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ELECTRONIC SPECTRA OF CATACONDENSED AND PERICONDENSED
AROMATIC HYDROCARBONS*

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Abstract

The electronic spectra arising from the excitations of pi-electrons in homo-nuclear conjugated bond systems are calculated for 37 aromatic hydrocarbons. The theoretical approach used takes into account overlap effects between different atoms, correlation between different electrons, variations in internuclear distances, and the influence of non-conjugated neighbors, hydrogen and carbon.

Four types of approximations are carried through for the molecules in order to obtain an estimate of the inadequacies of the theory. From the calculated transition energies and oscillator strengths, theoretical spectra are synthesized and compared with observed spectra. In order to help the interpretation, a decomposition of the transition dipoles into atomic contributions is introduced.

The spectra of alternant molecules are successfully predicted, but the limits of the underlying assumptions appear to be exceeded in the applications to non-alternant systems. The calculations are markedly successful for the peri-condensed systems, which had presented an obstacle to previous treatments. It is found that the calculated spectra are fairly sensitive to small variations in interatomic distances. Calculations with exact atomic positions, where available, give considerably better agreement with experimental spectra.

The calculations lead to an understanding of the general spectral pattern found in all aromatic hydrocarbons. On this basis the possibility of a general nomenclature of electronic transitions is examined.

CONTENTS

Introduction		
1. Description of Method Outline of Calculations Outline of Results Comparison between Theory and Experiment	3. Non-Linear Polyacenes Criteria for Grouping Naphthalene Group Anthracene Group	5. Azulene Family
2. Linear Polyacenes Transition Energies Intensities Comparison between Approximations	4. Pericondensed Molecules General Considerations Lowest Triplet and Lowest Singlets Pyrene Group Perylene Group	6. Influence of Sub- stituents Benzene Homologues Diphenyl and Fluorene
		7. Conclusions Assessment of Theory Review of Spectra Classification of Transitions

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INTRODUCTION

The quantum mechanics of aromatic molecules has continued to attract interest for several reasons. The molecules themselves are important, and their chemical and physical properties have been studied fairly extensively by experiment. Their spectra exhibit distinctive regularities which have permitted early empirical classification. Even relatively simple theoretical work can correlate reasonably well with various observed properties of at least a number of molecules. However an equal interest arises from the possibility of testing and proving more rigorous methods in molecular theory. For this purpose conjugated systems are exceptionally well suited, since attention can be focused upon interatomic molecular aspects with a minimum of purely atomic complications. This is so because, to a good approximation, each atom contributes but one atomic orbital and at most one electron, and, in hydrocarbons, all of the atomic orbitals are essentially identical. On the other hand, due to the variety in geometrical patterns, series can be formed which display systematic and often subtle relationships whose qualitative reproduction frequently provides a more reliable and sensitive test for the theory than isolated comparisons for individual molecules.

For some of the catacondensed molecules treated here, there have been carried out comparable calculations under certain simplifying assumptions, such as neglect of differential overlap between all atomic orbitals, neglect of the hydrogen atoms in the potential energy, neglect of the difference between joint- and non-joint carbon atoms, assumption of constant neighbor-distance and semi-empirical framework integrals and, in some cases, limitation of the configuration interaction. These are the calculations of Parr, Pariser, Pople, Ham and Ruedenberg.¹ The objective of the present study is neither to account

for the observed spectra of conjugated hydrocarbons with a minimum of theoretical effort, nor to achieve a maximum of agreement with experimental values; such objectives can obviously be better pursued by less rigorous, semi-empirical approaches. Rather the objective is the development and testing of a theory sufficiently rigorous and flexible so that (1) it can be extended to more complex systems, e.g., involving hetero-atoms; (2) it can give a realistic and sensitive indication of inadequacies in the assumptions, in particular of those errors which, in the semi-empirical treatments, are masked by compensation effects; (3) it might give a reasonably reliable indication of such unobservable quantities as molecular electronic wave functions.

The assumptions and approximations underlying the present work are those developed recently by one of the authors. ² Without full theoretical analysis, this treatment adopts the usual purely π -electronic approach, omitting specific interaction with the σ -electrons. However, in contrast to ^{all} previous work, the overlap-dependent contributions are taken realistically, though not completely, into account; two alternative approximations for the small elements of the overlap and one-electron energy-matrices are followed through: the "tight-binding" approximation and the "intra-ring approximation." Extensive, though not exhaustive, configuration interaction allows for electron correlation. The choice of atomic orbitals

involved gauging the short-range electron interaction and the atomic framework contributions by reference to the benzene spectrum and the carbon valence state.

The calculations permit an evaluation of the validity of these hypotheses. Limits of error for the tight-binding approximation and the intra-ring approximation should be found by comparing the calculations made under the two assumptions. For, the tight-binding approximation underestimates the smaller-than-neighbor matrix elements, whereas the intra-ring approximation ^{appears to} overestimate the smaller-than-neighbor energy elements. Any error due to either approximation should be smaller than that introduced, but hidden, in the studies based on the neglect of neighbor elements.

Furthermore, the inclusion of at least neighbor overlap renders the calculations responsive to the actual bond lengths. The effect of the latter on the spectra will be demonstrated in those, all too few, cases where the true bond lengths are well established and comparative calculations possible. Another effect traced by the present calculations is the corrections which arise by taking into account the differences between non-joint and joint atoms in the diagonal elements of the framework potential matrix.

The inadequacies due to the neglect of interactions with σ -electrons and these inherent in the gauging of atomic orbitals

could not be determined by comparative calculations. However, as there is no reason for consistent compensation between them in all molecules, an absence of sizeable unexplained disagreements between experiment and calculations would seem to imply that such errors are small. None-the-less, a bona fide analysis of the corresponding corrections would contribute valuable insights.

L. DESCRIPTION OF METHOD Outline of Calculations

The calculations were performed on an IBM-704 computer with a 32K core memory at the Midwest Universities Research Association, Madison, Wisconsin, by a completely automatic program. In the following, the course of the calculations executed is briefly described. For the mathematical details the reader must be referred to the derivations in reference 2.

The required input consists of the name of the molecule, the number of conjugated carbon atoms, and the cartesian coordinates of each of these. The non-conjugated neighbors are assumed to be hydrogens unless additional input specifies otherwise. Further, if there are symmetry planes perpendicular to the plane of the molecule or a center of symmetry, a list of symmetrically placed atoms may be added for the program's use.

From this input are computed all interatomic distances and, from these, the overlap integrals for the intra-ring ap-

proximation are calculated. The overlap matrix is diagonalized by Jacobi's procedure, the eigenvalues are ordered according to decreasing size, and the symmetries of the eigenvectors are determined if the previously mentioned symmetry input data had been supplied. In general the diagonalization procedure does not produce symmetrical and antisymmetrical eigenvectors for degenerate eigenvalues; such eigenvectors are constructed by a subsequent transformation. The overlap eigenvectors are then converted to eigenvectors of the neutral framework Hamiltonian matrix.

