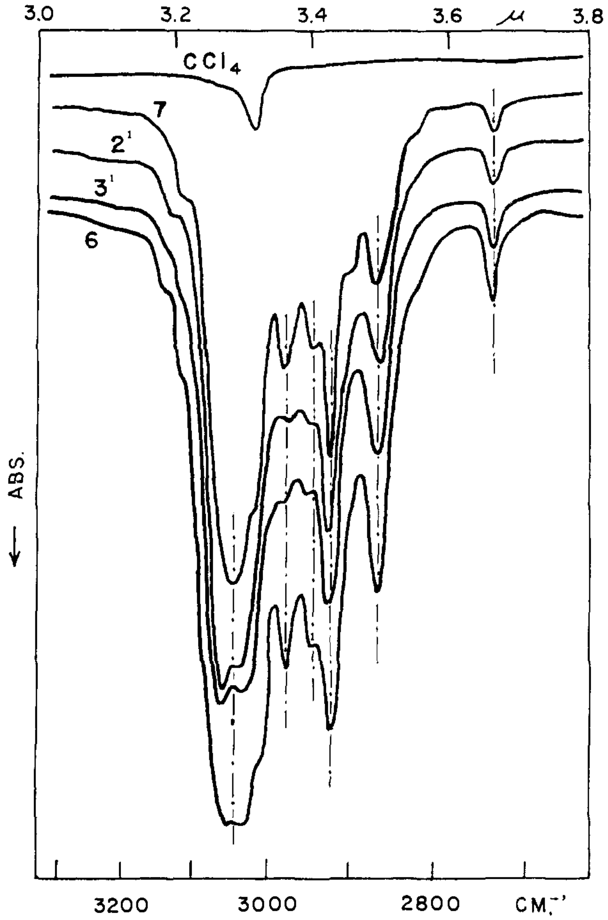

Fig. 7A.

Fig. 7.—CCl_4 solution spectra in the 3000 cm.$^{-1}$ region of the twelve monomethyl-1,2-benzanthracenes: (A) the four isomers (2'-, 3'-, 6- and 7-MBA) in which the methyl group is attached to a low free valence index carbon; (B) the contrast between a "low index isomer" (3'-MBA) and the "high index isomers" (10-MBA and 9-MBA); (C) the six "intermediate index isomers" (1'-, 4'-, 5-, 8-, 3- and 4-MBA).

fluorescence spectra,[53] magnetochemical properties[54] relative reactivity of ozmium tetroxide with the K-region aromatic double bond,[55] effect of picrate complex formation upon melting point,[23] dissociation constants and free energies of formation of complexes with 2,4,7-trinitrofluorenone[56] and equilibrium constants for the argentation reaction.[57] Columns F through N of Table IV give the results of these studies, and Figs. 8F through 8N make it clear that there is at least no simple correlation to be found between $\nu(CH)_{ar}$ and these other experimental data. However, anomalies in the infrared spectra of 1'-MBA and 9-MBA find a counterpart in the corresponding picrate melting points (Fig. 8L). Orchin[23] suggests that the melting point anomalies for the complexes formed

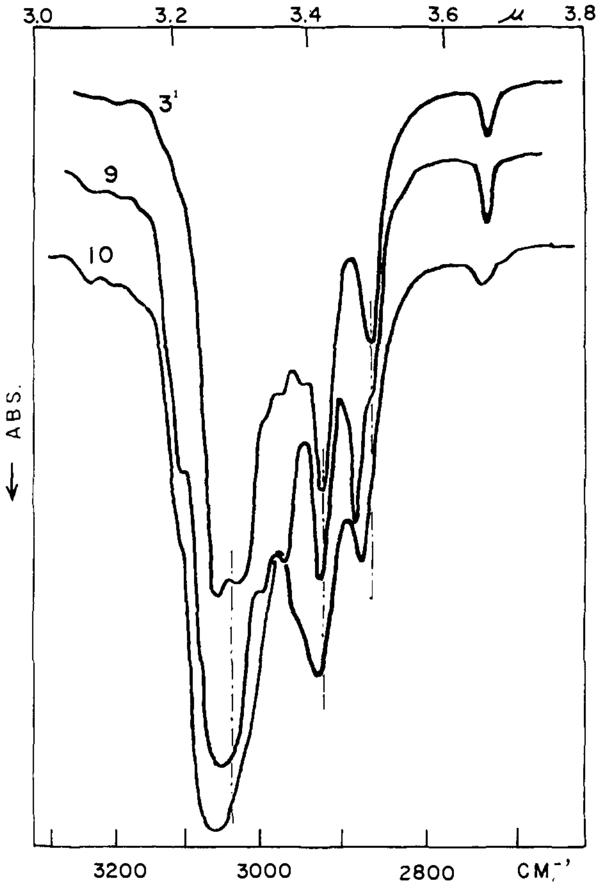

Fig. 7B.

