An estimate of the rate constant for this dissociation process can be obtained in the following way. Under favorable conditions triplet–triplet energy transfer in solution is found to be diffusion controlled, indicating that the nearest neighbor triplet–triplet energy-transfer rate constant is probably on the order of 10^9–10^{10}/sec.[17] If we assume a similar nearest neighbor energy-transfer rate constant for the crystalline systems which we studied, then the rate constant for the dissociation of *p*-diiodobenzene triplet states must be $\simeq(4 \times 10^3) \times (10^9\text{–}10^{10})$/sec $= 4 \times 10^{12}$ to 4×10^{13}/sec. The lifetime of the lowest triplet state of *p*-diiodobenzene must correspondingly be 2.5×10^{-13} to 2.5×10^{-14} sec.

It was noted that a significant portion of the $S_0 \rightarrow T$ absorption of *p*-diiodobenzene is due to a broad unassigned continuum which extends to *longer wavelengths than the structured* absorption.[3] This continuum absorption presumably is not due to impurities since it also appears in highly purified samples. Apparently it corresponds to a $S_0 \rightarrow T$ transition which is different in character from the one which gives rise to the structured absorption. Since the $n \rightarrow \sigma^*$ transitions in the alkyl iodides have significant intensities as far out as 3500 A,[14,18] we suggest that the long-wavelength continuum absorption in *p*-diiodobenzene also be assigned as an $n \rightarrow \sigma^*$ transition. Such an assignment would also account for the diffuseness of the absorption and the dissociative character of the triplet state. Alternatively, and less likely, it is possible that the continuum absorption represents a transition to a second π,π triplet state which, in order to account for lack of structure, we must presume dissociates with a rate constant which is even larger than 4×10^{13}/sec.

As a result of our assignment of the continuum absorption, we are inclined to attribute the broadness in structured $S \rightarrow T_{\pi,\pi}$ absorption to mixing between the discrete vibronic levels of the $T_{\pi,\pi}$ state and the underlying continuum T_{n,σ^*} levels.

The high-resolution crystal absorption spectra of other iodobenzene derivatives have not yet been reported, but, in view of the unusual PE spectra which these compounds also exhibited, anomalies similar to those observed in the $S_0 \rightarrow T$ absorption spectrum of *p*-diiodobenzene may be anticipated.

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Alternating Molecular Orbital Delocalization Energies of Symmetrical Alternant Polycyclic Polyenes.

$4n + 2$, $6n + 2$, $8n - 2$, $8n + 2$, and $8n + 4$ Effects

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Abstract: For a systematic series of symmetrical alternant polycyclic polyenes, LCAO–MO resonance energies calculated at any level of elaboration are divided into two parts: the first a reference function, the second the original simple Hückel delocalization energy multiplied by a constant amplifying factor. The factor can be chosen to minimize and render unimportant the oscillatory component of the reference function. It follows that alternations at any level of elaboration can be at least adequately studied by means of SHMO theory. Three $8n$ effects and a triple $2 + 6n$ effect in selected series are described and shown to involve the same algebraic features as the $2 + 4n$ effect of the annulenes.

Effective elaboration of the simple Hückel molecular orbital (SHMO) method of calculating resonance energies of aromatic hydrocarbons is limited by restrictions imposed by the assumed LCAO wave function. One of the restrictive effects appears in the alternating calculated stabilizations of the annulenes and of systematic series of symmetrical alternant polycycles.

It is shown that quantitatively, for the annulenes, elaboration merely multiplies the amplitudes of the $2 + 4n$ alternation by a constant factor as large as 3.4. For other series, there must be for each structure a single average exchange constant that will lead to the correct delocalization energy. Since this average β_N cannot vary much more through the series than the β_N of the annulenes, the conclusion for the annulenes must be applicable with adequate accuracy to alternating effects in other symmetrical series.

With the aid of a factoring method described in a separate section, the alternations in four symmetrical series are shown to be essentially the original $2 + 4n$ effect appearing with different periodicities. This means that the dubiously low result for cyclobutadiene is carried into the calculations for the depressed members of all the series. For this reason, the general reliability of any LCAO method, regardless of corrective elaboration, becomes questionable.