After determining the joint atoms, end atoms, and non-joint atoms, the program determines the applicable resonance integral, γ , and the joint correction, $\delta\alpha$, to the coulomb integral. Then the ground state bond order matrices, p and p' , are computed. Furthermore, from the interatomic distances, the interatomic two-electron interaction integrals

$$[PP|QQ] = G(PQ), \text{ are determined.}$$

Next, in preparation for the configuration interaction calculation, the one-electron excitations are examined as to transition energy and symmetry, if present. Discarded are those having transition energy in excess of 60,000 wave numbers or not having a dipole moment in transition with the ground state for symmetry reasons. If there is at least one perpendicular plane of symmetry, the remaining excitations split into two non-interacting groups with mutually perpendicular

dipole moments. For each group, the configuration matrices are now constructed and then diagonalized giving the energies and compositions of the excited singlets and triplets and the oscillator strengths for the singlets. From these results a theoretical spectrum is synthesized by a procedure to be discussed in the next section.

The calculations are carried out first for the intra-ring approximation, thereafter the procedure is repeated for the tight-binding approximation. In Figure 1, there are given the formulas for all 37 molecules which are treated in the present investigation. As indicated, 87 molecular calculations are carried through for these systems.

Outline of Results

The machine printed results are divided into two parts. The first contains the material pertaining directly to the spectra and aiding in their interpretation or assignment. The second part consists of basic information concerning the atomic contributions, which is needed for the calculation or estimation of molecular properties, including among others, spectra.

Spectral Data

In the first, spectral part it is assumed that in a molecule of N atoms there exist N molecular orbitals, well ordered according to increasing energies and numbered 1 to N . The excited wave functions are then merely characterized by their composition in terms of one electron excitations ($n \rightarrow \gamma$). For each of these jumps ($n \rightarrow \gamma$), the printed output follows the development of the energy, from the one-electron jump, through

the diagonal elements of the configuration interaction matrix (with and without joint correction), to the final state energy. The oscillator strength and the transition moment components are given for the transitions, and the moments are also supplied for the one-orbital excitations. A table containing this detailed information will be published elsewhere³. Tables which abstract transition energies and oscillator strengths for the major transitions are given in the sequel for the various groups of molecules to be discussed.

In these tables as well as elsewhere in the paper, the following abbreviations are used to denote the four types of calculations carried out for a given molecule: TBX \equiv tight-binding approximation (neighbors only) using exact internuclear distances, and IPX \equiv intra-ring approximation using exact internuclear distances (if exact distances are known); TBM and IRM \equiv tight-binding approximation and intra-ring approximation using the constant bondlength of 1.395 Å and the constant bond-angle of 120°, both "aromatic mean-values".

Synthetic Spectra

In order to permit direct comparison with experimental spectra, without the somewhat subjective intermediary of interpretive assignments, the program finally calculates, and automatically plots, theoretically predicted spectra. Smoothed vibrational-rotational broadening is simulated by assuming, for each transition, a triangular bandshape in the ϵ vs λ^{-1} spectrum. In accordance with the empirically observed average half width of 2kK, a base of 4kK is chosen for this triangle. Its height, $\epsilon(\text{max.})$, is found from the relationship between oscillator strength, f , and band area, viz.,

$$f = (\pi r_0)^{-1} \int d(\lambda^{-1}) \kappa(\lambda^{-1}) \quad (1)$$

where

$$r_0 = e^2/mc^2 = 2.81784 \times 10^{-13} \text{ cm}$$

is the classical "electron radius" and the "absorption coefficient" κ is related to the usual extinction coefficient, ϵ , by

$$\kappa = \epsilon(10^3 \ln 10/N) \quad (2)$$

with $N = \text{Avagadro number}$. One obtains

$$\epsilon(\text{max}) = (6.82188 \times 10^{-7}/Nr_0)f$$

$$\epsilon(\text{max}) = 115,813 f \text{ (liter/mole cm)} \quad (3)$$

whence

$$\log \epsilon(\text{max}) \approx \log f + 5. \quad (4)$$

After superposing all bands, a plot of $\log \epsilon$ vs λ is made and printed. Since the logarithm is plotted, in accordance with the usual spectral tracings, the initial choice of the individual bandshapes is practically irrelevant.

The spectra which are synthesized from calculated transitions and oscillator strengths are compared with the experimental ones in several figures to be discussed later on (Figs. 3, 4, 7, 8, 10, 11, 13, 14, 15, 18). In these figures the arrangement for each molecule is as follows: experimental spectra in the center, TB approximation above, IR approximation below. Three kinds of abscissae are used. For the experimental spectra/taken from A. Clar⁵, the abscissa is in Angstrom units, increasing from right to left; for the spectra taken from Friedel and Orchin⁶, the abscissa is in Angstrom units, increasing from left to right; for the spectra taken from Klevens and Platt⁷, the abscissa is in kilo-Kaysers (1 kK equals 1000 cm^{-1}), increasing from left to right. The synthetic spectra are plotted accordingly.

Dipole Maps

In order to trace similarities between individual transitions for a variety of different molecules, decompositions of the transition-dipole moments were machine plotted for all transitions with oscillator strength greater than 0.0005 in the following manner.

If, in the state function of a given excited state, the one-electron transitions ($n \rightarrow \nu$) occur with coefficients $C(n \nu)$, the transition dipole to the ground state is given by $\sum C(n \nu) \nu$

$$\vec{Q} = \sum_P \vec{R}_{P(n)} \sum_{(n)} C(n\mu) c'_{Pn} c'_{P\mu} (s_n + s_\mu) / \sqrt{2} \quad (5)$$

In order to exhibit the relative importance of the individual atomic contributions to the total moment, the scaled quantities,

$$\sigma 5 [N | \sum_{(n)} C(n\mu) c'_{Pn} c'_{P\mu} |]^{\frac{1}{2}} \quad (6)$$

(where σ is the sign of the sum before taking the absolute value) were considered optimal for display. They are printed, in map form, at the atomic positions. The $(s_n + s_\mu)/2$ are omitted because they are essentially constant, close to 2. Since the $c'_{Pn}, c'_{P\mu}$ are subject to a normalization involving summation over N atoms, the chosen quantities exhibit variation from -9 to +9. For the mapping they are truncated to integers.

For our more complex wavefunctions these dipole maps replace the nodal arguments used by Platt, in analogy to atomic spectra, for the perimeter model. It will be seen that there are interesting agreements as well as significant disagreements between the present analysis and the pattern of perimeter nodes.

Molecular Orbital Data

A second table of machine printed results consists of basic information concerning the molecular orbitals. Reference to their component atomic orbitals is based on a molecular map printed out to scale with the atomic numbering in the appropriate positions. The cartesian coordinates of these are printed beneath in units of $D = 1.395 \text{ \AA}$.

