Acenaphthylene and Pleiadiene (Cyclohepta[*de*]naphthalene): a Case of Approximate Orbital and State Cross-Pairing[1]

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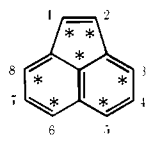
Abstract: The similar nature of ordinary and polarized absorption spectra of acenaphthylene (I) and pleiadiene (II), as well as the opposite nature of their MCD spectra, is readily understood within the framework of the PPP model as due to the existence of approximate pairing of the MO's and states of I and II, similar to that well known in the case of alternant hydrocarbons. This also accounts for certain other relationships between the properties of I and II. Among the low-lying states, K is intrinsic to the tricyclic nonalternant unit, L corresponds to a strongly perturbed L_a state of naphthalene, while M corresponds half to a perturbed L_b and half to a perturbed B_b state of naphthalene. The opposite halves of the sum total of naphthalene L_b and B_b states need to be used to construct the M state of I and the M state of II, and this can be used to account in detail for the opposite MCD signs in I and II. The correct absolute signs are obtained readily by inspection of HMO or PPP orbital expansion coefficients.

In the region of wavelengths longer than 250 nm, the electronic spectra of acenaphthylene[2] (I) and pleiadiene[3] (II) exhibit close similarity in the number of absorption bands, their location (except that the bands of II are red-shifted with respect to I), shape, intensity, and polarization. One might be tempted to conclude that the molecular orbitals ordinarily used for the interpretation of electronic transitions and their relative energies probably are quite similar in the two compounds, the additional two carbons in II representing only a minor perturbation. It is thus quite striking that in this spectral region their magnetic circular dichroic (MCD) spectra are complete opposites of each other. The MCD sign sequences, starting with longest wavelength MCD band, are +, +, −, −, . . . for I, and −, −, +, +, . . . for II, persist unchanged by substitution,[2-4] and appear to be inherent properties of these cyclic π-electron systems. The first three signs even survive an annelation of additional benzene rings.[5] This observation contradicts the notion that the above similarities of I and II reflect a great similarity of their MO levels and orbital coefficients. In this paper, it is shown that, instead, the spectral similarities as well as the MCD mirror image property are readily understood in MO terms as resulting from an approximate mirror-image pairing property[6] between orbitals and states of I on the one hand and II on the other. Also, low-lying electronic states of both nonalternant hydrocarbons, I and II, are related to those of their common formal precursor, naphthalene (III). The lowest three, labeled K, L, and M here, can be traced[5] throughout a larger family of conjugated nonalternants related to I and II.



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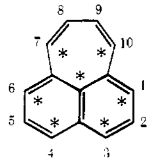

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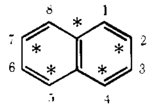

III

Results and Discussion

Approximate Pairing of Orbitals and States in I. The correlation of MO's of I with those of naphthalene and ethylene appeared in print some time ago,[7] and a similar argument can be made for II, using naphthalene and butadiene. The resulting correlation diagrams are shown in Figure 1. All three fragments are alternant hydrocarbons and their orbital energies are symmetrical with respect to the zero energy level, both in HMO and PPP models. In the following, we shall label bonding orbitals 1, 2, 3, . . . in the order of decreasing energy, and antibonding orbitals −1, −2, −3, . . . in the order of increasing energy. Occasionally, orbital 1 will be referred to as HOMO and orbital −1 as LUMO.