General Validity of SHMO Alternations

For [N]annulene, as a regular polygon, the LCAO assumption leads to a cyclic secular determinant containing $N + 2$ disposable constants. The not unreasonable orthogonality approximation eliminates half of these constants and causes the cancellation of the coulombic constant α from the delocalization energy summation, leaving $N/2$ exchange constants with absolute magnitudes β, γ, δ, etc., for 1–2, 1–3, 1–4, etc., interaction that require adequate evaluation.

If β, γ, δ, etc., are taken to decrease rapidly with distance, it is reasonable to neglect δ and take γ to be less than $\beta/2$. In this range, γ removes the symmetry of the energy level pattern relative to the usual zero without resolving the degeneracies, but cancels out of the energy summation over the occupied states. This leaves only two exchange magnitudes, β_N for [N]annulene and β_r for the corresponding reference polyene, that are required to calculate the resonance or delocalization energy (E_r). In general, either or both of these β's will vary with N, in any systematic series of alternant polyenes, in a manner that depends upon the extent and kind of departures from SHMO theory employed in calculating E_r.

To facilitate the study of the $2 + 4n$ or any other alternation that may turn up, E_r is divided into two parts, as in eq 1. In this equation DE, the limiting

$$E_r/N = \phi_N + \beta_6(DE/N\beta) \qquad (1)$$

SHMO value of E_r, is proportional to β, the chosen exchange constant of SHMO theory, which makes DE/β a fixed property derived from the cyclic determinant. Division by N permits finite evaluation of the property in the region of high N where $DE/N\beta$, ϕ_N, and E_r/N all become constants at any level of elaboration. The subscript in β_6 serves as a reminder that an independent E_r of benzene is usually used in the determination of the β values.

Arbitrary choice of any constant β_6 will divide the $2 + 4n$ or other alternation in E_r/N between ϕ_N and the amplified $DE/N\beta$. For present purposes there will be an optimum β_6 that minimizes the alternations in ϕ_N, at a magnitude near that of the true magnitude of the exchange energy β_N evaluated for benzene. If β_N differs from β_6 by the amount ϵ_N, ϕ_N will contain an alternating component $\epsilon_N(DE/N\beta)$ which could be either enhanced or diminished by alternations in ϵ_N or β_r. Trial estimates with reasonable assignments of β_6, E_r, β_r, and ϵ_N indicate that the $2 + 4n$ deviations of E_r/N are likely to remain within 5% of those in $\beta_6(DE/N\beta)$ in any realistic elaborated LCAO method.

As an example, as shown in Table I, ϕ_N is calculated from the E_r of the SPO semiempirical method of Chung and Dewar.[1]

A sensitive plot of the ϕ_N of Table I against N reveals no alternation, but a negligible alternation can be detected by examining the differences between successive values. The nearly optimum β_6 was obtained from the ratios of the differences between successive E_r/N values to the corresponding differences in $DE/N\beta$. These ratios were nearly constant at two levels, which occurred alternately for positive and negative differences because of the slope and curvature of ϕ_N. β_6 was chosen as the mean value of the two nearly constant ratios.

Table I. ϕ_N (ev) from the Annulene SPO Resonance Energies of Chung and Dewar (β_6 = 2.119 ev)

N	E_r/N	$DE/N\beta$	ϕ_N
4	−0.3585	0	−0.3585
6	0.2197	0.3333	−0.4867
8	−0.0880	0.2071	−0.5269
10	0.0674	0.2944	−0.5565
12	−0.0582	0.2440	−0.5753
14	0.0134	0.2841	−0.5887
16	−0.0537	0.2568	−0.5979
18	−0.0123	0.2797	−0.6050

The single exchange magnitude β of the original SHMO theory is half the assigned E_r of benzene, *i.e.*, 1.318/2 or 0.659 ev, and the ratio β_6/β is 3.2. According to eq 1 and Table I, the $E_r/N\beta_6$ ratios obtained for the annulenes by the SPO semiempirical method deviate from a nonalternating reference funtion ϕ_N/β_6 by the SHMO ratios $DE/N\beta$, which represent an invariant property of the cyclic determinant at each N level. Consequently, the $2 + 4n$ alternations in $E_r/N\beta_6$ are the same as those of SHMO theory. The alternations in E_r and E_r/N, however, are 3.2 times those of SHMO theory.