Next are printed the eigenvalues and eigenvectors of the overlap matrix and those of the neutral framework-hamiltonian matrix. The molecular orbitals are numbered in order of increasing one electron energy and characterized by their symmetry properties with respect to symmetry planes and centers of symmetry. Finally the Coulson-type bond order matrix, p , as well as the Mulliken-type bond order matrix, p' , are printed out. These tables will be published elsewhere. ✓

Comparison between Theory and Experiment

Before comparing the results of the calculation with experiment, it might be well to consider the limitations in the experimental spectra itself. The most obvious is the limitation of the available spectral range. Measurements must in general be made in solution, a solid solution in some cases, which restricts them to the range of transmission of the solvent and precludes measurement of the many short wave transitions. Consequently, except for certain molecules for which special pains have been taken, the available spectra are limited to a few of the lower transitions.

The interpretation is complicated by solvent shifts, dependent upon the transition involved as well as upon the solvent.

A more serious problem is that of ^{vibrational} interactions with electronic transitions¹⁰ to create broad, poorly defined maxima and to introduce peaks often indistinguishable from electronic transitions.

On the theoretical side the comparison is made difficult by the fact that the number of transitions that can be calculated is proportional to the square of the number of atoms and the fraction in the observable region increases for larger molecules. Thus, except for small molecules and except for the two, or three lowest transitions and the strongest transition, which remain clearly distinguishable for all molecules, experimental as well as theoretical spectra lose more and more of their distinctiveness with increasing molecular size.

Therefore the simpler hydrocarbons which have been the primary object of previous investigations will provide the more sensitive test of the present method in that their spectra are more characteristic and more thoroughly measured and assigned. The most critical test will lie in the still smaller

subgroup for which atomic positions have been determined with precision, since correct positions alone allow the present theory full scope.

The more complex molecules, which are not well treated by the semi-empirical theories, are also included to test the theory, to provide theoretical information on these molecules, and to provide a fairer comparison¹¹ between the present method and the semi-empirical methods. As for these molecules plots of assigned transitions vs calculated transitions tend to become rather arbitrary in the assignments. It was found more illuminating to compare the synthetic spectra for each molecule directly with a reproduction of the actual experimental spectra.

2. LINEAR POLYACENES

Transition Energies

Although the present study includes many molecules, the first five of the linear polyacenes remain a backbone of comparison with experiment for two reasons, both experimental. First of all, the experimental spectra for all but pentacene are more complete than usual and have been carefully studied and assigned to electronic transitions. In particular, measurements have been extended to shorter wavelengths, and for several transitions the polarizations have been determined and can be reasonably extended to the entire group. The second reason is that, of the four aromatic molecules whose atomic positions are known with confidence, three are members of this group, namely benzene, naphthalene and anthracene.

The results of the calculations for the linear polyacenes are presented in Table I. For the TBX and TBM cases, calculated and assigned transition energies are shown in Figure 2. Polarizations and relationships between transitions in different molecules are indicated only when considered justifiable. For the purpose of discussion it is convenient to divide the transitions into three groups; (1) the strongest and sharpest transition named 1B_D by Platt, (2) the families of transitions below 1B_D in energy, and (3) the remaining transitions with energies greater than or, in pentacene, comparable to 1B_D .

For the transitions below 1B_D , use of exact atomic positions yield a perfect fit between calculated and experimental energies and polarizations regardless of which approximation

(TBX or IRX) is used. However since exact distances are not known for the two largest molecules, the assumption of constant bond lengths and angles is unavoidable if all molecules are to be treated. With these incorrect distances, the results for the same transitions are not nearly as good. In particular, the lowest triplets fall three to five kK below the experimental values. The remaining three transitions per molecule are already well fitted by TBM and reasonably well fitted by IRM. It seems not unreasonable to expect that the use of correct distances would bring all transitions into close agreement with experiment.

The very prominent 1B_g transition shows a beginning of error even when exact distances are used. For TBX the calculated value is slightly high at anthracene and for the intraring approximation, IRX the error begins at naphthalene and is over a kK at anthracene. Use of the incorrect, average distances gives results that are a bit poorer for these two molecules and probably the same would hold for the two larger molecules. Even so the average error for all molecules and methods is roughly 2kK which is still considered fairly good.

Presumably, the higher transitions are not predicted as accurately, since the calculations are subject to increasing error as larger one-electron jumps are involved. It is however difficult to prove this disagreement for the larger molecules because of the increasing number of transitions predicted above 1B_g . This spectral region becomes crowded and rather confused for the larger molecules; for still larger ones ^{this "barrage" of transitions} would presumably appear more and more continuous. Under these circumstances, the synthetic

spectra become the most straight-forward means of comparing theory with experiment. For the linear polyacenes, they are given in Figures 3 and 4 (It should be kept in mind that strong transitions are in general subject to a red shift of about 1kK in liquid or solid solution).

Only two of the higher transitions can be observed in naphthalene and both are reasonably but not closely predicted by the TBX method. The results of the IRX approximation are for once quite a bit higher resulting in errors of 4 and 8 kK respectively.

While two high experimental transitions are also experimentally assigned in anthracene, all calculations place at least three theoretical transitions nearby. The synthetic spectra shows, however, that some of these are underlying and, as a whole, it exhibits a reasonable similarity to the actual spectrum.

Intensities

For all four methods of approximation, the intensities of a given transition are usually quite similar, and there is even greater resemblance between the two TB or the two IR methods. As in the previous semi-empirical calculations, the intensities of the strongest transitions are a bit too strong. The weaker ones suffer from this fault to a greater degree. For example the intensity of 1L_D in naphthalene is calculated 50 times weaker than 1B_D , whereas it should be 10 times weaker yet (Pariser gives 1L_D zero intensity; Ham and Ruedenberg, however, obtain the correct intensity ratio).

These observations are also verified by reference to the synthetic spectra in which the intensity results are incorporated as described earlier.

Comparison between Different Approximations

Both of the present approximations using exact distances ^{clearly} fit the experimental energies better than the semi-empirical methods, ³ but these in turn are better than the present approximations when constant bond lengths are assumed. These results imply rather strongly that the actual positions of the atoms are not negligible parameters.

Both approximations using exact distances yield equally perfect fits for the lower transitions, but the higher transitions seem to indicate, particularly in naphthalene, that TBX fits the experimental energy levels considerably better than IRX. (Pariser ~~too~~ calculated these transitions, but the energies obtained were even higher than IRX).

The somewhat unexpected conclusion would seem to be that neglect of the smaller-than-neighbor elements in the overlap and one-electron energy matrices, implicit in TBX, results in less error than taking them into account in the manner of IRX. To a large extent the explanation must lie in the particular manner in which the small matrix elements are approximated in IRX.

Another possible factor may be a greater sensitivity of the intra-ring approximation to the neglect of σ electrons. Whereas TBX gives a constant value of unity for all gross atomic populations, the latter are usually unequal, in the IRX approximation (of two neighbors greater than unity for one and less than unity for the other^v). The σ electrons in the bond between the atoms would, ^{perhaps} tend to compensate for this charge disparity, were they taken into account.

