Electron Configuration Analysis for Many-System Interactions. Electron Delocalization in Pyracylene, Acepleiadylene, and Dipleiadiene

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The method of electron configuration analysis for many-system interactions (ECAMSI) has been developed and applied to the π electronic structures of polycyclic molecules. The HMO-ECAMSI calculations have been carried out on acenaphthylene, pleiadiene, pyracylene, acepleiadylene, and dipleiadiene. Electron delocalization in the naphthalene core predominates in these molecules and remains unchanged from acenaphthylene to dipleiadiene; the central cross-linked π bond is not a small perturbation. There are four electron-delocalizing modes for the cyclic peripheral conjugation in acepleiadylene which give rise to an additional but appreciable delocalization, while the peripheral delocalization in pyracylene and dipleiadiene is almost completely depressed. The substituent effects on the delocalization have been predicted on the basis of the ECAMSI results and on the concept of the continuity-discontinuity of cyclic conjugation which has recently been developed.

The Hückel $4n+2\pi$ rule[1] is not directly applicable to polycyclic π conjugation. More than two decades ago two theoretical proposals[2,3] appeared about the "aromaticity" of the polycyclic systems. Platt[2] assumed that many polycyclic molecules were composed of peripheral polyene and intraannular cross-links. Assuming the cross-links are small perturbations, the Hückel rule may be applied to the peripheral polyenes. Craig's rules[3] predict the valence bond wavefunction of a given polycyclic system to be totally symmetric (aromatic) or not (pseudoaromatic). The qualitative evidence and the simple conclusions drawn stimulated many organic synthesists, but there are limitations.[4] The concept of resonance energy has frequently been used in both the LCAO and the VB methods for estimating the stabilities.[5-7] The improvement and the development of the methods are developing spheres of theoretical chemistry. A recent noticeable development has been the application of the graph theory.[8-12] The question of bond alternation, a measure of the electron delocalization is another property discussed for conjugated systems.[13,14]

In this paper a method for the electron configuration analysis for many-system interactions (ECAMSI) as an extension of the method of Baba *et al.* for two-system interactions has been presented.[15] The ECAMSI calculation enables the investigation of the constitution rather than the gross properties of the π electronic structures. The eigenfunctions have been analyzed from the point of view that polycyclic π conjugated molecules are composite systems of constituent ethylenic π subsystems. The main Kekulé structure of a given polycyclic system is uniquely determined and the mode of electron delocalization is visualized by investigating the mixing of electron-transferred configurations into the "zero" configuration which corresponds to the main Kekulé structure. The ECAMSI method has been applied to acenaphthylene (**1**), pleiadiene (**2**), pyracylene (**3**), acepleiadylene (**4**), and dipleiadiene (**5**). The tetracyclic nonbenzenoid hydrocarbons, **3**—**5**, were of theoretical interest.[16-19] The ECAMSI calculations have numerically solved such interesting questions as to whether the peri-bridges conjugate with the naphthalene core such that the intrinsic conjugation in the naphthalene substantially breaks down; the vinyl cross-links are involved almost exclusively in a naphthalene-like conjugation or the electrons are delocalized on the periphery without disturbing the naphthalene conjugation.

Theoretical

The total wavefunction of polycyclic π electron systems may be expressed as a linear combination of a basis set of electron configuration functions constructed as Slater determinants from the orbitals of the constituent subsystems. An electron configuration is denoted by the zero-configuration, Φ_0, where neither electron transter from one ethylenic unit to another nor electron promotion within any unit takes place. The second type of configuration is the electron-transferred configuration, $\Phi_{K\to L}$, in which an electron is shifted from the π bonding orbital of one ethylenic unit (K) to the π^* antibonding orbital of another (L). The third type of configuration is the locally excited configuration, Φ_{K^*}, in which an electron is promoted from the π orbital to the π^* orbital within the same unit (K). The other configurations have been neglected for simplicity in this study. The total wavefunction is then approximated as