The same conclusion is reached for each of the several other approximations to the E_r of the annulenes tabulated by Chung and Dewar, except that each approximation has its own different amplifying factor. The lowest factor is 1.2, the highest 3.4.

For a systematic series other than the annulenes, the problem of alternations in E_r relative to those in DE could involve the occurrence of larger variations in β_r and the mean effective value of β_N. When such variations are held within reasonable limits, they do not significantly decrease the accuracy with which alternations in $E_r/N\beta_6$ can be represented by those in $DE/N\beta$.

In the present study of the nature and interrelation of alternations in several systematic series of alternant polycyclic hydrocarbons, the $DE/N\beta$ values of SHMO theory are used throughout as adequately representative. They show the character of the alternation more clearly than the corresponding E_r/N values of more elaborate theories.

Within the LCAO framework, the $2 + 4n$ effect of the expanded annulenes is determined by the double degeneracies of the energy level pattern and their position on the energy scale. The above discussion shows that the alternations are not sensitive, except for the amplitude, to reasonable elaborations of the original SHMO theory. Unfortunately, there is no evident way to subject the alternations to a convincing theoretical or experimental test. The apparent instability of aromatic [$4n$] annulenes is negative evidence that does not exclude positive delocalization energies; practical instability could involve strain effects and be due to the availability of more stable conformations, structures, or decomposition products.

It is possible that the $2 + 4n$ alternations may represent a serious algebraic error of oversimplification that is introduced by the LCAO assumption and is not likely to be removed by any reasonable elaboration of the theory. Departure from the LCAO framework could change the energy level pattern enough to modify seri-

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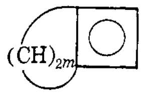
(1) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, 42, 756 (1965).

ously or even eliminate the 2 + 4*n* effect. For example, effective screening of the positive ring charge by individual electron pairs could lead to a vibrator-like pattern of nondegenerate states that would not show a 2 + 4*n* effect. Again, hybridization of the orbitals of the 4*n* structures to degenerate pairs at intermediate positions on the quantum number scale would eliminate the alternation. This latter suggestion is electrostatically reasonable.

The above speculations support a suspicion that the calculated stabilizations of the lower [4*n*]annulenes are seriously in error relative to the 2 + 4*n* structures. Further support for this supicion comes from the calculated valence-bond (VB) resonance energies of the annulenes which do not show a 2 + 4*n* effect. The evident association of the 2 + 4*n* effect with the high symmetry of the annulenes directs attention to the possibility of related alternations in other series of symmetrical structures. If the 2 + 4*n* effect is incorrect, related alternations in other symmetrical series are also likely to be wrong.

An indication of where to look for other alternations comes from the series obtained by converting each annulene except cyclobutadiene into a bicyclic alternant polyene by means of a single transannular 1↔4 bond



$m \geqslant 1$

The per electron SHMO stabilizations of the first several structures are shown in Table II in β units. All structures of the series have a twofold symmetry axis that bisects both rings, and only the first one, bicyclohexatriene, has a second perpendicular twofold axis and, of course, a center of symmetry. The first entry shows a symmetry depression; otherwise, there is no indication of an alternating effect. The alternation in the first three entries is opposite to the 2 + 4*n* effect.

Table II. Per Electron SHMO Delocalization Energies of 1,2-Substituted Cyclobutadienes

N	6	8	10	12	Large
m	1	2	3	4	$(N-4)/2$
$DE/N\beta$	0.276	0.298	0.284	0.283	0.273

It can be inferred that alternations of the per electron delocalization energy may occur in selected series of bicyclic and polycyclic structures with two perpendicular twofold symmetry axes. Calculations for several such series showing a triple 2 + 6*n* effect and three forms of an 8*n* effect are summarized below.

