Nonalternant Hydrocarbons: a Classification of Excited States in Acenaphthylene and Pleiadiene (Cyclohepta[*de*]naphthalene) Families[1]

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Abstract: A classification of low-lying electronic states of hydrocarbons derived from acenaphthylene and pleiadiene (cyclohepta[*de*]naphthalene) by union with an alternant fragment and their relation to the states of naphthalene are discussed. Experimental energies of three transitions (K, L, M) in 11 hydrocarbons change as a function of the structure of this fragment and its mode of attachment in a regular way, which agrees with PPP calculations, but can also be rationalized very simply already at the level of PMO theory. The lowest transition (K) lies at disproportionately low energies, considering the orbital energy difference involved. This is proposed to be a consequence of its intramolecular charge-transfer nature, which is also reflected in its weak intensiy and in a small singlet–triplet splitting.

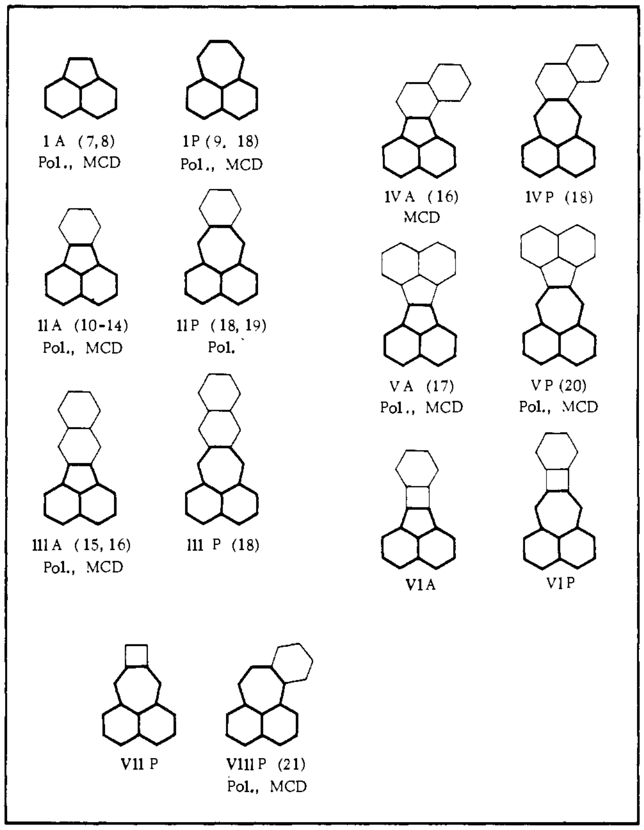
Electronic states of benzenoid hydrocarbons have been the subject of several successful systematic correlation schemes,[2] in particular Clar's empirical α, p, β, β' nomenclature and Platt's ^1L_b, ^1L_a, ^1B_b, ^1B_a, . . . nomenclature based on the free-electron perimeter model, which can also be expressed in terms of MO configurations for the best known bands ($\alpha = {}^1L_b = (1 \rightarrow -2) - (2 \rightarrow -1)$; $p = {}^1L_a = (1 \rightarrow -1)$, $\beta = {}^1B_b = (1 \rightarrow -2) + (2 \rightarrow -1)$, $\beta' = B_a = (2 \rightarrow -2)$. More recently, correlations between states of related hydrocarbons were discussed in terms of the molecules-in-molecules method,[3] etc. On the other hand, no such systematic and general classification of states exists for nonalternant hydrocarbons. An extension of Platt's scheme to hydrocarbons of the azulene series and to benzotropylium ions has been reported,[4] but an attempt to extend it to acenaphthylene and fluoranthene was not fruitful.[5]

In view of the variety of types of such hydrocarbons, it appears useful to study them family by family. Various subdivisions of nonalternant hydrocarbons according to structural type are possible. In our work, we use a scheme proposed in ref 6. We have now completed an experimental investigation[7-21] of two families of hydrocarbons derived from members of the group of pericondensed tricyclics, namely acenaphthylene (IA) and pleiadiene (IP). It turns out that their low-lying electronic states can be classified jointly and approximately related to states of naphthalene. We propose such a classification in the present communication, using simple MO theory as a guide.