$$\Psi \simeq C_0\Phi_0 \sum_{K,L} C_{K\to L}\Phi_{K\to L} + \sum_K C_{K^*}\Phi_{K^*}, \qquad (1)$$

where

$$\Phi_0 = N_0|a\bar{a}b\bar{b}\cdots z\bar{z}|,$$

$$\Phi_{K\to L} = \frac{1}{\sqrt{2}}N_{K\to L}\{|a\bar{a}b\bar{b}\cdots k\bar{l}^*\cdots z\bar{z}| + |a\bar{a}b\bar{b}\cdots l^*\bar{k}\cdots z\bar{z}|\},$$

$$\Phi_{K^*} = \frac{1}{\sqrt{2}}N_{K^*}\{|a\bar{a}b\bar{b}\cdots k\bar{k}^*\cdots z\bar{z}| + |a\bar{a}b\bar{b}\cdots k^*\bar{k}\cdots z\bar{z}|\}.$$

The normalization factors for Φ are denoted by N with the subscript. The π and π^* orbitals of A, B,···Z are denoted by a, b,···z with and without an asterisk. The total wavefunction,

$$\Psi = N|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_n\bar{\phi}_n|,$$

can be expanded by applying the following relation,

$$\phi_i = \sum_X(\lambda_{ix}x + \lambda_{ix^*}x^*).$$

The occupied MO's of the whole system are denoted by ϕ's and x and x* are the bonding and antibonding molecular orbitals of the subsystem, X, λ being the coefficient. The coefficients of the configurations are

then (the overlap integrals having been neglected):

$$C_0 = D_0^2,$$

$$C_{K\to L} = \sqrt{2}\, D_0 D_{K\to L},$$

$$C_{K^*} = \sqrt{2}\, D_0 D_{K^*},$$

where

$$D_0 = \begin{vmatrix} \lambda_{1a} \cdots \lambda_{1k} \cdots \lambda_{1z} \\ \vdots \quad \vdots \quad \vdots \\ \lambda_{na} \cdots \lambda_{nk} \cdots \lambda_{nz} \end{vmatrix},$$

$$D_{K\to L} = \begin{vmatrix} \lambda_{1a} \cdots \lambda_{1l}^* \cdots \lambda_{1z} \\ \vdots \quad \vdots \quad \vdots \\ \lambda_{na} \cdots \lambda_{nl}^* \cdots \lambda_{nz} \end{vmatrix},$$

$$D_{K^*} = \begin{vmatrix} \lambda_{1a} \cdots \lambda_{1k}^* \cdots \lambda_{1z} \\ \vdots \quad \vdots \quad \vdots \\ \lambda_{na} \cdots \lambda_{nk}^* \cdots \lambda_{nz} \end{vmatrix}.$$

Polycyclic π conjugated molecules have usually many Kekulé structures. Each of them can be a basis set of ethylenic units in the ECAMSI calculations. The use of the main Kekulé structure as a basis set is, however, chemically the most acceptable. The main Kekulé structure may be defined as a set of ethylenic units of which the corresponding zero-configuration represents the most appropriate electronic structure, that is, a Kekulé structure which has the largest C_0. In this sense the coefficient of the zero-configuration can be used as an index demonstrating the degree of contribution from a given Kekulé structure.

The degree of electron delocalization in a molecule has been examined by investigating the magnitude of the coefficients, $C_{K\to L}$. Direct comparison between the coefficients of the different molecules may, however, make no chemical sense since a large molecule usually has a large number of possible configurations and then a small C_0. Reasonable comparison is made in terms of the absolute value of the coefficient ratio (CR), $|C_K/C_0|$.

A relative value as the criterion to determine the significant configurations has been proposed. The comparable units in **1**—**5** have been denoted by the same letters, A, B,···I (see **1a**—**5a**). The value, δ, has been defined as the difference between the maximum and the minimum of the CR's for a set of the configurations represented by the same symbol, K→L or K*. One or more significant configurations may then be found in the set of the configurations with a large δ. Tentatively 0.05 was chosen as the critical value, δ_c. A second critical value, CR_c, has been used. Whether $\delta > \delta_c$ is not important if each configuration in a set has a small CR or contributes little to the corresponding molecule. No account has been taken of the sets of configurations in which all CR's are smaller than $CR_c(=0.2)$, even if $\delta > \delta_c$.