by these two isomers can be explained by steric interference between the 1'-hydrogen and the 9-methyl group (and *vice versa*). We suggest that steric hindrance could also explain, for example, the low position of the 9-MBA point in Fig. 8A and in Fig. 8N. With the exception of this 9-methyl isomer, and of 3-MBA and 4-MBA which might be expected to be anomalous because of the complexing taking place at the C_3–C_4 bond (K-region), there is an almost linear relation between $\nu(CH)_{ar}$ and K_1 (see Fig. 8N).

Correlation of Infrared Spectra with Carcinogenic Activity

Many aromatic hydrocarbons are included in the category of substances having carcinogenic potency[58] and what might be considered minor changes in molecular structure of such compounds often completely alters the biological effects induced by them. As a supplement to the essential but time-consuming biological tests for carcinogenic activity of chemical compounds, it would be helpful if a physical means of differentiating between carcinogens and non-carcinogens could be found. Many such avenues of approach have been and are being explored.[50–54] In particular the utility of infrared spectroscopy for this purpose was first investigated by Pacault and Lecomte,[59] who searched for an absorption band

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[53] R. Schoental and E. J. Scott, *J. Chem. Soc.*, 1683 (1949).

[54] A. Pacault and J. Hoarau, *Compt. rend.*, **233**, 689 (1951).

[55] G. M. Badger, *J. Chem. Soc.*, 456 (1949), 1809 (1950); G. M. Badger and K. R. Lynn, *ibid.*, 1726 (1950).

[56] K. H. Takamura, M. D. Cameron and M. S. Newman, THIS JOURNAL, **75**, 3280 (1953).

[57] R. Kofahl and H. J. Lucas, *ibid.*, **76**, 3931 (1954).

[58] J. W. Cook, *J. Chem. Soc.*, 1210 (1950).

[59] A. Pacault and J. Lecomte, *Compt. rend.*, **228**, 241 (1949).

characteristic of cancer-producing compounds but with a negative result.

Before discussing our MBA infrared results in the light of the range of biological activity of the MBAs, we summarize a theory of carcinogenesis which has been one of the stimulants to experimental investigations of K-region reactivity. A. and B. Pullman have proposed[7,8,40,48,60] that cancer growth caused by polynuclear aromatic compounds is initiated by a reaction between the biological cell and the K-region (*ortho*, phenanthrene-like, active region) of the aromatic compound if the K-region possesses a sufficiently high reactivity; that, with some exceptions, high reactivity is associated with high electron density in the K-region; that interactions of the L-region (*para*, anthracene-like, active region) with the biological cell are *not* cancer stimulating and that to the extent that L-region reactions occur they tend to replace or hinder K-region reactions and thus to inhibit carcinogenic activity. Thus a polycyclic aromatic compound such as is illustrated by Fig. 2 tends to be carcinogenic if the electron density in the K-region is high while the L-region is only slightly reactive.[61]

The Pullmans calculate the effect on electron density at the K-region of methyl substitution at various points on the aromatic nucleus (Table IV, columns C and D) and obtain a positive correlation between this index and carcinogenic activity for the MBAs (Table IV, columns O and P). Exceptions are 3-MBA and 4-MBA (steric hindrance) and the four primed-ring MBAs (anomalous behavior).[62] On the other hand, except for silver ion[57] and osmium tetroxide[55] activity, the experimental results cited in the preceding section (columns F through N of Table IV) show no significant correlation either with K-region electron density or with carcinogenic activity.

We now comment on the degree of correlation of our MBA infrared spectra with the carcinogenic potency of these compounds. The bands associated with the asymmetric stretching and deformation and with the wagging vibrations of the methyl group cannot be utilized as they are complicated by, and often superimposed upon, other bands. Those associated with the symmetric stretching and deformation of the methyl group are clearcut, but of these only the former show even a slight correlation with carcinogenic activity. We have already seen, however, that the "center-of-gravity" wave number, $\nu(\mathrm{CH})_{\mathrm{ar}}$, associated with aromatic CH stretching vibrations correlates quite well with the K-region electron density (Figs. 8C and 8D). It also provides the best infrared indication of carcinogenic potency, a result that might be anticipated from the theory of the Pullmans in view of the K-region correlation just cited.[63] Thus, from columns O and P of Table IV one sees that of the molecules tested, the two having highest potency, *viz.*, 10-MBA and 9,10-diMBA, show significantly higher values of $\nu(\mathrm{CH})_{\mathrm{ar}}$ than do the other MBAs. There is no consistent correlation, however, for molecules of low or intermediate activity.