Results and Discussion

Schematic formulas of representatives of the two families of fully unsaturated hydrocarbons for which π-electron calculations have been performed are shown in Chart I. Obviously, numerous additional members of each family can be readily envisaged and many are actually known, in particular, numerous benzofluoranthenes. We believe, however, that a sufficient number of members of each family have now been studied such that extrapolations to further hydrocarbons of this type should be relatively safe. Of the hydrocarbons listed, all but two (VIA and VIP) have been prepared,[22] although some (IIP, IIIP, and IVP) were too reactive to be isolated in substance.[18] All but three have been investigated experimentally in the present series of investigations, and appropriate references are listed in Chart I. In about half of the instances, substituted derivatives and/or hetero analogues of the hydrocarbon were incorporated in the studies in order to derive more detailed information. In addition to low-temperature absorption measurements, polarized emission and/or absorption and magnetic circular dichroism were also measured if experimental conditions permitted. This is noted in Chart I as pol and MCD, respectively. This combination of measurements produced quite unequivocal and detailed assignments of low-lying electronic states. Only in the cases of IIIP and IVP were the results and assignments less detailed. Invariably, the experimental results were in good agreement with PPP theory.

Chart I



In two pioneering studies,[23,24] some of the presently noted correlations were predicted from Hückel MO calculations. The existence of a correlation of some of the experimental bands in some of the compounds has also been noted previously.[12,15,20,21,25]

Hydrocarbon VP is presently considered to be derived from IP by union with a naphthalene unit, and is analogous to VA. It could also be considered to result from IA by union with

Table I. Experimental Characteristics of Transitions K, L, and M

Transition	Ordering[a]	Intensity	Pol[b]	Franck–Condon	*B* Term[c] A	*B* Term[c] P
K	1	w	—	Forbidden	−w	+w
L	2	s	∣	Allowed[d]	−s	+s
M	3	m–s	—	Allowed	+s	−s

[a] In some instances K may lie above L. [b] Directions referring to formulas in Chart I. [c] Opposite in sign to the observed MCD peak. A: acenaphthylene family, P: pleiadiene family. VP behaves as a member of the pleiadiene family, except that its K band has negative *B* term. In IIIA and IVA, the *B* term of transition M is negative, presumably because it is not determined by magnetic mixing of excited state M with excited state L as usual, but by stronger mixing with the next higher excited state, which is very close in energy in these two hydrocarbons. [d] Or weakly forbidden.

1,8-dimethylenenaphthalene. This is less useful for the present purposes, since the interaction with such a biradical would be quite strong and of a different type than those found throughout the rest of the series.

Of the basic experimental characteristics of an electronic transition, its energy, intensity, polarization, band shape, and MCD *B* term were considered in the present work. Using these for guidance, three low-energy transitions could be traced throughout the whole series of hydrocarbons. We propose the labels K, L, and M for these transitions. Their characteristics are listed in Table I and their location in the spectra is indicated in Figure 1. Except in IIIA, they are always ordered K, L, and M in the order of increasing energy, and except in IIP (and probably IIIP and IVP), they are the lowest three experimentally identified transitions.

Results for IA and IP permit an extrapolation to the electronic states of naphthalene:[26] the L band of IA and IP represents a strongly perturbed ^1L_a (p) band of naphthalene, their M band correlates half with the ^1L_b (α) band and half with the ^1B_b (β) band of naphthalene (this influenced our choice of labels: L for L_a, M for mixed). Their K band has no analogy in naphthalene alone and has been described in a simplified manner as due to charge transfer between the naphthalene moiety and the peribridging unit.

Simple PPP theory and the concept[27] of approximate orbital and state pairing showed the presence of approximate mirror-image symmetry between the MO levels of IA and those of IP, and an approximate pairing of their electronic states, thus accounting for the great similarity of their ordinary and polarized spectra and the opposite (mirror image) character of their MCD spectra.[26] According to this interpretation, the K, L, and M transitions in the pleiadiene family are not directly related to the K, L, and M transitions in the acenaphthylene family, in spite of the coincidence of most of their characteristics, but rather, are their "mirror images" in terms of the MO energy levels involved, and this accounts for the opposite MCD signs in the two families (Table I). The orbitals 3, 2, 1, −1, and −2 of IA are paired with orbitals −3, −2, −1, 1, and 2 of IP, respectively (bonding orbitals are labeled by positive integers in the order of decreasing energy, antibonding ones by negative integers in the order of increasing energy). In IA, transitions K, L, and M are approximately described by one-electron jumps $1 \rightarrow -1$, $2 \rightarrow -1$, and $3 \rightarrow -1$, respectively, and in IP, by jumps $1 \rightarrow -1$, $1 \rightarrow -2$, and $1 \rightarrow -3$, respectively.