π-Interactions between positions 1 and 8 of naphthalene on one side and the termini of ethylene or butadiene on the other form odd-membered rings and destroy the pairing symmetry. The manner in which this happens is clear from Figure 1: with respect to a symmetry plane which interconverts the naphthalene positions 1 and 8, naphthalene orbitals 1 and −1 are both antisymmetrical, and 2, −2, 3, and −3 are all symmetrical. On the other hand, the LUMO of ethylene and HOMO of butadiene are antisymmetrical, and the HOMO of ethylene and LUMO of butadiene are symmetrical. When the π-electron fragments are united, the LUMO of ethylene interacts strongly with the LUMO of naphthalene, but their HOMO's cannot interact, and the HOMO of butadiene interacts strongly with the HOMO of naphthalene, while, in turn, their LUMO's cannot interact. This provides I with a low-lying empty orbital and II with a high-lying occupied orbital, both delocalized over the whole tricyclic system. The resulting high-electron affinity of I and low ionization potential of II are in good agreement with classical resonance structures for the corresponding radical ions, which would place a negative charge in a five-membered ring and a positive charge in a seven-membered ring, in agreement with the organic chemist's intuition. Naphthalene orbitals 2 and −2 are almost unaffected by union with either olefinic fragment, since their coefficients at positions 1 and 8 are very small (zero in the HMO approximation). The HOMO of ethylene and LUMO of butadiene interact with orbitals 3 and −3 naphthalene, respectively, and are both shifted closer to the zero energy level. The resulting picture of energy levels shows an interesting pairing (Figure 1): the behavior of bonding levels of naphthalene on going to I is similar to that of its antibonding levels on going to II, and vice versa. The resulting mirror image symmetry of the shifts is only approximate, because the HOMO and LUMO of butadiene are closer to the zero energy level than those of ethylene, and since their coefficients on the terminal atoms are smaller. Also, it only holds for levels which are relatively close to zero energy (and thus of interest in optical spectroscopy), i.e., those shown in Figure 1, since for these, interactions with the other two π-orbitals of butadiene, which have no counterpart in ethylene, are quite small. Thus, while the occupied bonding energy levels of III are paired with the unoccupied antibonding energy levels of III, within the above stated limi-

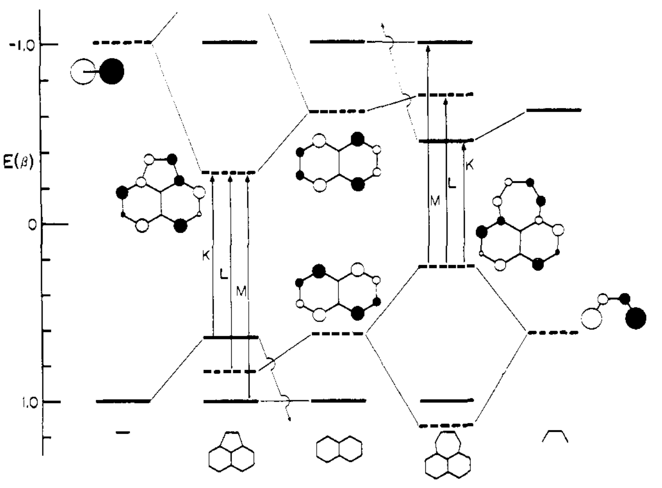

Figure 1. A correlation of MO energy levels of I, II, and III, with assignments of the K, L, and M transitions, showing their mirror-image symmetry in I and II. Orbitals symmetric (antisymmetric) with respect to mirroring, which interconverts naphthalene positions 1 and 8 are shown in full (dashed) lines. Expansion coefficients of several of the MO's are shown (sign is indicated by shading).

tations the positions of the occupied bonding levels of I present an approximate mirror image of the unoccupied antibonding levels of II, and vice versa.

On closer inspection, it is seen that the corresponding MO coefficients in the 1,8-dimethylenenaphthalene portions of I and II also are related in the sense of alternant pairing. In these portions of the molecules, the LCAO coefficients of the HOMO of naphthalene, orbital 2 of I, and orbital 1 of II look very much alike, and the same close similarity is noted for the LUMO of naphthalene, orbital −1 of I, and orbital −2 of II. Since the coefficients of the HOMO and LUMO of naphthalene are mutually related, as required by alternant symmetry in the PPP model (they are the same on starred atoms and differ only by sign on unstarred atoms; cf. the naphthalene portions of formulas I, II, and III), the coefficients of orbital 2 of I are related in the same manner to those of orbital −2 of II, and those of orbital −1 of I to those of orbital 1 of II. These relations are only approximate, but are fulfilled to a surprising degree of accuracy, as can be verified by inspection of Figures 1 and 2.

Similarly, the naphthalene orbital 3, which is admixed in antibonding fashion into the ethylene HOMO to yield orbital 1 of I (the bonding combination gives MO 4 of I), is paired with the naphthalene orbital −3, which is admixed in bonding fashion into the butadiene LUMO to yield orbital −1 of II (the antibonding combination gives MO −5 of II). The nodal properties of ethylene and butadiene orbitals and the requirements for their bonding and antibonding modes of interaction with the naphthalene moiety combine in such a way that even the MO coefficients on atoms 1 and 2 in I and those on atoms 7 and 10 in II obey the pairing requirements, if starring is performed as indicated in the formulas.