Results

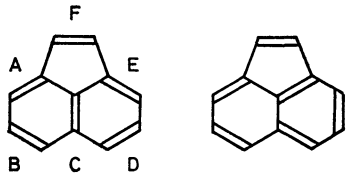
The main purpose of this paper has been to present a procedure which allows a numerical examination of the qualitative many-system interaction theory[20,21] applicable to polycyclic π conjugated molecules where many subsystems interact with one another. A sophisticated molecular orbital calculation was not necessary. The HMO method was employed.

TABLE 1. KEKULÉ INDICES[a]

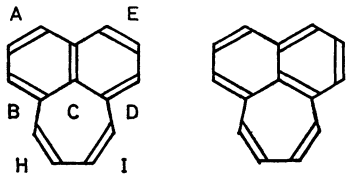
	a	b	c
1	0.299	0.257	
2	0.255	0.219	
3	0.264	0.225	0.000
4	0.159	0.140	0.098
5	0.185	0.160	0.000

a) See the definition in the text.

The Kekulé indices of the possible structures of **1**—**5** were calculated and are listed in Table 1. The values show that the main Kekulé structures contain benzenoid ones, **1a**, **2a**, **3a**, **4a**, and **5a**, in both six-membered rings of the naphthalene cores. The contribution from any quinonoid structure is small. A further important implication is found in the Kekulé indices of **3c**, **4c**, and **5c**. These structures should contribute more or less if the molecules enjoy the peripheral delocalization of electrons; a complete delocalization gives the equivalent Kekulé indices for **a** and **c**. The zero values for **3c** and **5c** indicate the absence of peripheral delocalization in **3** and **5**, while a non-zero value (0.098) implies that the electrons in **4** delocalize to some degree.



1a **1b**



2a **2b**

The CR's of the transferred configurations are listed in Table 2; those of the locally excited configurations have been omitted since they are much smaller (<0.069) than CR_c. Table 2 shows that the degree of electron shift depends on the distance between the ethylenic units where the shift occurs. The CR's for the adjacent-unit shifts range from 0.265 (F→A of **3**) to 0.547 (B→A of **4**) while the maximum for the nonadjacent-unit shifts is 0.260 (H→A of **4**). This result may be explained in terms of the perturbation theory for many-system interactions.[20,21] The adjacent-unit shifts correspond to first-order mixing of the transferred configurations while the nonadjacent-unit shifts correspond to higher-order mixing.

In the Platt model, the intraannular cross-links in **3**—**5** are assumed to be small perturbations and the electron shifts from and to the central double bond are negligibly small. In the first-order approximation of the naphthalene-core conjugation the delocalization is

Table 2. Absolute values of the coefficient ratios[a)]

	1	2	3	4	5	δ[b)]
A → B	0.431	0.437	0.455	0.430	0.466	0.036
A → C	0.444	0.420	0.453	0.431	0.409	0.044
B → A	0.485	0.480	0.455	0.547	0.466	0.092
B → C	0.436	0.416	0.453	0.421	0.409	0.044
C → A	0.407	0.431	0.397	0.408	0.437	0.040
C → B	0.415	0.434	0.397	0.418	0.437	0.040
A → F	0.373		0.345	0.402		0.057
F → A	0.275		0.265	0.288		0.023
B → H		0.289		0.294	0.294	0.005
H → B		0.364		0.399	0.347	0.052
H → I		0.367		0.383	0.358	0.025
A → D	0.181	0.154	0.109	0.230	0.103	0.127
A → E	0.137	0.029	0.091	0.178	0.049	0.149
B → D	0.044	0.082	0.091	0.142	0.049	0.098
B → E	0.029	0.057	0.109	0.057	0.103	0.080
A → H		0.145		0.163	0.154	0.018
A → I		0.077		0.119	0.058	0.042
B → F	0.174		0.126	0.246		0.120
B → I		0.109		0.139	0.096	0.043
C → F	0.000		0.000	0.000		0.000
C → H		0.088		0.075	0.089	0.014
F → B	0.148		0.132	0.173		0.041
F → C	0.148		0.133	0.114		0.034
H → A		0.182		0.260	0.164	0.096
H → C		0.039		0.040	0.037	0.003
H → D		0.205		0.249	0.182	0.067
H → E		0.101		0.189	0.058	0.131
F → G			0.000			
F → H				0.112		
H → F				0.202		
H → J					0.011	
H → K					0.060	