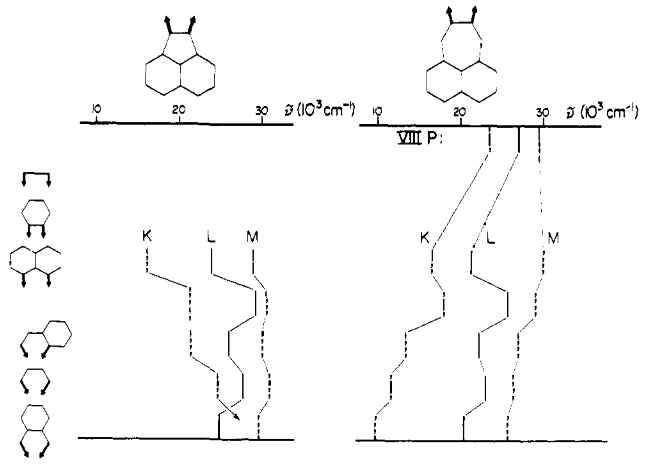


Figure 1. Experimental energies of transitions K, L, and M in hydrocarbons of acenaphthylene and pleiadiene families (0–0 band).

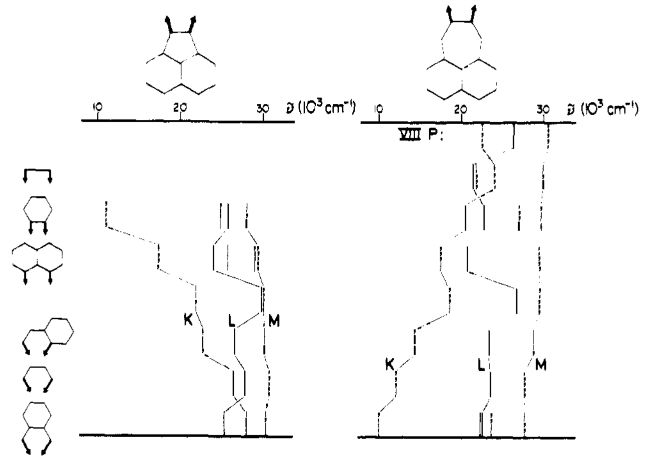


Figure 2. Calculated (PPP) energies of transitions K, L, and M in hydrocarbons of acenaphthylene and pleiadiene families (vertical transition).

Figure 1 shows interesting regularities and contrast in the response of the K, L, and M transitions of the hydrocarbons of the two families to ring annelation. The effect on transition L is about the same in the two families, but those on transitions K and M show opposite trends, K being by far the more sensitive of the two. Figure 2 presents results of PPP calculations for the same group of hydrocarbons at a uniform level of approximation (CI with all singly excited configurations, Mataga–Nishimoto[28] electron repulsion integrals, one-center repulsion integral $\gamma_0 = 10.84$ eV, all resonance integrals equal to −2.318 eV, regular geometries with all bond lengths 1.40 Å). Numerical agreement with experiment (Figure 1) could be improved by consideration of real bond lengths, and the low-lying doubly excited state in IIP (most likely present also in IIIP and IVP) can be accounted for by more extensive CI,[19] but such refinements are not essential for the present discussion and for tracing the qualitative behavior of transitions K, L, and M. Detailed inspection of the results of the calculations permit a safe identification of the excited states of these transitions in all cases. In several instances, additional low-energy symmetry-forbidden transitions are predicted to lie in the same region, so that K, L, and M need not always be the lowest three states. Comparison of Figures 1 and 2 shows that the trends shown by the three transitions are well reproduced by the theory.

It is perhaps more interesting to ask whether the observed trends can also be rationalized in simple terms. This can indeed be achieved by consideration of the effect of the interaction of the added part of the hydrocarbon on the energies of the MO's of the basic tricyclic unit, IA or IP. In the various hydrocarbons, such interaction occurs in analogous positions (Chart I),