Factoring and Calculation

Beyond the monocycles and the structures of Table II, only series consisting of linear condensed successions of even-numbered rings with two perpendicular twofold symmetry axes are considered. In such cases the secular determinant for the N-center problem can be written at the outset as the vanishing product of four determinants of degree $(N + 2)/4$, $N/4$, or $(N - 2)/4$. These factors are used in tracing the relation of the alternations in the several symmetrical series to the 2 + 4*n* effect. Numerical extraction of the necessary roots from the factored secular equation by desk methods is simple and becomes more expeditious than computer procedures. To obtain the SHMO delocalization energy it is only necessary to expand half the determinantal factors and extract not more than $N/4$ roots. For example, in the diphenylene ($C_{12}H_8$) case it is sufficient to extract one root of each of two cubic equations.

With α the coulombic energy, $-\beta$ the exchange energy, E the energy, and x set equal to $(E - \alpha)/\beta$, the Nth degree secular determinant has a complete row of uniform main diagonal elements x with unit elements elsewhere corresponding to interaction of neighboring atomic orbitals. All other elements are set equal to zero. For this kind of vanishing determinant, the sum of the roots is zero. Demonstration of this practically obvious property can be made in a simple manner. The expanded determinant, in polynomial form, is the algebraic sum of $N!$ N-fold products with each product involving not more than one element from any row or column. Inclusion of one off-diagonal element therefore excludes two x's from the product. It follows that the coefficient on x^{N-1} in the polynomial form of the secular equation is zero. The completely diagonalized determinant, in terms of the roots x_i of the secular equation, is the product of N factors $(x - x_i)$. Conversion of this product to the polynomial includes multiplying x^{N-1}, in turn, by the negative of each x_i, so that the coefficient on x^{N-1}, which has just been shown to be zero, is the negative of the sum of the roots.

The structures chosen for study here can be formulated from the monocycles by introducing one or more transannular bonds parallel to two opposite peripheral bonds and therefore perpendicular to a twofold symmetry axis that does not pass through any atomic centers. For convenience, the atoms are numbered consecutively around the perimeter with atoms 1 and N on opposite sides of the symmetry axis. Arrangement of the determinant in the corresponding order places all the interaction elements due to the transannular bonds in the secondary diagonal, and yields a determinant that is symmetrical about both diagonals.

With this symmetry, and with N always even, the SHMO secular determinant (D) is readily factored into two determinants (D_+D_-) of degree $N/2$. Each element of column 1 is augmented by the element in the same row of column N, and each element of column N is reversed in sign and augmented by the element in the same row of column 1. According to the theory of determinants, the first of these operations by itself leaves D unchanged and the second by itself reverses the sign of D. Simultaneous performance of both modifications, however, doubles D and reverses the sign. Columns 2 and $N - 1$, 3 and $N - 2$, etc., are now modified in the same manner, and the rows of the resulting determinant are subsequently subjected to the same set of modifications. At this point the original determinant has been factored and multiplied by 2^N. Normalization requires dividing each element of both factors by 2.

As a consequence of the uniform main diagonal element x in D, each root from one factor is the negative of a root from the other, and the roots from either factor will reveal the entire energy level pattern. When one factor is expanded to the polynomial form, the number of positive roots is equal to the number of sign reversals between consecutive coefficients. The positive (or negative) roots are extracted, whichever are less numerous, and the sum of the negative (or positive) roots is obtained from the coefficient on $x^{(N-2)/2}$, the negative of the sum of the roots. The sum of the negative roots of both factors, which determines the DE, is now evident. The DE of a ten-center structure with the prescribed symmetry requires the extraction of two roots from a fifth degree equation.

Each structure of the several alternating series studied here has a second perpendicular twofold symmetry axis that may or may not pass through atomic centers. In either case, D_+ and D_- are symmetrical about both diagonals and subject to factoring as described for D into two determinants of degree $(N + 2)/4$, $N/4$, or $(N - 2)/4$. As a result, the original secular equation is factored as

$$D = D_+D_- = D_{++}D_{+-}D_{-+}\,D_{--} = 0 \qquad (2)$$

D_+ has $x + 1$ on the diagonal when the atom is linked to its reflector across the primary symmetry axis, otherwise x, and contains two complete rows of unit interaction elements adjacent and parallel to the main diagonal, with all remaining elements zero. D_- is formulated from D_+ by replacing each diagonal element $x + 1$ by $x - 1$.