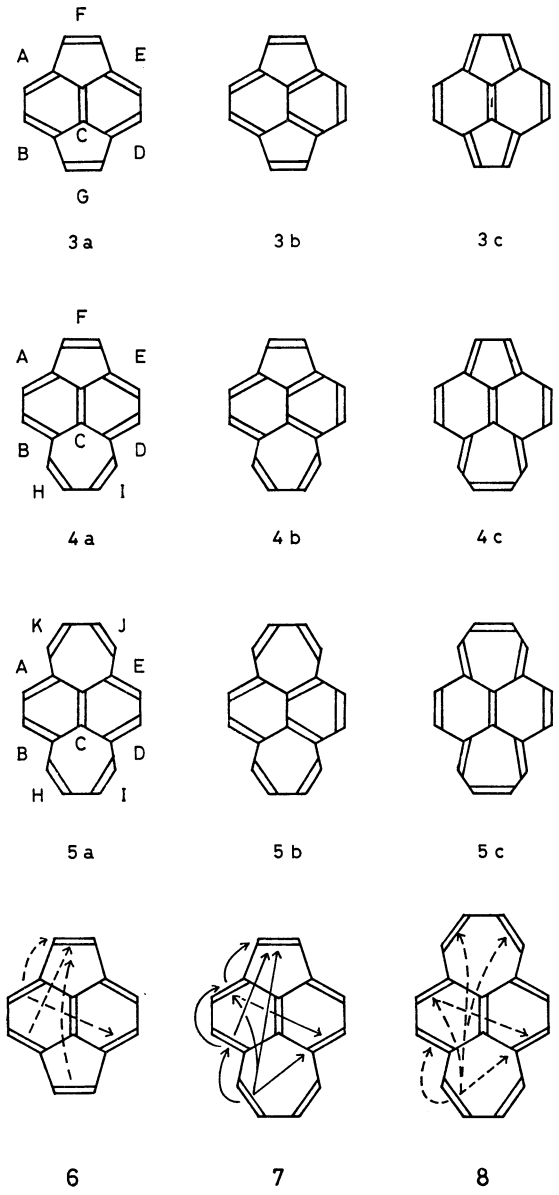
a) $|C_M/C_O|$. b) The difference between the maximum and the minimum values in the row (see the text).

discussed in terms of the adjacently transferred configurations. These configurations contain A→B, A→C, B→A, B→C, C→A, C→B, and the eqivalents. Each set of configurations has δ smaller than δ_c except in the case of B→A. The large δ value for B→A is due to an extraordinarily large CR for **4**. These results show that the electrons in **1**—**5** delocalize in the naphthalene cores to a similar degree although the B→A shift in **4** is appreciably enhanced. This argues against the Platt assumption that the intraannular cross-links are small perturbations.