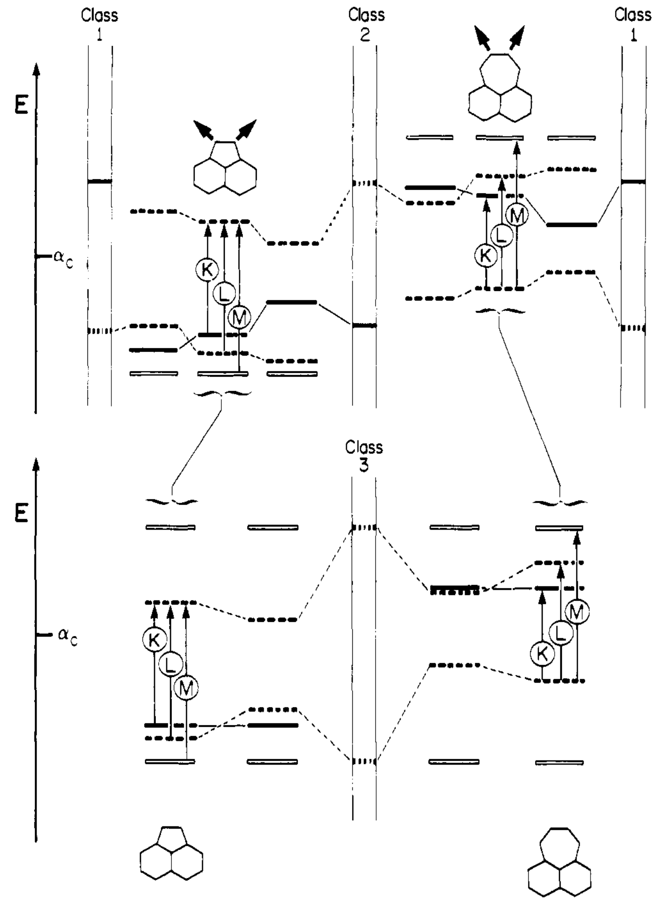


Figure 3. Effects on MO energies of IA and IP resulting from the interaction with alternant fragments of classes indicated on top at positions indicated by arrows. Full lines: symmetric orbitals; dashed lines: antisymmetric orbitals; double lines: symmetric orbitals with very small coefficients at the position of attachment.

except for VIIIP, which will be briefly mentioned later. To estimate the effect of the interaction on the orbitals involved in transitions K, L, and M in a qualitative fashion, we shall concentrate on their interactions with the HOMO and LUMO of the fragment which is being attached in the spirit of the simple PMO[29] method.

The results are shown in a schematic fashion in Figure 3. Energies of orbitals which have coefficients of equal signs at the two points of interaction with IA or IP (symmetric orbitals in those cases in which there is overall C_{2v} symmetry) are shown in full lines, those which have coefficients of opposite signs (antisymmetric) in dashed lines. Since the fragments which are being attached are themselves alternant, their HOMO and LUMO will be disposed at the same distance from the energy zero. Styrene, butadiene, and o-xylylene fragments have a symmetric LUMO and antisymmetric HOMO (fragments of class 1). In view of orbital energies and coefficient size, the strength of their interaction with both IA or IP should increase in the above named order. Benzene and ethylene have an antisymmetric LUMO and symmetric HOMO (fragments of class 2). Benzene also has an additional symmetric LUMO and antisymmetric HOMO with smaller coefficients at the points of attachment, which will complicate matters somewhat, but a more detailed discussion does not seem warranted, since no experimental data are available for this type of derivative. Naphthalene LUMO and HOMO are both antisymmetric at positions 1 and 8 (fragment of class 3). No experimental data are available for the effect of fragments whose LUMO and HOMO are both symmetric (class 4).

Table II. Shift of Transition Energies Expected from PMO Model

Fragment class	Substrate	Transition energy shift K	L	M
1	IA	+	−	(+)
	IP	− −	−	−
2	IA	− −	−	−
	IP	+	−	(+)
3	IA	−	− −	−
	IP	−	− −	−
4	IA	−	(−)	0
	IP	−	(−)	0

Choosing an arbitrary HOMO-LUMO energy splitting for the fragment being added and permitting orbitals of the same nodal properties (symmetry) at the positions of newly formed bonds to interact, we get simple diagrams, depicted in Figure 3 for fragment classes 1-3. The reason orbitals 3 of IA and −3 of IP hardly interact with the orbitals of the fragment at all even when the symmetry is favorable is the negligible size of their coefficients at the points of attachment (zero in HMO approximation). The size of shifts indicated in Figure 3 was chosen arbitrarily; however, the relative shifts are more or less correct, based on the size of the coefficients and energy differences involved. The qualitative conclusions to be drawn from Figure 3 are summarized in Table II. Agreement with experiment (Figure 1) and PPP calculations (Figure 2) is astonishing, considering the crude approximations made in the procedure, and should permit extrapolations for additional members of the two families of hydrocarbons. The different response of the K band in the two families, A and P, is again seen to be basically due to the approximate mirror-image properties of the cross-paired orbitals of IA and IP.

As for VIIIP, which differs in the mode of attachment of the butadiene fragment, nodal properties of the orbitals of IP are such that a PMO argument similar to the above predicts some stabilization of orbital 1 and a larger one of orbital −2, destabilization of orbital −1, and little effect on orbital −3. Thus, blue shift of transition K, small red shift of transition L, and small blue shift of transition M are expected from the simple argument, in reasonable agreement with experiment (Figure 1) and PPP calculation (Figure 2).