In summary, not only are the MO energies paired as already mentioned, but also the coefficients of the MO's of I (4, 3, 2, 1, −1, −2, −3) are approximately related to those of II (−5, −3, −2, −1, 1, 2, 3, respectively) in the sense of alternant symmetry. Coefficients on atoms 8 and 9 of II, which are without counterparts in I, remain outside the pairing scheme. In the determination of directions of transition dipoles and transition currents, they play a subordinate role and only slightly modify the magnitudes which would be obtained from the rest of the molecule. Also, some orbitals of II must, of necessity, lie outside the pairing scheme, since I has two fewer orbitals than II. These originate in the lowest bonding and highest antibonding orbital of butadiene, heavily admixed into orbitals 4, 5, and −4, −6 of II, respectively, and are not involved in low-energy electronic transitions in II.

In the PPP model, according to a well-known theorem,[8,9] two systems whose MO's fulfill pairing relations also have paired many-electron states. In particular, such paired systems have identical absorption spectra (transition energies, intensities, and polarization) and identical π-electron spin and charge (except for sign) distributions, as well as identical bond orders within the conjugated system. Finally, the MCD spectra of such paired systems are predicted to stand in mirror-image relation to each other.[10] Since I is approximately paired with II in the sense of alternant symmetry within the limitations outlined above, the close similarity of their electronic transition energies, intensities, polarizations, and overall band shapes (which depend on geometry changes upon excitation, and thus on changes in bond orders), as well as the mirror-type relation between the signs of their MCD spectra, all mentioned at the outset, are to be expected. The vibrational substructure of the K band fulfills expectations least well and this is readily understood, since this excitation involves an orbital heavily localized in the olefinic portion of the molecule, in a region in which vibrations of I and II, of necessity, must differ. In this picture, the overall red shift of the transitions in II compared to I originates in the greater proximity of the HOMO and LUMO of butadiene to the zero energy level compared with the HOMO and LUMO of ethylene. The assignment of the −1 orbital of II as a perturbed LUMO of butadiene is in excellent agreement with the measured spin distribution in the anion of II.[11] The approximate pairing of I with II also accounts for similar spin distributions in the naphthalene moiety of the anion of I[12] and cation of II.[11] The distribution is quite different in the anion of II;[11] that in the naphthalene part of the cation of I has not been determined, but can be expected to resemble that found in the anion of II. Similarly, one can expect that the so far unknown electronic absorption spectra of the radical cation (anion) of II will be similar to those of the radical anion (cation)[13] of I (except for a red shift of some transitions and blue shift of others). Further, the spectrum of the double cation of II should resemble that of the double anion[14] of I, except for a blue shift, while their MCD spectra ought to be mirror images of each other, etc. The existence of the approximate pairing also is in accordance with the apparently complementary distribution of charge in neutral I and II, as deduced[15] from ^{13}C NMR spectra and calculations (and resulting in dipole moments predicted to point in opposite directions). However, this argument is not compelling, since a summation over all occupied orbitals is required to determine total electron densities, and analogues of the most bonding and most antibonding orbitals of butadiene, which enter into the MO's of II, are missing in I. Qualitatively, it is reasonable, since the most bonding orbital of butadiene, which is without analogue in I, effectively contributes two π electrons exclusively to the butadiene unit of II (all orbitals resulting from its interaction with orbitals of the naphthalene unit are doubly occupied). Therefore, to a good approximation, it does not affect the overall π-electron population in the naphthalene portion of the molecule nor its detailed distribution.

It is amusing to note that such diverse properties as mirror-image relation of the MCD spectra of I and II, similar relative intensities of bands in their absorption spectra, high electron affinity of I and low ionization potential of II, similar spin distributions in the naphthalene portions of I^- and II^+ ions, etc., can all be related to the difference of nodal properties (symmetry) of the HOMO and LUMO orbitals of ethylene on the one hand and butadiene on the other, thus to the same difference which also lies at the heart of arguments concerning allowed and forbidden pericyclic reactions,[16] arguments concerning the presence or absence of barriers in photochemical reactions,[17] etc. However critical one may be of the use of semiempirical and approximate models in organic chemistry, their ability to interconnect and rationalize diverse phenomena is impressive.