For a $2 + 4n$ structure, the degree of D_+ is odd, and that of the reflecting factors D_{++} and D_{-+} is $(N + 2)/4$ while the degree of the reflectors D_{+-} and D_{--} is $(N - 2)/4$. The central row and column are not modified in the factoring operations, and the elements of the central column are not divided by 2 in the normalization.

For anthracene, as an example

$$D_{++} = \begin{vmatrix} x+1 & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x+1 & 2 \\ 0 & 0 & 1 & x \end{vmatrix} = (x^2 - 2)(x^2 + 2x - 1) = 0$$

$$(3a)$$

$$D_{+-} = \begin{vmatrix} x+1 & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x+1 \end{vmatrix} = (x^2 - 1)(x + 2) = 0$$

D_{++} is the corner quartic minor from D_+ with one off-diagonal element doubled, and D_{+-} is the unchanged corner cubic from D_+. In the anthracene case, D_{+-} is the D_+ of the benzene solution.

For a $4n$ structure the degree of D_+ is even and that of all four factors of D is $N/4$. D_{++} reflects D_{--}, and D_{+-} and D_{-+} are reflectors. For diphenylene, as an example

$$D_{++} = \begin{vmatrix} x+1 & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x+2 \end{vmatrix} = x^3 + 3x^2 - 3 = 0$$

$$(3b)$$

$$D_{+-} = \begin{vmatrix} x+1 & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x^3 + x^2 - 2x - 1 = 0$$

In D_{++} the lowest corner element of the lead cubic minor of D_+ has been increased by unity, and in D_{+-} the same element has been decreased by unity. The single positive roots of the two cubics are, respectively, 0.878 and 1.248, and the DE in β units is $2[3 + 1 + 2(0.878 + 1.248)] - 12 = 4.504$, a well-known result.

The D_{++} and D_{+-} of eq 2 can be written down at the outset, and the DE calculation will require the extraction of not more than $N/4$ roots (three for anthracene, $N/6$ for diphenylene).

Under these circumstances, calculations of the values tabulated here have been made by desk methods, since computer methods would involve a waste of time. A considerable fraction of the tabulated values have appeared before in the literature as DE or DE/β values. Because of the simplicity of computation, they have all been independently recalculated for present purposes.

The Alternating Series

Annulenes (Polymethines), $C_{2m}H_{2m}$. For these structures, it is well known that with the substitution $x = -2 \cos \theta$, the HMO secular equation reduces to $\cos N\theta = 1$ and the roots x are the quantities $-2 \cos (2\pi n/N)$ obtained with any N consecutive integers n.

The terminal roots at ±2 can be factored out for the monocycle in the same manner as for the linear crystal[2] to give, for the secular equation, with the substitution

$$x = -2 \cos \theta$$

$$D = D_+D_- = (x^2 - 4)E^2_{(N-2)/2} = (x^2 - 4) \sin^2 (N\theta/2)/\sin^2 \theta = 0 \qquad (4)$$

The E determinant has x at each main diagonal position, two complete rows of unit elements adjacent and parallel to the diagonal, and all other elements zero. The equation calls for degenerate pairs at $\theta = 2\pi n/N$ with the integer n in the range $1 \leqslant n \leqslant (N - 2)/2$. Equation 4 proves that $\cos N\theta = 1$ for even N and sets up the form for a general solution for the "ladder" series discussed below.

Each electron in an occupied level at the angular position θ contributes $(2 \cos \theta - 1)\beta$ to the calculated DE, which then becomes the sum of these quantities over the angles in the first quadrant. At very high N the ratio $DE/N\beta$ is the integrated average of the function $(2 \cos \theta - 1)$ over the first quadrant. The limiting value $(4 - \pi)/\pi$ or 0.2732 is approached from above by the $[2 + 4n]$annulenes and from below by the $4n$ structures.

For N greater than 20, $0.2732N\beta$ is a good first approximation to the SHMO delocalization energy of any higher alternant monocycle. This can be corrected empirically, adequately for a $2 + 4n$ structure and quite accurately for a $4n$ structure, by adding or subtracting $4\beta/N$.