It will be noted that the energy of transition K is out of proportion to the corresponding orbital energy difference. In particular, compared with that of transition L, it is too low, and K is the lowest transition even in some members of the series in which the calculated orbital ordering is changed with respect to the parent IA and IP, i.e., when K no longer corresponds to the 1 → − 1 excitation (e.g.,[10,12] in IIA). The singlet excitation energy for transition $i \rightarrow j$ is given by $\Delta\epsilon_{ij} - (J_{i,j} - 2K_{i,j})$, where $\Delta\epsilon$ is the orbital energy difference, $J_{i,j}$ is the energy of electrostatic repulsion between a charge distribution $\rho_{i,i}$ due to an electron in orbital i and a charge distribution $\rho_{j,j}$ due to an electron in orbital j, and $K_{i,j}$ is the energy of electrostatic repulsion of the transition density $\rho_{i,j}$ of transition $i \rightarrow j$ with an identical density $\rho_{i,j}$. The anomalously low excitation energy of transition K indicates that $J_{i,j} - 2K_{i,j}$ is larger than usual (for most of the compounds IA-VIA and IP-VIIIP, $i = 1, j = -1$). This can be understood as a consequence of the charge-transfer nature[26] of this transition peculiar to A and P families. Since orbitals i and j are largely located on different atoms in the molecules, $\rho_{i,j}$ is small everywhere, and its self-repulsion $K_{i,j}$ is also relatively small (so is the dipole moment of $\rho_{i,j}$, resulting in weak intensity of the transition). On the other hand, for the L band, $K_{i,j}$ is about as large as for naphthalene L_a transition, which involves similar orbitals, and thus is "normal". Independent support for this rationalization can be obtained in the case of IA from the reported[7,30] energy of its lowest triplet state, which is also believed to correspond to $1 \rightarrow -1$ excitation. The singlet–triplet splitting is $2K_{1,-1} = 4800\ \text{cm}^{-1}$, to be compared with 13 700 cm^{-1} in naphthalene ($^1L_a - {}^3L_a$).[31] A similar situation has already been noticed for azulene and discussed in detail.[32] It probably prevails throughout the A and P families discussed here.

In summary, we believe that low-lying electronic states of the two title families of nonalternant hydrocarbons are now reasonably well understood. Some simple interpretations can be made even for higher states of certain of the compounds, but they are not generally applicable throughout the series, since they involve orbitals which are too profoundly modified by the various attached fragments and transitions whose description in terms of ordinary MO's requires considerable configuration mixing, and thus are of less interest for a simple classification scheme.

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Structure of Transition States. 4. MINDO/2 Study of Rearrangements in the C_6H_{10} System

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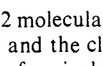
Abstract: A portion of the potential energy surface for C_6H_{10} is examined using the MINDO/2 molecular orbital method. The reactions include [3,3] sigmatropic shifts, double methylene isomerization of 1,5-hexadiene, and the cleavage and inversion of bicyclo[2.2.0]hexane. The calculations involve the location of 16 stationary points on this surface including geometries that characterize reactants, products, intermediates, and transition states for the various isomerizations. From the calculated force constants and vibrational modes together with the use of group theoretical theorems governing the symmetries of reaction paths, a picture of this energy surface is constructed and mechanistic information is deduced and compared to available experimental evidence. The various isomerizations are divided into two sets of HOMOmeric reactions corresponding to two molecular orbital energy surfaces in such a way that reaction paths between two structures on different surfaces are LUMOmeric.

Introduction

One of the earliest studied isomerizations of C_6H_{10} is the [3,3] sigmatropic shift or Cope rearrangement[2] of 1,5-hexadiene. The now classic experimental work of Doering and Roth suggested that the most facile route for this rearrangement involved a four-centered (chair-like) transition state.[3] The kinetic parameters for this "chair" rearrangement were subsequently determined.[4] More recently, the kinetic parameters for a Cope rearrangement involving a "boat-like" transition state have been obtained,[5] as have also the parameters for the inversion and stereospecific cleavage of bicyclo[2.2.0]hexane.[6] There is some controversy concerning the detailed mechanism of the latter.[7]

In the above investigations the species 1,4-cyclohexylene (**1**)



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emerges as the central structure involved in these reactions. In particular, one can assign detailed structures to **1** such as chair, boat, twist-boat, or planar, analogous to the cyclohexane system, and one can also identify these structures with isotopically or stereochemically distinct reactions.[8]