One criticism of the simple PPP model, which has recently resulted from high-quality ab initio calculations on benzene,[18] should be mentioned here. It stems from the failure of the ab initio results to reveal evidence for pairing properties in this alternant π-electron system. The authors concluded that such pairing apparently is an artifact of the semiempirical model. This conclusion appears unwarranted. There is a large body of experimental evidence which is accounted for nicely by the pairing properties of the HMO and PPP models for alternant hydrocarbons and lack thereof for nonalternant ones, such as almost identical absorption spectra and/or spin density distributions in variously charged paired systems and the predicted[10] and very recently observed[19] mirror image nature of their MCD spectra, extremely weak intensities of transitions into "minus" states of hydrocarbons paired with themselves, approximately constant value of the sum of their electron affinity and first ionization potential, etc. Accordingly, there is no question about the existence of an approximate pairing of states in alternant, but generally not in nonalternant, systems, and the large body of experimental evidence must be reproduced by any sufficiently accurate model or theory. Pairing of MO's is another matter in that they are not observable and only occur in some theories. Possibly, one will be able to recast accurate ab initio results for an alternant system into a form which will exhibit something very close to the PPP MO pairing, perhaps for quasiparticles[9,20] rather than electrons.

Obviously, the PPP model is only approximate and all of the above-mentioned experimental evidence shows small deviations from perfect pairing of states. This is, however, a strong point in favor, rather than against, the use of a hierarchy of models which includes the PPP model as a first-order approximation, for it will facilitate the discovery of approximate relations, which tend to be rather general. It is in this light that we view some of the recent comments[21] on orbital pairing in naphthalene based on results from a higher member of the hierarchy of models (CNDO).

Correlation with States of Naphthalene. Absolute Signs of *B* Terms. A correlation of the low-lying electronic states of I and II with those of naphthalene is suggested by data in Figure 1. As pointed out earlier[7] in the case of I, such a correlation can be only approximate, since the olefinic bridge strongly perturbs the naphthalene unit. Accepting the correspondence of MO's of the three species outlined in Figure 1, we conclude that the L bands of I and II can be viewed as a strongly perturbed $\mathrm{L_a}$ (p, $1 \rightarrow -1$) band of naphthalene, while the K band of I and II has no counterpart in naphthalene and is characteristic of the integral tricyclic nonalternant unit. In I, it corresponds to charge transfer from the ethylene section to the naphthalene part of the molecule,[7] and this interpretation is in agreement with the observed[22] reversal of the direction of the molecular dipole moment upon excitation. In II, the K band corresponds to charge transfer in the opposite direction, from the naphthalene to the butadiene subunit. Such charge-transfer transitions have small transition density (product of two orbitals mostly localized in different parts of space) and this is in good agreement with the weak intensity of the K band. The large degree of weakening of the quasiolefinic double bonds in both instances, by removing one electron from what is essentially an ethylene HOMO or by placing one into what is essentially a butadiene LUMO, accounts for the observed Franck-Condon forbidden band shape.

In the PPP model, the $\mathrm{L_b}$ and $\mathrm{B_b}$ transitions of naphthalene are approximately represented[23] by out-of-phase and in-phase one-to-one mixtures of degenerate configurations $1 \rightarrow -2$ and $2 \rightarrow -1$. Figure 1 shows that interactions with ethylene or butadiene in positions 1 and 8 destroy the degeneracy of the two configurations by moving orbitals 1 and -1 to lower energies in I and to higher energies in II. As a result, the two corresponding configurations in I and II are uncoupled. In I, $3 \rightarrow -1$ is considerably below $2 \rightarrow -2$, and represents the excited state of transition M, while in II, $1 \rightarrow -3$ is considerably below $2 \rightarrow -2$, and represents the excited state of transition M. As already noted, configuration $3 \rightarrow -1$ in I is paired with $1 \rightarrow -3$ in II, just as $2 \rightarrow -1$ naphthalene is paired with $1 \rightarrow -2$ in naphthalene.