Ladder Series, $C_{2m}H_4$. This series is formulated by introducing the maximum number of parallel transannular bonds into a monocycle to set up a condensed linear succession of four-membered rings. For the resulting ladder-like structures D_+ has the form of the E determinant of eq 4, except that the uniform diagonal element is now $x + 1$ instead of x. In D_- the diagonal element is $x - 1$.

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[2] J. O. Halford, *J. Chem. Phys.*, **19**, 1375 (1951).

Table III. Per Electron SHMO Delocalization Energies in the "Ladder" Series, $C_{2m}H_4$. The 2 + 6 n Effect

N	4	6	8	10	12	14	16	18	20	22	38
$DE/N\beta$	0	0.276	0.309	0.293	0.350	0.361	0.353	0.377	0.382	0.378	0.391

With the substitutions $x + 1 = -2\cos\theta$ in D_+ and $x - 1 = -2\cos\theta$ in D_-, the x values for the ladders are given by

$$x = -2\cos\theta \pm 1 \text{ with } \sin[(N + 2)/2]\theta/\sin\theta = 0 \quad (5)$$

The roots occur at θ equal to $2\pi n/(N + 2)$ with all x values included for n, an integer, in the range $1 \leqslant n \leqslant N/2$. For each such θ there are two x values, at $-2\cos\theta \pm 1$. With N always even, the solutions for θ occur in matched pairs, at θ and $\pi - \theta$. At each θ there are two states separated by two units on the x scale. Both states are occupied, at $-2\cos\theta \pm 1$, only if θ is less than $\pi/3$, and the matching states with θ between $2\pi/3$ and π are unoccupied.

When θ lies between $\pi/3$ and $2\pi/3$ the matching states with $x = -2\cos\theta - 1$ at θ and $\pi - \theta$ are both occupied but those with $x = -2\cos\theta + 1$ are all in the unoccupied region. For two matched occupied states in this region of θ, the contribution to the delocalization energy, with m electrons in each state, is

$$\{2m - m[2\cos\theta + 2\cos(\pi - \theta) + 2]\}\beta = 0 \quad (6)$$

Consequently the states with θ values between $\pi/3$ and $2\pi/3$ do not contribute to the SHMO delocalization energy.

A pair of states with a common θ value less than $\pi/3$ and with $x = -2\cos\theta \pm 1$ will contribute to the SHMO delocalization energy at the average rate per electron of $(2\cos\theta - 1)\beta$, the same as in the monocycles. The limiting per electron contribution at high N for this group of states, by integration over θ from 0 to $\pi/3$, is $(3^{3/2} - \pi)\beta/\pi$. This is the average contribution of the $2N/3$ contributing electrons. The per electron value for all the electrons is two-thirds of the above quantity, or $(2 \times 3^{1/2} - 2\pi/3)\beta/\pi = 0.4360\beta$, a little more than 50% greater than the limit for the monocycles. Calculated per electron stabilizations are all below this limit, evidently because of the absence of zero θ from the solutions of eq 5.

The SHMO delocalization energy of a ladder is, very simply, 8β times the sum of the quantities $(\cos\theta - 0.5)$ over all θ values $2\pi n/(N + 2)$ from $2\pi/(N + 2)$ to $\pi/3$. For the bicyclic six-membered ladder, this is $8\beta \times 0.2071 = 1.657\beta$ and for the eight-center ladder it is $8\beta(\cos 36° - 0.5) = 2.472\beta$. If $(N + 2)$ is an integral multiple of 3, so that $\pi/3 = 2\pi n/(N + 2)$, it follows that $N = 6n - 2$, with x values from the angles at $\pi/3$ and $2\pi/3$ of 2, 0, 0, and -2. In common with the $4n$ monocycles, the $6n - 2$ ladders include the entire cyclobutadiene pattern and show corresponding depressed SHMO delocalization energies. For $6n$ and $6n + 2$ ladder structures the SHMO stabilizations lie on smooth curves at higher levels, each curve retaining to a degree the features of the curve for $2 + 4n$ monocycles.