Criteria for Forming Families of Transitions

Previous Approaches

- (1) Several criteria have been used in the past for classifying the electronic transitions into families whose members can be traced through all polyacenes. On the basis of regularities concerning energies, intensities, and vibronic structure found empirically in the actual spectra, A. Clar⁵ pointed out that, usually, three distinct and characteristically different bands could be recognized in each aromatic hydrocarbon. These he called the α band, the β band, and the p band.
- (2) Later theoretical calculation led to the grouping of the

excited states according to irreducible representations of the molecular symmetry group. The linear polyacene singlets fall into four groups. Only two of these, however, ${}^1B_{2u}$ ($A_{1g}, S_{//}$) and ${}^1B_{3u}$ ($S_{1g}, A_{//}$) have a dipole transition with the ground-state and may thus contribute to the observable spectra. Each group has a specific polarization, which can be experimentally determined. As two main directions of polarization are also found for but approximate symmetry, the two classes of characteristic polarizations are indeed fundamental. They alone, however, do not furnish sufficient subdivision for a satisfactory classification.

(3) Platt ¹² stressed that, in view of Clar's observations, these molecules must exhibit certain quantum mechanical similarities in addition to the symmetry properties just mentioned. Basing his arguments on the perimeter model and drawing analogues to the use of angular momentum in simple atomic spectra, he characterized the transitions by the nodal behavior of their one-electron jumps and proposed a system of classification which accounted for the families of Clar and moreover suggested additional families frequently hidden under stronger transitions or in an optically inaccessible region. His classification retained the division according to polarization.

(4) Moffitt ¹³ and Pariser ¹ developed a different explanation for Clar's relationships, based on the fact that, in the neighborhood of the highest occupied orbital, viz. the $(N/2)^{th}$ orbital,

the one-electron energies are fairly evenly spaced. Consequently, the 4 lowest transitions, fall roughly into the following order: $[N/2 \rightarrow (N/2) + 1] < [(N/2) - 1 \rightarrow (N/2) + 1] \approx [N/2 \rightarrow (N/2) + 2] < [(N/2) - 1 \rightarrow (N/2) + 2]$. The first yields essentially 1L_a , the second and third are known as "paired excitations" and interact to form 1B_b and 1L_b , while the fourth essentially becomes 1B_g . In the neglect-of-differential-overlap approximation used by these authors, these paired excitations, as well as other higher, excitation pairs, are degenerate and the resulting states are 1:1 mixtures, viz., the + and - combinations. Since the minus combinations interact only with each other, Pariser suggested a division of the actual transitions into + and - states as a subclassification within the group theoretical species.

Unfortunately this subdivision is limited to alternants, and even there the + combinations are much more numerous and but two of them, ${}^1B_{2u}^+$ and ${}^1B_{3u}^+$, account for almost all observable transitions in the linear polyacenes. Hence this subdivision is not too helpful.

In the present more accurate calculation, it is still true that the lowest three transitions arise from the first three excitations mentioned above; but Pariser's +- classification loses its meaning. On the other hand, the essence of Platt's classification was seen as a structural analysis of

the transition moments. For the trigonometric wave functions of the perimeter model, his analysis of nodes alone provided a complete description. For the present more complicated wave function, a more thorough analysis of the transition dipole structure is needed to establish clearly kinships between different molecules.

Present Approach

(1) It proved possible to determine such finer features with the help of the graphical dipole decomposition

described earlier. The transitions on which Clar's and Platt's identifications agree are clearly related by common characteristics and so are a number of additional transitions. In some molecules, it is found that a relationship is disrupted by extensive configuration interactions which had been absent in smaller molecules. These relationships can be seen from the dipole maps reproduced in Figure 5. The numerical values are truncated to one figure, they have sufficient variation for good resolution, but not so much as to create confusion. The relationships between transitions in different molecules are exhibited by connecting lines, bearing the corresponding label, in Figure 2.

(2) Consider first the four low transitions, 1L_a , 1L_b , 1B_b and 1B_a in Platt's nomenclature. The dipole maps reflect, of course, the well known symmetry properties: 1L_a and 1B_a are symmetrical about the short axis, anti-symmetrical about the long axis, while 1L_b and 1B_b are anti-symmetrical about the short axis, symmetrical about the long.

The 1L_2 is characterized by having a node in every bond just as Platt suggested. The values at the atoms alternate in sign, but are not uniform as they would be in the perimeter model. The two largest magnitudes are found in the short axis; succeeding values of the same sign diminish towards the outside within one quadrant. The values of opposite sign have their smallest magnitude next to the short axis and increase away from this axis. The envelopes of the two groups are essentially parallels.

The dipole map of 1B_D , too, exhibits the nodal properties suggested by Platt, viz., one single node only along the short axis. In addition the following details occur consistently. The atomic contributions increase gradually from the central node, but after a short inflection peak suddenly to a high value at the end atoms. This is the origin of the very strong intensity of 1B_D .

In contrast, the 1L_D dipole does not have the multiple nodes derived by Platt from the perimeter model; instead it has a single node like 1B_D . The resemblance to 1B_D is in fact very close in all particulars, except that the magnitudes involved are much smaller, resulting in the very small transition moment. Indeed, to the extent that 1L_D and 1B_D arise from paired transitions, the atomic dipole contributions of

1L_D must be proportional to those of 1B_D in any calculation--not just the present. Our result for 1L_D is not in complete disagreement with Platt's picture: the simple perimeter model produces nodes at all atoms, and the present atomic contributions are small. They would indeed vanish if, instead, the results of Pariser's approximation would be plotted in like manner. The major difference from Platt's diagrams lie in the dipole contributions assigned to the bond regions. While the free-electron perimeter model suggests antinodal behavior, the actual bond contributions are smaller than those from the atoms. Similar limitations of the free-electron model are found whenever the number of nodes equals the number of atoms.

The " 1B_2 " transition differs from the previous ones in that there exists no characteristic dipole pattern for it which would persist to the higher molecules of the polyacene series. This is a consequence of the increasing amounts of configuration interaction to which 1B_2 is subject because of its constantly high one-electron excitation energy. In naphthalene it has the single node along the long axis that Platt proposed. The dipole structure is similar to that of 1L_2 , however, in that for both it fluctuates strongly, although the fluctuations in 1B_2 are not strong enough to produce nodes through all bonds. In anthracene, however, eight additional nodes are produced --only four short of 1L_2 . In naphthacene two

additional transitions have moved down to interact very strongly ($>50\%$) with the $[(N/2 - 1) \rightarrow (N/2 + 2)]$ one-electron jump to form transitions with new and varying characteristics. Conclusions concerning this transition are further complicated since it is one where the differences between TBM and the more nearly correct TBX are greatest and the fine details provided by the dipole analysis are sensitive to such considerations. The correct distances needed for TBX are not available for the very molecules in which the complications arise.

(3) In order to describe the relationships for the remaining transitions, it is convenient to have short state labels. Since the nomenclature derived from the perimeter model does not really fit, and since it seemed premature to promulgate another general scheme on the basis of the present work alone, the following simple nomenclature is used in the following discussion. The long axis polarized states are labeled L1, L2, L3, L4,.... The short axis polarized are labeled S1, S2, S3, S4,....

Naturally in larger molecules, additional transitions arise. If some appear to resemble those of an already existing family, such branching is brought out by using symbols like L1', S2', L3', L3'' etc.