Thus, the M bands of I and II correlate with transitions to the $2 \rightarrow -1$ and $1 \rightarrow -2$ configurations of naphthalene, respectively, i.e., half with its $\mathrm{L_b}$ band and half with its $\mathrm{B_b}$ band. Each of the transitions has about half the intensity of the naphthalene $\mathrm{B_b}$ band (the intensity of its $\mathrm{L_b}$ band is negligible), comparable to the intensity of the L band in I and II. A similar, though not nearly as complete an uncoupling of the $1 \rightarrow -2$ and $2 \rightarrow -1$ configurations in naphthalene can be achieved by introduction of a heteroatom or a substituent, and in this case a considerable intensification of the $\mathrm{L_b}$ band is also observed. In this limited sense, I is analogous to, for example, quinoxaline (configuration $2 \rightarrow -1$ expected to lie below $1 \rightarrow -2$ in energy from the perturbation theory), and II, for instance, to phthalazine ($1 \rightarrow -2$ expected to lie below $2 \rightarrow -1$ in energy).

The mirror image relation between the K, L, and M excitations in I ($1 \rightarrow -1$, $2 \rightarrow -1$, $3 \rightarrow -1$) and II ($1 \rightarrow -1$, $1 \rightarrow -2$, $1 \rightarrow -3$), obtained from theory and clearly displayed in Figure 1, is not at all apparent from ordinary or polarized absorption spectra. Here, MCD spectroscopy proved to be of unique value as a probe. It is of some interest to investigate in more detail how the mirror image relation of MCD signs comes about and where the absolute signs originate. Parenthetically, it can be noted that the different expected mechanisms for uncoupling of the $1 \rightarrow -2$ and $2 \rightarrow -1$ configurations in quinoxaline and phthalazine have also been verified by MCD spectroscopy.[24]

For naphthalene and other uncharged alternant hydrocarbons, the PPP model predicts zero B terms for all transitions,[25] as a result of cancellation of contributions. For instance, the contribution to the B term of the $\mathrm{L_a}$ band which originates from magnetic mixing of the $\mathrm{L_a}$ state with the nearby $\mathrm{L_b}$ state can be written[26] as

$$B(\mathrm{L_a}\text{ from }\mathrm{L_b}) = \mathrm{Im}\{\langle \mathrm{L_a}|\hat{\mathcal{M}}|\mathrm{L_b}\rangle \cdot \langle 0|\hat{M}|\mathrm{L_a}\rangle \\ \times \langle \mathrm{L_b}|\hat{M}|0\rangle/\Delta E\}$$

where Im stands for imaginary part of, $\hat{\mathcal{M}}$ is the magnetic dipole moment operator, $\hat{M}$ is the electric dipole moment operator, ΔE is the energy of the $\mathrm{L_b}$ state minus the energy of the $\mathrm{L_a}$ state, and $|0\rangle$ refers to the ground state. In the usual approximation for naphthalene states,

$$\begin{aligned}\mathrm{Im}\{\langle \mathrm{L_a}|\hat{\mathcal{M}}|\mathrm{L_b}\rangle \cdot \langle 0|\hat{M}|\mathrm{L_a}\rangle \times \langle \mathrm{L_b}|\hat{M}|0\rangle\} \\ = \mathrm{Im}\{\langle (1 \rightarrow -1)|\hat{\mathcal{M}}|a(1 \rightarrow -2) - b(2 \rightarrow -1)\rangle \\ \cdot \langle 0|\hat{M}|(1 \rightarrow -1)\rangle\langle a(1 \rightarrow -2) - b(2 \rightarrow -1)|\hat{M}|0\rangle\} \\ = (a^2 - b^2)\mathrm{Im}\{\langle 2|\hat{\mu}|1\rangle \cdot \langle 1|\hat{m}|-1\rangle \times \langle 1|\hat{m}|-2\rangle\}\end{aligned}$$

where $\hat{\mu}$ and $\hat{m}$ are one-electron analogues of operators $\hat{\mathcal{M}}$ and $\hat{M}$, respectively, $a = b = 1/\sqrt{2}$ are the mixing coefficients of the $1 \rightarrow -2$ and $2 \rightarrow -1$ configurations, and the relations $\langle -j|\hat{\mu}|-i\rangle = \langle i|\hat{\mu}|j\rangle$ and $\langle i|\hat{m}|-j\rangle = \langle j|\hat{m}|-i\rangle$, easily verified by direct substitution (cf. ref 10), have been used. The contribution vanishes in spite of the sizable values of the three vectors it contains, since for naphthalene itself, $a = b$ in the PPP model. If this exact balance of configuration mixing is destroyed and the configurations $1 \rightarrow -2$ and $2 \rightarrow -1$ are uncoupled, $a \neq b$, and the contribution to B ($\mathrm{L_a}$) which is due to mixing with $\mathrm{L_b}$ no longer vanishes. If $1 \rightarrow -2$ is lower than $2 \rightarrow -1$ and, therefore, prevails in the $\mathrm{L_b}$ state, $a > b$, and if $2 \rightarrow -1$ is lower, $a < b$, so that opposite signs prevail in the two cases if other factors are the same. This permits quite generally