For the $2 + 4n$ monocycles, the θ value of the highest filled states is short of the limiting value $\pi/2$ by the interval π/N, resulting in a decreased average x value for the occupied states. Correspondingly, the highest θ involved in the $6n$ ladders is short of the limiting $\pi/3$ by one-third of the interval $2\pi/(N + 2)$, and the relatively stable $6n + 2$ ladders show a corresponding deficiency of two-thirds of the interval.

Per electron SHMO ladder delocalizations fall on three smooth curves with increasing N, with the curve for $6n + 2$ structures highest and that for $6n - 2$ structures lowest. In the intervals from $6n - 2$ to $6n$ and $6n$ to $6n + 2$, the per electron value increases, but a decrease occurs in each change from $6n + 2$ to $6n + 4$ or $6(n + 1) - 2$. This produces a $6n + 2$ alternation involving three classes of structures, within each of which, without any alternation, the structures have alternately $4n'$ and $2 + 4n'$ centers. All patterns for the least stable $6n - 2$ structures inherit the entire cyclobutadiene level system.

The approach to the calculated limit for high N at 0.436β per electron is relatively slow with the value reaching 0.419 for N at 70($6n - 2$) and 0.422 for N at 78($6n$). The per electron SHMO delocalization energies of the first several ladders are shown in Table III.

Anthracene Series, $C_{4m+6}H_{4m+2}$. Anthracene is the principal member of a series consisting of a condensed linear succession of three even-numbered rings in the form of a symmetrically substituted benzene ring. The ring-size successions are 4–6–4, 6–6–6, 8–6–8, . . ., $(2m + 2)$–6–$(2m + 2)$. For this series the product of the factors D_{+-} and D_{--} (eq 2) is the complete solution for the $2m + 2$ monocycle. Between successive members of the anthracene series, m increases by one unit and N by four. Consequently the $2m + 2$ monocycle involved is alternately a $4n$ and a $2 + 4n$ structure, and the anthracene series inherits the $2 + 4n$ effect, but now on a cycle of 8 units in N. All members of the series are $2 + 4n$ structures, but the calculated stabilizations are enhanced for $8n' - 2$ structures and depressed for $8n' + 2$ cases.

Table IV shows the calculated SHMO per electron delocalization energies for the first several members of the anthracene series. Obviously the values for the more stable $8n - 2$ cases must approach from above the same limit as the monocycles at 0.2732. The depressed $8n + 2$ values must also approach the same limit.

Table IV. Per Electron SHMO Delocalization Energies in the Anthracene Series $C_{4m+6}H_{4m+2}$. The $8n - 2$ Effect

N	10	14	18	22	26
$DE/N\beta$	0.268	0.380	0.302	0.333	0.310

Diphenylene Series, $C_{4m}H_{4m-4}$. Diphenylene, $C_{12}H_8$, is the principal member of a series consisting of a condensed linear succession of three even-numbered rings in the form of a symmetrically substituted cyclobutadiene. The ring-size successions are 4–4–4, 6–4–6, 8–4–8, . . ., $2m$–4–$2m$. The factors D_{++} and D_{+-} of eq 2 for this series are, successively, similar perturbations of the D_+ factors of the $2m$ monocycles which apparently still contain the major part of the $2 + 4n$ effect. As a result the SHMO stabilization for odd m

is relatively greater than that for even m, and an alternation again occurs on a cycle of 8 in N, as shown in Table V.

Table V. Per Electron SHMO Delocalization Energies in the Diphenylene Series, $C_{4m}H_{4m-4}$. The $8n + 4$ Effect

N	8	12	16	20	24
$DE/N\beta$	0.309	0.375	0.309	0.332	0.301

Although all members of this series have $4n'$ centers, those with $8n + 4$ centers are alternately more stable than the $8n$ structures. The eight-center structure, a depressed $8n$ member of the diphenylene series, is one of the most stabilized $6n + 2$ ladders. For this series, the limit at high N is again the 0.2732 calculated for the monocycles.

The relation of the $8n + 4$ alternation to the $2 + 4n$ effect of the monocycles is indirect but still traceable. D_{++} and D_{+-} of the N-membered structure are simple perturbations of the D_+ factor of the $N/2$ monocycle. In every case the perturbations add a substantial increment to the per electron value of the related $N/2$ monocycle. The increments alternate in the direction opposed to the $2 + 4n$ effect of the related monocycles, but only enough to damp out a relatively small fraction of the monocycle alternation. The remaining major part of the $2 + 4n$ effect is then inherited by the diphenylene series.