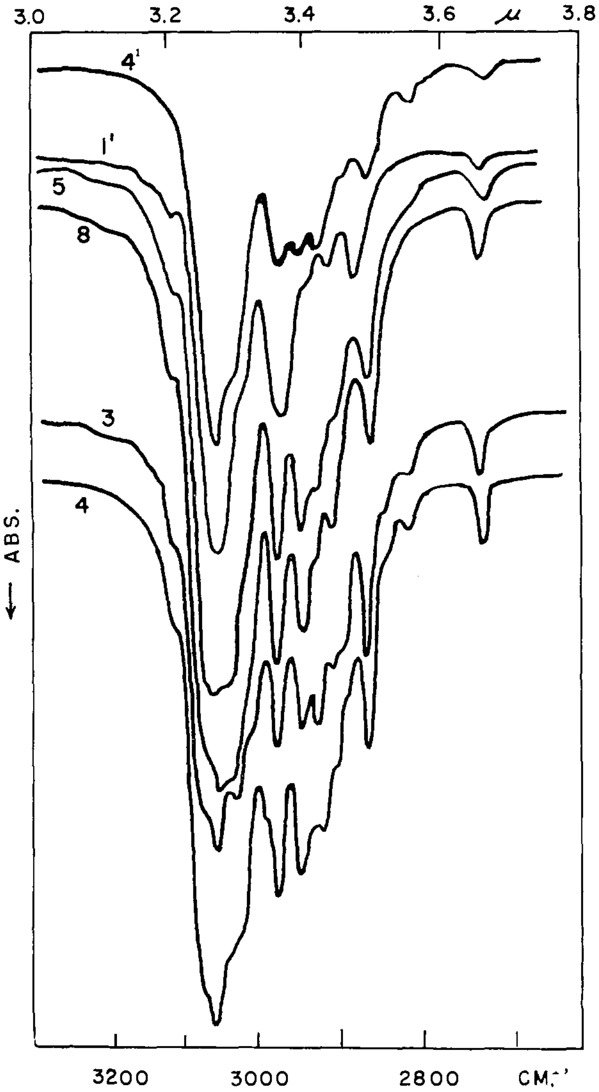

Fig. 7C.

While no broad generalization can be drawn from these results, they do show the desirability of further infrared studies in order to ascertain, for instance, whether a relatively high wave number for $\nu(\mathrm{CH})_{\mathrm{ar}}$ is in any sense typical of carcinogenic potency for other isomeric sets of methylated aromatic compounds. Furthermore, the behavior of a unique bond closely associated with specific points of substitution in the molecule would be expected to provide a more definitive indication of activity than does $\nu(\mathrm{CH})_{\mathrm{ar}}$. Accordingly, we are considering the feasibility of investigating deuterated isomers of the substituted MBAs with a view to isolating such a band, possibly one of those now contributing to the $\nu(\mathrm{CH})_{\mathrm{ar}}$ complex.

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(60) Reference 8, chap. 3.

(61) We suggest that this condition of low reactivity of the L-region would be one consequence of steric hindrance resulting from the replacement of a hydrogen by a CH_3 group in the L-region, as for example in 9 MBA, 10 MBA and 9,10 diMBA.

(62) Reference 8, pp. 142-144.

(63) However, whereas the Pullmans postulate an opposing effect for the activity of the K- and L-regions, the spectral shift in $\nu(\mathrm{CH})_{\mathrm{ar}}$ represents an average or additive effect from all CH groups remaining on the molecule.