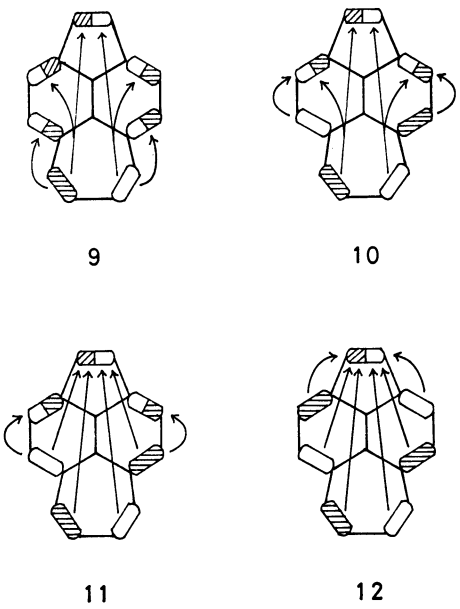
Secondly, adjacent-unit transfer has been restricted to five- and seven-membered rings, *i.e.*, A⇄F, B⇄H, and H⇄I. The CR's of these configurations are smaller (0.265—0.402) than those of the configurations corresponding to the electron shifts in the naphthalene cores (0.397—0.547). This shows that electrons delocalize in the five- and seven-membered rings to a lesser extent than in the naphthalene cores. The peri-bridge double bond, F, in the five-membered ring was found to accept rather than donate electrons (compare the CR's between A→F and F→A in **1**, **3**, and **4**). The butadienic parts (H or I) in the seven-membered ring tended to release electrons (compare the CR's between B→H and H→B in **2**, **4**, and **5**). An important observation was that the electron shifts to the five-membered ring and from the seven-membered ring were enhanced in **4** and depressed in **3** and **5** to an appreciable degree. Both A→F and H→B have δ values larger than δ_c while the others do not. The CR of A→F is largest in **4** and smallest in **3**, and the CR of H→B is largest in **4** and smallest in **5**.

Some distantly transferred configurations characterize the electronic structures of **3**—**5**. The B→F, H→A, H→D, and A→D configurations have δ larger than δ_c. They are enhanced in **4** but depressed in **3** and **5**. A significant difference in the transfers between the peri-bridges should also be noted. The H→F in **4** has a large CR while the F→G transfer in **3**, the H→J and H→K transfers in **5** have small ones. The ECAMSI results are summarized in **6**—**8**. The characteristic transfers are all enhanced in **4** (→) and depressed in **3** and **5** (⇢).

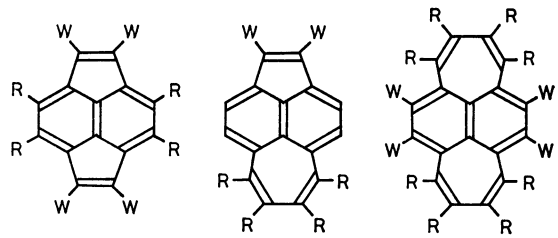
Now the cyclic electron delocalization on the molecular periphery will be examined. A cyclic delocalization among n units is described as a set of n−1 modes of transfer which have particular relations with one another.[21] Firstly, an adjacent-unit transfer mode is necessary. The transferred electron in the acceptor should be shifted further to a neighboring acceptor,



or the resulting hole in the donor should be supplied with an electron by a neighboring donor. These processes are expressed as the interaction of the first transferred configuration with the second configuration where an electron is shifted from the first donor to the second acceptor or from the second donor to the first acceptor. The second configuration is required to interact with the third one which satisfies a similar condition. The complete description ends with another adjacently transferred configuration. For **4** four electron-delocalizing modes (**9**—**12**)[21] can be constructed from the enhanced transfers (**7**). The shadow and the blank represent the orbital phase relation. The coupled shadow-blank and the single shadow or blank stand for the LUMO and the HOMO of the ethylenic π-bond units, respectively. It may be seen that **9**—**12** meet the orbital-phase continuity requirements for electron delocalization among many systems.[20,21] As a result, the peripheral delocalization is unequivocally confirmed by the ECAMSI calculations while the delocalization is depressed in **3** and **5**.