In particular the previously discussed states are now denoted as follows:

$$L_b = L1, B_b = L2, L_a = S1, B_a = S2.$$

On the whole it is surprising how many of the transitions can be placed into families with quite consistent characteristics. This is indicated by the many connecting curves on Figure 2. The only case where such correlations are really hopeless and therefore omitted in this figure is the group of heavily interacting states into which ${}^1B_a = 1S2$ disappears from naphthalene on.

Best characterized are the long axis-polarized transitions. In fact all L transitions below 55 kK except L1 and L2, seem to belong to one clan denoted by L3, L3'.

The main branch, L3, has the almost identical structure as $S1({}^1L_a)$ except that there is a node rather than a maximum on the short axis. It has nodes in every bond. The next branch, L3', is characterized by maintaining the total numbers of nodes and the general appearance of L3 in anthracene through the larger molecules, and hence does not have nodes in every bond.

The remaining long axis polarized transitions all seem to be characterized by being flat and of one sign from the central nodes to the next to end atom and then changing sign strongly to attain the maximum magnitude. Thus these transitions are all classed together as L4.

The remaining short axis polarizations do not carry a rigid pattern from the first member of a family to the last, but must be followed from molecule to molecule. The lower energy S3 has a considerable resemblance to S4 but the considerable difference in energy led to their being assigned to separate families. S4 is one of the transitions which enter into interaction with S2 ($1B_2$) and its characteristics can be partially found in several of the highly mixed S states of naphthalene and pentacene. The S transition at 35.26 kK in Pentacene is an almost pure state of new characteristics hatched in this molecule.

3. NON - LINEAR POLYACENES

Criteria for Grouping

Because of their great number, the non-linear polyacenes must be divided into groups for calculation and display. Under the influence of the perimeter model it has been customary to form groups of molecules having the same number of carbon atoms. However, the strong variations in energy found in such a group both experimentally and theoretically indicate considerable distortions from the perimeter model. In contrast we observed that similarities in the positions of the lower energies exist between those aromatics which agree as to the largest linear polyacene contained in the molecular structure, and this may indeed be a general rule. Within such a group, energy variations are much finer and present therefore a greater challenge to theoretical calculation than the larger variations found in the aforementioned grouping. They are therefore chosen for the present work. Representative members of two groups will be considered: one based on naphthalene and one based on anthracene.

Naphthalene Group

The numerical results for the Naphthalene group are reproduced in Table II. The experimental and theoretical transition energies are compared in Figure 6, for the TBM approximation. The agreement between the lower assigned and calculated transitions is reasonable and comparable with the results for the linear polyacenes and better than what Ham and Ruedenberg have previously obtained for several of the present molecules. Note that the TBX approximation again improves the triplet value for Naphthalene.

The spectra of the non-linear polyacenes are more complicated than those for the linear polyacenes, since they have at most one symmetry plane (not including the molecular plane). The presence of one plane will create two sets of transitions with mutually perpendicular polarisations, but none of them will be dipole forbidden. The only exception is chrysene which has a point of symmetry, so that the symmetric states are dipole forbidden. But the remaining states, all anti-symmetric, are all mutually interacting and without limitation as to the polarization directions.

Thus many excited states are to be expected in the present group, and it is rather surprising that most of them seem to fall in the region around the strong transition where they are hidden or higher where observation is difficult. The lowest two singlets are remarkably separate. It is still true that their polarizations are mutually orthogonal except for chrysene which has the lowest state polarized along the long axis of the molecule and the next at an angle of less than 30° with it. These similarities in polarization, intensity, dipole map, etc. are expressed by the connecting lines in the figures.

In the 40 kK region, all molecules typically show a strong transition, long axis polarized, with a fairly strong satellite less than two kK higher. The latter is short axis polarized except in chrysene where both transitions are almost

equally strong and bracket the long axis between them. These two transitions resemble 1L_2 (1B_b) and 1S_2 (1B_a) in naphthalene. This similarity appears to support the present grouping. The discussed relationships are again indicated by connecting lines on the figures.

While the appearance of the two low weak transitions and the strong higher transitions in all molecules is quite similar to naphthalene, the situation is more complicated as regards symmetry and pairing properties. In all cases, except naphthalene, the long axis is orthogonal to the symmetry plane which is perpendicular to the molecular/^{plane}(if existing). If this perpendicular/^{symmetry} plane contains atoms, "the paired excitations" are long-axis polarized; if it bisects a bond, then the "paired excitations" are short-axis polarized. In fact, it emerges that the pairing properties play a negligible role in the make-up of the wave functions. Also the dipole maps do not show the same structure as in the linear polyacenes. Almost absent, for instance is the picture with a single node found there for 1B_b , 1B_a , and 1L_b and predicted generally by the perimeter model for the 1B_b and 1B_a states. Also the present dipole maps are more difficult to systematize.

In spite of all these considerable complications and differences the spectra display remarkable uniformity in certain features: a low lying triplet, two low lying weak transitions some 8kK higher, and two stronger transitions some 5kK higher yet. On these points there is agreement between calculations and experiment. Consequently, a gratifying correspondence exists between experimental and synthetic spectra, as shown in Figures 7 and 8.

Anthracene Group

The numerical results for the anthracene group are given in Table II. They are compared with the assigned transitions in Figure 9. The principle of grouping seems to be justified in as much as the energies of the transitions remain generally constant throughout the group and are consistently lower than those of the naphthalene group. Moreover the non-linear members appear to have acquired a third, low lying, weak transition in addition to the two found in the naphthalene group.

These results are reproduced in the calculations, which are however somewhat high on these transitions. Also in 1,2,3,6-dibenzanthracene, one of the three is dipole forbidden according to the calculation and its observation must be justified by vibrational interactions similar to 1L_b in benzene and coronene. The experimental spectrum of pentaphene has a rather unique appearance in that the single strong peak seems to be replaced by two or three fairly strong peaks. Calculations reproduce this rather peculiar feature.

A comprehensive comparison of all calculated singlet transitions with experiment is given in Figures 10 and 11 by reproducing together experimental and simulated theoretical spectra. Again reasonable agreement is found. The general analogy to the naphthalene group is close enough to make further discussion unnecessary.

It would be valuable to have measurements on the triplets of these molecules.

4. PERI-CONDENSED MOLECULES

General Considerations

The peri-condensed aromatic hydrocarbons have long been a stumbling block for theoretical understanding. Unlike the cata-condensed systems, they have resisted attacks based on simple models as well as on more rigorous calculations. Not only have their spectra special characteristics, but in some cases even the extent of the conjugation over the molecular framework has been the object of controversy. It is therefore very gratifying that the present work leads to results remarkably close to experiment.

To be sure the calculations were handicapped by the lack of information on the exact nuclear positions. While X-ray measurements are available for all molecules, it is presently recognized that, so far, their degree of analysis is inadequate. Nevertheless these measured distances were used in the present calculation in the hope that on the average they would represent an improvement over the use of mean distances.