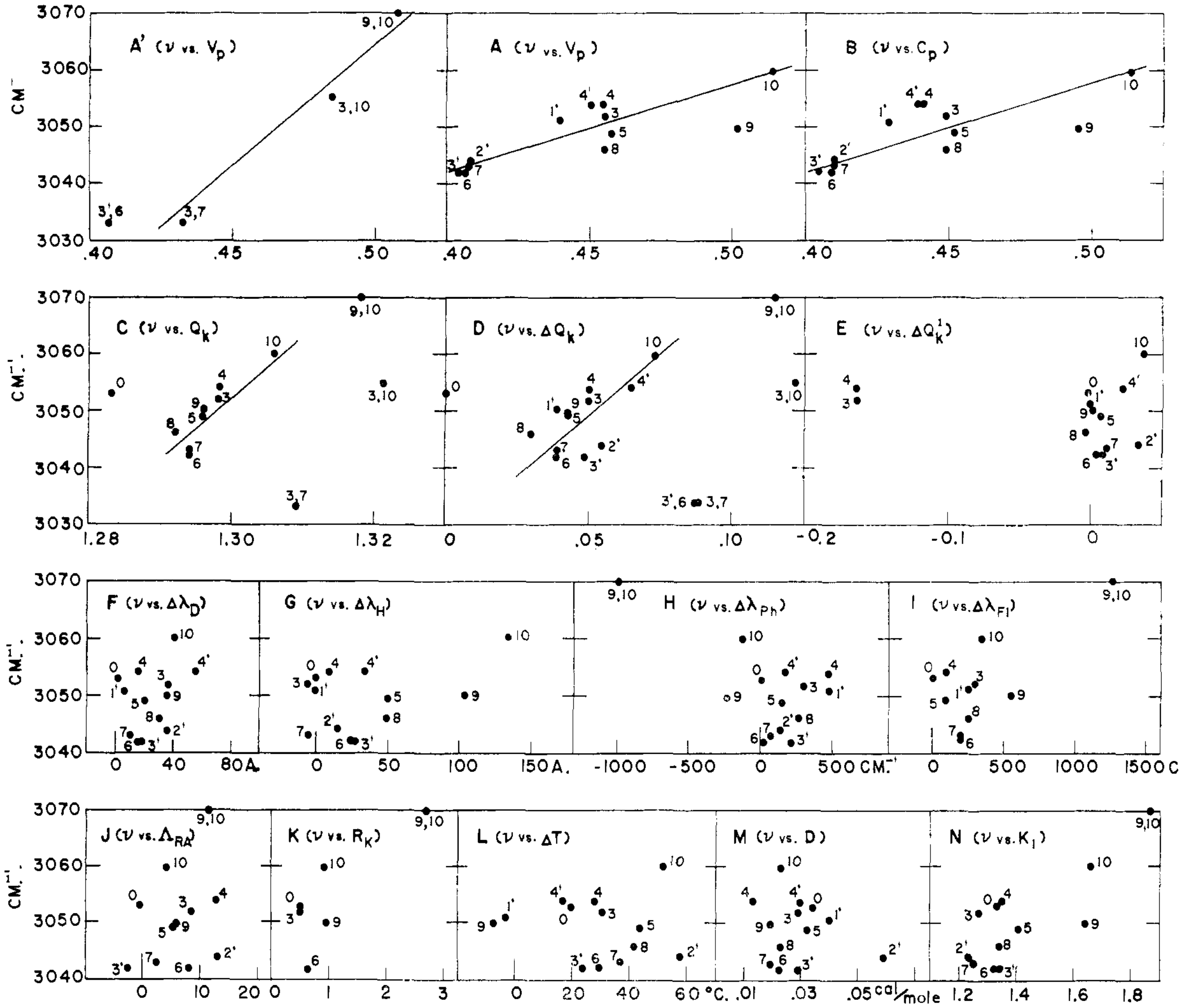

Fig. 8.—Plots of $\nu(\text{CH})_{ar}$ of the methyl-1,2-benzanthracenes with corresponding calculated indices and experimental measures, as follows: (A′) ν(di-MBA) *vs.* average of the free valence index[7] for the two 1,2-benzanthracene carbons involved; (A) ν(mono-MBA) *vs.* corresponding 1,2-benzanthracene free valence index[7]; (B) ν *vs.* corresponding 1,2-benzanthracene conjugating power ($\beta \times$ self polarizability)[44]; (C) ν *vs.* K-region electron density (V.B. calcd.)[40]; (D) ν *vs.* added electron density on the K-region (V.B. calcd.)[8,48]; (E) ν *vs.* added electron density on the K-region (M.O. calcd.)[49]; (F) ν *vs.* shift, produced by methyl substitution, of the 1,2-benzanthracene ultraviolet absorption band "D" at 2900 Å.[50,51]; (G) ν *vs.* shift produced by methyl substitution, of the 1,2-benzanthracene ultraviolet absorption band "H" at 3400 Å.[50,51]; (H) ν *vs.* shift, produced by methyl substitution, of the 1,2-benzanthracene phosphorescence band at 16,500 cm.$^{-1}$[52]; (I) ν *vs.* shift, produced by methyl substitution, of the 1,2-benzanthracene fluorescence band at 26,950 cm.$^{-1}$[53]; (J) ν *vs.* electronic delocalization relative to anthracene (a measure of the magnetochemical effect)[54]; (K) ν *vs.* relative reactivity of osmium tetroxide with the K-region aromatic double bond[55]; (L) ν *vs.* elevation of MBA-picrate melting points[23] above the melting point of picric acid; (M) ν *vs.* dissociation energy of trinitrofluorenone-MBA complexes[56]; (N) ν *vs.* equilibrium constant of the argentation reaction.[57]

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