From this the effects of electron-releasing (R) and -withdrawing (W) substituents on the stabilities of **3**—**5** may be predicted. The delocalization in the naphthalene core has been found to be insensitive to the peri-bridges and is probably so to other substituents. The stabilities are, therefore, expected to depend on the peripheral delocalization. All electron-delocalizing modes, **9**—**12**, of **4** contain the diene bridge as a donor and the monoene as an acceptor, the peripheral parts on the naphthalene playing the dual roles. This suggests that the introduction of R into the diene and of W into the monoene (**14**) enhances the delocalization. In **3** the peri-bridges tend to accept electrons. The derivatives with R on the naphthalene core and with W on the bridges (**13**) may be more stable than the parent molecule. The electron-donability of the diene parts in **5** suggests that R-substituents on the dienes and W-substituents on the naphthalene core (**15**) stabilize the derivatives. Fortunately, the donor and acceptor groups arrange alternately along the periphery in the substituted molecules, **13** and **15**. Such alternation has recently been shown to make the cyclic conjugation discontinuous.[21] The degree of delocalization is not restricted by the Hückel rule; **13** and **15** avoid the disadvantage of 4n π periphery.



Discussion

Pullman *et al.*[16] calculated the HMO delocalization energy which predicted that **4** would be aromatic.

Zahradnik *et al.*[17] also drew a similar conclusion. Boekelheide and Vick[22] synthesized **4** and showed that **4** did not react with maleic anhydride under the conditions under which maleic anhydride gave the Diels-Alder adduct with **2**. Afterwards Jones *et al.*[23] concluded from the relatively narrow carbon-13 chemical shift range and the high-field shifts of the intraannular quarternary carbon atoms that **4** was highly conjugated on the periphery. The properties of **4**, predicted theoretically and suggested by the observed chemical reactivity and NMR shifts, seem to substantially confirm Platt's peripheral conjugation of $4n+2\pi$ electrons.

Yamaguchi and Nakajima,[18] using the semiempirical SCF LCAO-π-MO method, showed that the bond lengths of the naphthalene core of **4** were almost the same as those of the free naphthalene molecule, and that there was a marked bond fixation in the remainder of the periphery although the extent was smaller in **4** than in **3** and **5**. This implication is in good agreement with the ECAMSI results: (1) the degree and the mode of electron delocalization in the naphthalene core remains almost unchanged on the peri-bridging, (2) the degree of electron delocalization is smaller between the naphthalene core and the peri-bridges than in the naphthalene core, (3) electrons delocalize on the molecular periphery to an appreciable degree. As a result, the peripheral delocalization is significant but additional to the naphthalene-core delocalization.

The application of Platt's peripheral conjugation model suggests a description of **3** and **5** as antiaromatic perturbed [12]annulenes. This contradicts the prediction made by Craig's rules that they are aromatic. Using the HMO method, Zahradnik *et al.*[17] predicted that **3** and **5** were unstable. Pyracylene has been synthesized by Trost and Bright[24] while **5** is not yet known. The up-field shift of the NMR spectrum and the unusually low value of the first half wave potential were found and from this the conclusion drawn was that the peripheral model was a better representation than the peri-bridged naphthalene core model. Comparison of carbon-13 NMR spectra of **3** and its dihydro derivatives supported the indication that **3** exhibits paratropism.[25] The relative instability was suggested from the failure to isolate **3** and the reluctance of pyracene into **3**.[26] These results are compatible with Platt's model.

Lo and Whitehead[19] concluded from PPP-MO calculations that the most stable configuration of **3** corresponds to the peri-bridged naphthalene core model, a result similar to that of Yamaguchi and Nakajima.[18] The ECAMSI calculations also support this model. The degree and mode of electron delocalization in the naphthalene core are very similar to those in other molecules, the peripheral delocalization being appreciably depressed.

Conclusion

The ECAMSI calculations contribute to the understanding of the electronic properties of molecules as well as the nature of the interactions of many molecules. In this paper the polycyclic nonbenzenoid aromatics have been investigated. The ECAMSI calculations numerically showed how the polycyclic molecules were composed of the constituent ethylenic π bond units, *i.e.*, the kinds of electronic rearrangements occuring among the subsystems in the molecules. The calculations were successful in disclosing the mode of electron delocalization on the periphery and in estimating the degree of it.

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