The numerical results are given in Tables IV and V. For some of the molecules, the assigned transitions are compared with the calculated TBX (where X indicates measured, not necessarily exact distances) values in Figure 12. For all molecules experimental spectra are compared with the synthesized singlet spectra in Figures 13, 14 and 15.

Lowest Triplet and Lowest Singlets

Unfortunately only two triplets have been assigned. The theoretical value is four kK low in pyrene, but only one kK off (high) in coronene. The error in ^{pyrene} / is reminiscent of those found in the polyacenes when average, rather than exact distances, were used.

As in the polyacenes, two transitions follow between 16 kK and 32 kK in all molecules, weak in the pyrene group, but one of them strong in the perylene group. Agreement between theory and experiment is near perfect for most of these. The remaining two, both perpendicularly polarized, are three kK low.

Pyrene Group

Pyrene

Towards higher energies, where the polyacenes exhibit one strong band, the pyrene spectrum is distinguished by having three rather intense peaks of nearly equal strength. This characteristic feature is satisfactorily reproduced by the present study.

The lower two of these correspond to what has been known as 1B_b (the lower) and 1B_a (the higher) in the polyacenes, the former containing the paired excitations and being parallel to the horizontal axis in Figure 12. In contrast to the polyacenes this axis is not the longest

in pyrene, but the one perpendicular to it is somewhat longer. This circumstance is the origin of the comparable strength of the two bands with the 1B_a -like transition a bit stronger.

Between these two transitions and the third strong band at higher energy with its accompanying barrage of weaker transitions lies a clear gap of seven kK, free of transitions both weak and strong. This theoretically predicted gap is clearly apparent in the observed spectrum.

The prediction of the intensities in the two highest bands, which are also the two strongest, are not completely satisfactory. Whereas experimentally, the highest is slightly weaker, theory gives it slightly stronger than the second highest.

Benzperylene

The calculations in 1,12 benzperylene are not as successful in the upper energy region as they were for the preceding molecule. The energies fit experiment reasonably well in its prominent features. The gap referred to previously has, however, been filled in by fairly weak transitions, whereas it is still shown by experiment. True it is less prominent and may cover weak absorptions. As noted earlier, agreement is very good in the placement of the two low transitions.

Unsatisfactory are the intensities. The experimental spectra has again three comparably strong bands, but, unlike in pyrene and perylene, theory fails to provide adequate intensity for two of these (at 25 kK and 47 kK) and provides possibly a bit too much for the strongest (at 35 kK), which according to theory is a pair of almost degenerate strong transitions. The experimental peak possibly supports this latter prediction.

On the whole it is consoling that, in reporting the measured distances, Robertson indicated that the benzperylene distances was the least reliable and that several of the important distances could not be determined. The comparison of transitions is after all reasonably good, but suffers from comparison with other molecules of the sequence.

Anthanthrene

Anthanthrene differs from pyrene by the addition of two benzene rings; it differs from Benzperylene merely in the location of one of these two additional ring. Yet there are distinct differences in the spectra of these molecules. These differences are reproduced by the calculations, as can best be seen by comparing the experimental with the synthetic spectra. In fact, the agreement between the TBM spectrum and the experimental in anthanthrene is almost too good to be true.

Coronene and Ovalene

The lower transitions of coronene have been discussed previously. The doubly degenerate very strong transition is matched perfectly by the calculated energies. Above this transition the experimental absorption curve falls monotonically up to the cutoff at 39 kK, forming the first part of a gap in complete agreement with theory which predicts the next peak at 44 kK. It would be helpful to have the experimental spectra extended to higher wavelengths.

Ovalene apparently is particularly difficult to dissolve for its experimental spectra is restricted to wavelengths longer than 3000\AA . To the extent that the experimental spectra has been observed it seems to agree with the theoretical values. For this molecule a more complete experimental spectra would be even more desirable.

Perylene Group

Perylene

Perylene differs from the other molecules of this study in that negligible conjugation is indicated by the consideration of Kekule structures for the two central bonds joining the two naphthalene groupings. Support for this conclusion has been seen by some in the large measured length of 1.50\AA for the bonds in question. Undoubtedly the existence or non-existence of such conjugation should be reflected in the spectra. But so far the latter has presented a puzzle, even to qualitative understanding, because of certain unique features to be discussed. All of these aspects seem to have contributed to the feeling that perylene would be a tough nut to crack.

In the present work the central bonds were treated no differently than the other conjugated bonds, and with this assumption excellent agreement was found between theoretical and experimental spectra. In view of the fact that, even in the TBX calculation (!) the LCAO-MO bond order in the central bond is only 35% lower than the average perylene bond order, it is

indeed very hard to see why there should not be appreciable conjugation over the central bond. The excessive length of this bond is very likely due in part to steric hindrance¹⁵ as has been fairly well proven for a similar, unquestionably conjugated bond¹⁶ in chrysene.

The spectra of perylene is very distinctive indeed. The lowest singlet, weak in all other molecules, is here the strongest peak. Also the two low transitions are separated by an unusually wide spacing between them. Unlike pyrene, only one of the transitions around 40kK (1B_g) is fairly strong. But, similar to pyrene, there follows another band of about equal strength some 8 kK higher.

These spectral features are matched by the excellent fit between theoretical and experimental energies and the good fit (subject to the usual empirical scaling factor), of the strong intensities. Also there is again a gap at high energy, in the calculated transitions, before the onslaught of the barrage. This distinctive gap is found in experiment.

Terrylene and Bisanthene

Terrylene and bisanthene differ from perylene in that both have three additional rings. Both molecules preserve the two typical central bonds of perylene; but whereas terrylene has altogether four bonds of this type, bisanthene has only three of them.

The appearance of the spectra of perylene, terrylene and bisanthene is remarkably alike, and the characterization of the

perylene spectrum applies equally to the other two molecules. The distinctive difference between them is that corresponding parts of their spectra stretch over larger and larger wavelength regions. The perylene spectrum between 2400 and 4400 Å corresponds to the terrylene spectrum between 2300 and 5400 Å, and to the bisanthene spectrum between 2900 and 7100 Å. ¹⁷ All these experimental observations are excellently reproduced by the calculations as is shown by the synthetic spectra in Figures 14 and 15.

Dipole Maps

The dipole maps are very interesting and display, as expected, radial as well as angular nodes, although the structure is more complex than indicated by nodes alone. The parallel transitions have dipole regularities even more striking than were observed in the linear polyacenes, which makes it easy to trace the transitions. The regularity is such that the patterns can be adequately recognized by the first and last members of the sequence, ^{which are displayed in Figure 16.} As in the linear polyacenes naphthalene and pentacene transitions of the perpendicular polarization have much less regularity. The reason is presumably that the parallel excitations contain the paired excitations.

5. THE AZULENE FAMILY

The results for the non-alternant, azulene family compare very poorly indeed with experiment. Particularly in view of the good results that have been obtained for the alternant aromatics, this failure may be quite illuminating with regards to the assumptions of the underlying theory. The results, which are also listed in Table V, are considerably too low, most notably for the lower two.¹⁸ Only the TBM and IRM approximations were carried through. While use of exact distances might yield some improvement, it is unlikely to remedy the basic deficiency.