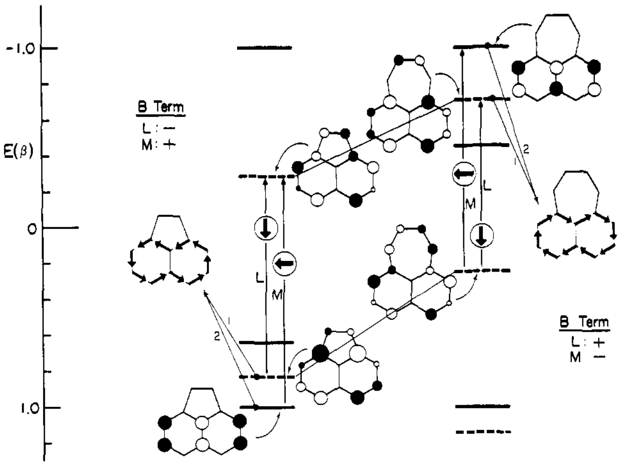

Figure 2. Derivation of the absolute signs of the B terms of L and M transitions in I and II by inspection. Orbital symmetry and expansion coefficients are indicated as in Figure 1.

a determination of the "decoupling mechanism" which operates. In derivatives of alternant hydrocarbons with substituents or heteroatoms, the uncoupling mechanism can be predicted from the form of Hückel molecular orbitals, and ΔE is known, so that an extremely simple scheme for prediction of the MCD spectra of such species results and could be of possible value in structural analysis. This will be reported in detail elsewhere.[24] Unsubstituted uncharged alternant hydrocarbons have nonvanishing MCD spectra in reality, with signs determined by second-order effects which are absent in the PPP model (deviations from perfect pairing) and require calculations by more elaborate methods.[27] Such secondary effects appear to be negligible as soon as a first-order effect described within the PPP model is present. In the case of I and II, the order of state energies is the same, K < L < M, and the above simple considerations show in detail the origin of the opposite MCD signs in the two paired species as due to opposite uncoupling mechanisms.

To elucidate the origin of absolute MCD signs, we note first that the signs of the MCD bands of transitions K, L, and M can be attributed to magnetic mixing of the excited states of these three transitions alone, other contributions being negligible[2,3] (the B term of the K band in both compounds is reinforced by a mixing of its excited state with the ground state, which can be analyzed in an analogous fashion). The signs of the L and M bands are determined by the mutual magnetic mixing of their excited states, and the sign of the weak K band is determined by the mixing of the excited states of transitions K and L. Since each transition can be adequately represented by a single electron jump between MO's, the qualitative three-sign rule[28] provides a simple means for deriving the absolute MCD signs (Figure 2; a positive MCD peak has a negative B term and vice versa). For instance, for the B term of transition L, we obtain a positive first sign, since M is of higher energy than L, and a negative second sign, since the head of the L transition dipole is rotated less than 180° counterclockwise from the head of the M transition dipole (these directions are deduced by inspection of the transition densities obtained by multiplication of orbitals shown in Figure 2, and are the same in I and II, in accordance with the approximate pairing properties of the MO coefficients). The third sign is positive in I and negative in II, since the "transition currents" from orbital 2 to 3 in I and from orbital −2 to −3 in II are counterclockwise and clockwise, respectively. Their directions were deduced by inspection of the MO coefficients in Figure 2 and the difference in sign is again in agreement with the pairing theorem (cf. ref 10). Thus, we expect in I, $B(\mathrm{L}) < 0$, $B(\mathrm{M}) > 0$, and in II, $B(\mathrm{L}) > 0$, $B(\mathrm{M}) < 0$, in agreement with numerical calculations and with experiment.[2,3] A similar qualitative argument accounts for $B(\mathrm{K}) < 0$ in I and $B(\mathrm{K}) > 0$ in II.

In concluding, we would like to point out the probable existence of other pairs of nonalternant hydrocarbons whose electronic states could be profitably discussed in terms of approximate mutual pairing in the sense of alternant symmetry.

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