Naphthalene Series, $C_{4m+2}H_{4m}$. Each member of this series, like naphthalene, is an alternant $2+ 4\,n$ bicyclo-[$2m.2m.0$]polyene, with m any positive integer. The succession of even-numbered rings is ($2m + 2$)–($2m$ 2), that is, 4–4, 6–6, 8–8, etc. The per electron HMO delocalization energy shows a marked alternation on a cycle of 8 in N, as illustrated in Table VI.

Table VI. Per Electron SHMO Delocalization Energies in the Naphthalene Series, $C_{4m+2}H_{4m}$. The $8n + 2$ Effect

N	6	10	14	18	22
$DE/N\beta$	0.276	0.368	0.293	0.314	0.289

The ultimate per electron value at high N in the naphthalene series is again 0.2732, the same as for the monocycles. Inheritance of the alternating effect from the $2 + 4n$ effect of the monocycles is again indirect but traceable. For this series, the factors D_{+-} and D_{--} are exactly the same as those of the perimeter $2 + 4n$ monocycle $C_{4m+2}H_{4m+2}$, and yield for the roots one component of each of the degenerate pairs of the monocycle pattern. D_{++} and D_{-+}, however, are simple perturbations of the D_+ and D_- factors of the lower $(N + 2)/2$ monocycles which are alternately $4n$ and $2 + 4n$ structures. In each case the perturbations add an increment to the per electron delocalization energy calculated for the related $(N + 2)/2$ monocycle. The increments alternate in the direction opposed to the $2 + 4n$ effect but only enough to cancel out a relatively small fraction of the monocycle alternation. The remaining major part of the $2 + 4n$ effect of the related $(N + 2)/2$ monocycles is inherited by the naphthalene series.

Analysis of the patterns of the naphthalene series from another point of view is of some interest. In each case, the pattern is that of the perimeter monocycle with $(N + 2)/4$ of the occupied states perturbed, alternately upward and downward on the energy scale and by approximately equal distances. When the number of perturbed states is odd, the stabilizing perturbations predominate, but, when this number is even, the perturbations tend to cancel and leave the result close to that of the perimeter monocycle. For naphthalene, with three perturbed occupied levels, the per electron increase above cyclodecapentaene is 0.074, while for the following 14-center case, the corresponding increase is only 0.009.

Discussion

In three of the five alternating series discussed here, the cyclobutadiene levels appear unchanged in the SHMO solutions for all structures of minimal calculated stability. In the other two series the level pattern of each depressed member includes one or two moderate perturbations of the pattern of a lower $4n$ monocycle. Since the [$4n$]annulene pattern always contains the cyclobutadiene levels which, when moderately perturbed, will still contribute very little to the DE, the depressions in the naphthalene and diphenylene series are merely somewhat less directly inherited from cyclobutadiene.

Algebraic limitations imposed by the assumed LCAO wave function cause the SHMO alternations, in amplified form, to comprise the preponderant part of the alternating effect obtained with elaborated LCAO procedures.

Calculated resonance energies of a large number of symmetrical structures are thus affected by the inclusion of the cyclobutadiene SHMO result which, to say the least, is dubious. The degree to which perturbations of the cyclobutadiene result might affect the calculations for less symmetrical structures is at present a matter for speculation.

These considerations bring into question the general validity of any LCAO procedure, regardless of the degree of corrective elaboration.

While the tabulated SHMO delocalization energies provide valid illustrations of the alternating effects, it is generally agreed that they are not quantitatively reliable for predicting stability. It is true, however, that a high enough calculated SHMO stabilization energy can be indicative of probable stability. The minimum significant DE value, however, is not readily determined and is likely to vary with the number and size of the rings condensed into the structure. In spite of their high DE values, the heavier ladders are probably destabilized by a four-membered ring effect. Some of the structures with large rings may be stable enough in the aromatic form, but should be even more stable in nonaromatic less strained conformations.