Azulene itself has also been treated by Ham and Ruedenberg and by Pariser. Their results have been somewhat, but not significantly closer to experiment than the present one. Pariser's calculation, the best one due to the inclusion of configuration interaction in the ground state, falls three kK below the peak of 1L_b and more than five kK below the peak of 1L_a . The present authors feel that, in all treatments carried out so far, some fundamental physical effect has been given inadequate consideration.

The basic reason for the failure seems to be related to the fact that the atomic populations in non-alternants differ greatly from unity in all approximations. In some higher azulenes they go even up to 1.3, as can be seen from the

Coulson bond order matrix. As a consequence, the average potential needed to determine adequate molecular orbitals must be composed of contributions from non-neutral atoms and hence have long range, coulombic components. Such adequate molecular orbitals must therefore be different from the Hückel-type eigenvectors of the overlap matrix.

This inadequacy of the present molecular orbitals is more serious for the ground state, which by hypothesis has been taken as a single determinant, than for the excited states, which have been subjected to extensive configuration interaction. There is in fact evidence that the ground state configuration as presently used may interact appreciably with the excited configurations. This is indicated by the fact that, for the lowest transition in azulene, electron interaction decreases the one-electron jump energy of 16.4 kK by 3 kK whereas in alternants it consistently introduces an increase of 6-20 kK. The inference may be drawn that, in contrast to the situation in alternants, certain excited states may now contain less internal electronic repulsion than the ground state, and this can indeed be related to the charge accumulations indicated by the atom populations. Admitting configuration interaction to the ground state would not be the only, or necessarily a sufficient, remedy (Pariser lowered the ground state 2.44 kK by this means); proper modification of the molecular orbitals would be another possibility.

If it should be necessary to use slightly different atomic orbitals for the different atoms, this would lead to further, but not insurmountable, complications.

Finally it is not unlikely that the interplay with σ electrons is considerably more important in the non-alternants than in the alternants. Neglect of σ electrons has been justified on the basis that they are localized in a bond between two atoms and thus their ability to correlate with the mobile π electrons is severely restricted. However they are free to move within a bond, and, if the bonded atoms have an unequal charge due to the π electrons, the σ electrons may be expected to shift within the bond to partially neutralize the inequality. This would lower the energy of those states having the greatest electron interaction energies which in the present case would include the ground state.

6. INFLUENCE OF SUBSTITUENTS

Benzene Homologues

After having treated so many large molecules it appeared tempting to consider several small homologues of benzene characterized by conjugated and unconjugated substituents.

The methyl substituted derivatives toluene, xylene, and mesitylene were dealt with by changing the framework potential, i.e. the contribution of one neutral hydrogen atom was replaced by that of a neutral carbon atom. Hence for the conjugated carbon atom next to the methyl group, the neutral framework potential was assumed to be the same as that of a joint atom. Thus the treatment can be said to include the inductive effect in its most general form, but omitted hyperconjugation.

On this basis of the theory developed in the earlier sections this change of the framework potential does not affect the molecular orbitals, but enters the calculation in two ways: the resonance integral γ is lowered, and certain joint correction contributions enter the configuration interaction matrix.

The numerical results are listed in Table VI. The comparison with the experimental assignments is shown in Figure 17. The trend to longer wavelengths is reasonably reproduced. In Table VII, the change of each transition is decomposed, for each molecule, into two contributions; the first arising from the modifica-

tion of the resonance integral, γ , the second from the joint correction mentioned in the preceding paragraph. Contrary to assumptions popular in some simple models, the former is the greater of the two.

Figure 17 also contains the result for styrene as an example of α conjugated substitution. Although the free ending chain must give rise β certain effects not properly accounted for by the present treatment, the agreement between theory and experiment is relatively satisfactory.

Table VII. Energies of the benzene homologues

		1_{B_b}	1_{B_a}	1_{L_b}	1_{L_a}
Benzene		56.05	56.05	40.23	48.59
Toluene	No joint corrections	54.62	54.62	38.81	47.16
	Joint corrections	54.83	54.79	38.95	47.33
M-xylene	No joint corrections	53.91	53.91	38.09	46.45
	Joint corrections	54.11	54.08	38.23	46.61
Mesitylene	No joint corrections	53.19	53.19	37.37	45.74
	Joint corrections	53.37	53.37	37.55	45.91

Diphenyl and Fluorene

Another simple case where the influence of unconjugated substituents could be tested was the comparison between diphenyl and fluorene. The results, also given in Table VI, give rise to the synthetic spectra in Figure 18. The shift of the lower diphenyl band in fluorene is given incorrectly, the shift of the upper band, though in the right direction, is too small. However the split of the lower in Fluorene, due to increasing separation of the involved transitions, is reasonably reproduced. The application of the present method,

presupposing a planar molecule, seems much more justified for fluorene than for diphenyl, which is known to twist around the central bond. It is therefore gratifying that, among the two, the agreement between theoretical and experimental spectra is better in fluorene.

7. CONCLUSIONS

Assessment of Theory

While the present approach is more rigorous than past pi-electronic work, it does involve approximations without which molecules as big as the one considered here would be untractable. The calculations represent therefore a test of their validity.

The calculations have proved successful, as judged by comparison with experiment, for the alternant hydrocarbons investigated. There are aspects, to be sure, which are in need of serious improvements, in particular as regards the intensities. The lack of contrast in allowed intensities, encountered in all calculations to date, remains a disconcerting puzzle. Notable achievements were the markedly successful treatment of the peri-condensed systems, the first of its kind, and the even better results for those cata-condensed molecules whose exact atomic positions were available. It was established that the calculated spectra are fairly sensitive to variations in the atomic positions.

The synthetic spectra have proved to be very helpful, and they compare encouragingly with the experimental ones. There are in fact cases of isomers (e.g., tetraphene and anthracene, or more interestingly, anthanthrene and 1,12-benzperylene) where a decision regarding the molecular structure could be made by comparing the experimental spectra with the calculated synthetic spectra. To be sure, in certain cases the proper choice of an appropriately simpli-

ried model can explain, or at least rationalize such differences without an elaborate calculation. There is something to be said, however, for a computer program which automatically "grinds" out the synthetic spectra as soon as it is supplied with the cartesian coordinates of the atoms.

The limits of the assumptions and approximation are clearly overstepped in the applications to the non-alternant systems.

Review of Spectra

In comparing so many experimental spectra with their reasonably corresponding theoretical counterparts, one is struck by certain features common to all molecules. Consistently one finds, above the lowest triplet, two, or in a few cases three, low lying singlets. This theoretical result agrees with the empirical observation that the considerable broadness of these bands is clearly recognizable as vibrational fine structure. Towards shorter wavelengths, there follow in general one or two much stronger absorption bands and, traditionally, their fine structure, too, is interpreted as vibrational, although this can hardly be inferred from the line shapes and little of it is found in the simple molecules. The theoretical calculations furnish in general as many strong transitions as observed. In larger molecules, these are accompanied however by varying numbers of medium or weak transitions which extend from this vicinity to higher energies, resembling a barrage and presumably going into the Rydberg transitions. The existence of such a multitude of states cannot be a surprise from quantummechanical considerations. Remarkable is rather that they do not extend into lower re-

gions. In view of these results, we feel that the majority of the fine structure of the strong bands at higher energies is presumably not vibrational but electronic in character. This conclusion seems to be supported by the synthetic spectra. Although the calculations of the very high transitions (above 60 kK) are of course much less reliable, we predict an almost continuous fairly strong absorption in the short wavelength region which is presently unobserved due to technical difficulties..

Classification of Transitions

Is it possible, within this general spectral pattern to relate specific transitions in different molecules to each other ?

In addition to symmetry, we used the transition-dipole maps to trace kinships of this kind. In families of molecules with enough symmetry throughout the series, they provided indeed a sensitive fingerprint of particular transitions. In more irregular sequences, formed by less closely related molecules, they proved rather to sensitive to the molecular variations for establishing connections.

We see therefore no basis for a nomenclature which could express intimate similarities in the transitions of all aromatics. The most practical convention would be to take over, from the linear polyacenes, the symbols 1L_a , 1L_b for the generally observed lower transitions and the bymbols 1B_a , 1B_b for the higher and generally strong transitions, without however associating with them the characteristics of the dipole structures found in the polyacenes or the original model concepts of Platt. In those few cases where there are

more than two transitions of one kind, they may be denoted by 1L_a , 1B_b etc. If a clear gap does exist above the B-bands, then the next strong transitions following at shorter wavelength should receive different names, say C_a , C_b etc. In alternants the indices a, b indicate behaviour with respect to symmetry planes, "b" states being polarized parallel to a plane intersecting bonds and "a" states polarized parallel to a plane containing atoms, regardless of the length of the corresponding molecular axes. In unsymmetric molecules, these subscript can be used if there is a clear enough relationship to states in closely related symmetric molecules. It appeared unnecessary to invent a special nomenclature for the many moderate transitions in the high energy region. These practices have been followed in the present investigation, since they do justice to the observed spectra as well as to the theoretical results with a minimum amount of complication.

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- ⁸See Eqs. (3.18) and (4.12) of the first paper in reference 2.
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- ¹⁰As an illustration of the difficulties, consider the low transitions 1L_a and 1L_b in the standard sequence of the linear polyacenes. Platt's earlier assignment of the stronger one (1L_a) differs from Ham's later assignment by more than 2000 wavenumbers in two cases. The weaker one can be picked out of the spectra only for the first and the last member of the sequence. In anthracene it was located by polarized light in a carefully prepared solution crystal, but in naphthacene it has not been experimentally located to date.
- ¹¹Semi-empirical methods may be expected to show up more favorably relative to a more theoretically restricted theory for a family of molecules used in fitting the parameters. This advantage fades as the molecules differ more and more from those used in the gauging.


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- ¹⁴Indeed, in perylene and 1, 12 benzperylene many of the atomic positions are not located by experiment.
- ¹⁵The bonds in the two concave sections of well measured chrysene are 0.04 Angstrom longer than predicted by bond order. The final refinement of the determination indicates confirming displacements of the hydrogen atoms. D. W. Cruickshank and R. A. Sparks, *Proc. Roy. Soc. (London)* A258, 270 (1960).
- ¹⁶Singly bonded carbons normally are able to stagger their hydrogens and reduce steric interaction. Rotational activation energies of the order of 3 Cal. are therefore a lower limit for the increased energy of the un-staggered hydrogens in perylene-type geometry.
- ¹⁷The shift to long wavelength in bisanthene is presumably related to the fact that the "building block" increases from naphthalene to anthracene. Note however that anthracene itself has its longest transition below 4000 Angstrom.
- ¹⁸The experimental assignments are taken from E. M. Layton, *Journal of Molecular Spectroscopy*, 5, 181 (1960).

Captions for Tables I to VI

- TABLE I.** Calculated Transitions of the Linear Polyacenes.
 Explanation: One set of data occupies two lines. The first two entries on the first line are a counting integer referring to the chemical formula in Figure 1 and the name of the molecule. The first two entries on the second line give the method of approximation (TBX, IRX, TBM, IRM) and the transition energy of the lowest triplet. The remaining entries on both lines consist of pairs of numbers of which the first gives the transition energy of a singlet transition and the second its oscillator strength.
- If the molecule possesses a symmetry plane perpendicular to the molecular plane, the first line contains the singlets of S symmetry and the second line contains the singlets of A symmetry.
- If the molecule possesses two planes of symmetry perpendicular to the molecular plane, the first line contains the singlet of SA symmetry and the second contains the singlets of AS symmetry, where the first symmetry specification refers to the long axis and the second to the short axis.
- If the molecule possesses a center of symmetry, only the A states are listed (since the S states are symmetry forbidden), and they occupy both lines. In the absence of any symmetry, too, the second line is merely a continuation of the first.
- TABLE II.** Calculated Transitions of the Non-Linear Polyacenes. Naphthalene Group. See Table I for explanations.
- TABLE III.** Calculated Transitions of Non-Linear Polyacenes. Anthracene Group. See Table I for explanations.
- TABLE IV.** Calculated Transition Energies of Pericondensed Aromatics. I. See Table I for explanations.
- TABLE V.** Calculated Transitions of Pericondensed Aromatics, II, and of Azulene Derivatives. See Table I for explanations.
- TABLE VI.** Calculated Transitions of Benzene and Diphenyl Derivatives. See Table I for explanations.

Captions for Figures

- Fig. 1. Chemical formulas of molecules treated. The numbers refer to the entries in Tables I to VI.
- Fig. 2. Assigned and calculated transitions in the linear polyacenes.
- Fig. 3. Experimental and synthetic spectra for linear polyacenes. I. For explanation see Sec. 1 after Eq. (4).
- Fig. 4. Experimental and synthetic spectra for linear polyacene. II. Explanation in Sec. 1 after Eq. (4).
- Fig. 5. Dipole maps for electronic transitions of linear polyacenes.
- Fig. 6. Assigned and calculated transitions for naphthalene group.
- Fig. 7. Experimental and synthetic spectra for naphthalene group. I.
- Fig. 8. Experimental and synthetic spectra for naphthalene group. II.
- Fig. 9. Assigned and calculated transition for anthracene group.
- Fig. 10. Experimental and synthetic spectra for anthracene group. I.
- Fig. 11. Experimental and synthetic spectra for anthracene group. II.
- Fig. 12. Assigned and calculated transitions for pericondensed molecules.
- Fig. 13. Experimental and synthetic spectra for pericondensed systems. I.
- Fig. 14. Experimental and synthetic spectra for pericondensed systems. II.
- Fig. 15. Experimental and synthetic spectra for pericondensed systems. III.
- Fig. 16. Experimental and synthetic spectra for pericondensed systems. IV.
- Fig. 17. Dipole maps for electronic transitions of pericondensed systems.
- Fig. 18. Assigned and calculated transitions for substituted benzenes.
- Fig. 19. Experimental and synthetic spectra for diphenyl and fluorene.



END