

occurs for hydrogen abstraction reactions by fluorine and in substitution at silicon. In this case, silicon is large enough to accommodate five atoms around it at the transition state with a minimum of steric repulsion, and thus the actual barrier is fairly low. The spurious repulsions thus result in the bond being formed being much too long at the transition state and the bond being broken being much too short. This distortion of the transition-state geometry appears to occur for many strongly exoergic reactions. In the case of substitution at carbon, there is a substantial actual activation barrier because of its smaller size, so that the spurious repulsions at longer distances do not make much of a contribution to the overall predicted activation energy. Nevertheless, MNDO compares very favorably with good ab initio calculations for predicting reaction energies, particularly in the analysis of trends in related series of compounds. If one is careful to take into account these known discrepancies, MNDO can be useful in modeling large silicon-containing molecules.

For the cases of fluorine atom attack on methane, we predict much easier abstraction to form HF than substitution. For attack on silane, either substitution or abstraction should be quite easy.

For fluoride attack on methane, again abstraction is much more likely, although not as likely as in the neutral fluorine atom case. Fluoride attack on silane is complicated by the formation of a stable, trigonal-bipyramidal intermediate that will persist, at least in solution. If enough energy is available to decompose this complex, both substitution and abstraction should be quite easy. In general, the ease of substitution in the silicon case reflects both the strength of the Si-F bond and the stability of pentacoordinate silicon relative to carbon.

Acknowledgment. We thank Professor Michael J. S. Dewar of the University of Texas, Austin, for many helpful discussions. Two of us (M.S.G. and K.K.B.) acknowledge the computer time made available by the North Dakota State University Computer Center. The work was supported in part by grants (to M.S.G.) from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (No. CHE-8309948).

Registry No. F, 14762-94-8; F⁻, 16984-48-8; CH₄, 74-82-8; SiH₄, 7803-62-5.

The Structure Corresponding to the Reference Polynomial of [N]Annulene in the Topological Resonance Energy Theory

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Abstract: A directed weighted graph for [N]annulene, G1', is studied in which directed edge $r \rightarrow s$ is weighted $\exp(iv_{rs})$. It is shown that an appropriate choice of v_{rs} gives "reference" [N]annulene in the topological resonance energy theory. The relationships are discussed between Hückel, "reference", Möbius, and field-perturbed [N]annulenes. The analytical expression for the eigenvalues of the adjacency matrix of G1' is given, which allows one to get a mnemonic device for obtaining the roots of the reference polynomial of [N]annulene.

The topological resonance energy (TRE)¹⁻⁴ is known to be an excellent index for aromaticity of conjugated molecules. The clue to the success of the TRE theory is the mathematical definition of the reference structure. The coefficient of the reference polynomial is computed by dropping all Sachs graphs with cyclic components. So the reference polynomial of a conjugated system is considered to be the characteristic polynomial of the hypothetical "acyclic polyene-like" reference structure. The TRE value of a system, i.e., the difference between the total π -electron energy of the system and that of its reference structure, reflects the degree of π -electron cyclic delocalization arising from the presence of rings in the structure. London susceptibility (and ring current), which has been used as a criterion of aromaticity,^{5,6} is also closely related to the presence of ring.⁷⁻¹⁰

Since the definition of the reference polynomial was purely combinatorial in nature, it was not evident what was the adjacency matrix corresponding to the "structure" of the reference polynomial until Aihara,¹¹ Schaad et al.,¹² and Graovac¹³ obtained the adjacency matrices corresponding to the reference polynomials for a few simple systems. However, their purpose was the proof that the roots of the reference polynomial are real.^{14,15} So the properties of the matrices have not been discussed sufficiently.

All information on the physical property of a system is involved in the adjacency matrix because it reflects the structure of the system. Therefore, it is very important to study the properties of the matrix (and the graph) corresponding to the reference polynomial. In the present paper a directed edge-weighted graph for [N]annulene will be studied in detail, which is slightly more general than the graphs given by Aihara, Schaad et al., and Graovac. The investigation of the graph will clarify some prop-

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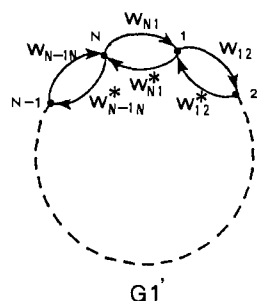


Figure 1. Directed edge-weighted graph G_1' .

erties of the reference "structure" of annulene. The results will deepen one's understanding of the concept of aromaticity.^{16,17}

Directed Edge-Weighted Graph and "Reference" Annulene

Consider a directed edge-weighted graph G_1' shown in Figure 1, in which the directed edge $r \rightarrow s$ is given weight $w_{rs} = \exp(i\nu_{rs})$. Now we assume that

$$v_{sr} = -v_{rs} \quad (1)$$

which ensures that the adjacency matrix of G_1' , $A(G_1')$, is Hermitian and hence its eigenvalues are all real. The graphs for Hückel and Möbius¹⁸⁻²⁰ annulenes are a special kind of directed edge-weighted graph G_1' . If w_{rs} 's of all the edges are unity, then G_1' represents Hückel $[N]$ annulene, and if w_{rs} of one edge is -1 and those of other edges are unity, then G_1' represents Möbius $[N]$ annulene. Further, if²¹⁻²³

$$v_{rs} = (e/\hbar c)S_{rs}H \quad (2)$$

then G_1' represents the molecular graph for $[N]$ annulene in the presence of a uniform, external magnetic field H , perpendicular to the molecular plane. In eq 2 e , \hbar , and c are the usual fundamental constants with these symbols, H is the strength of the field, and S_{rs} is the signed area of the triangle formed by an arbitrary origin and bond $r-s$:

$$S_{sr} = -S_{rs} \quad (3)$$

It is easily seen that the weights w_{rs} have no effects on the reference polynomial of Hückel $[N]$ annulene, G_1 ,

$$R_{G_1'}(X) = R_{G_1}(X) \quad (4)$$

where $R_{G_1}(X)$ and $R_{G_1'}(X)$ are respectively the reference polynomials of G_1 and G_1' . Equation 4 also shows that the reference polynomial for Möbius annulene is identical with that for Hückel annulene.²⁴ The characteristic polynomial of G_1' is expressed as

$$P_{G_1'}(X) = R_{G_1'}(X) - w_{12}w_{23}\dots w_{N-1N} - w_{21}w_{32}\dots w_{NN-1} = R_{G_1}(X) - 2 \cos V_C \quad (5)$$

where we have used V_C defined by

$$V_C = v_{12} + v_{23} + \dots + v_{N-1N} \quad (6)$$

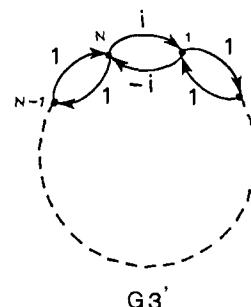


Figure 2. Directed edge-weighted graph for "reference" $[N]$ annulene, G_3' .

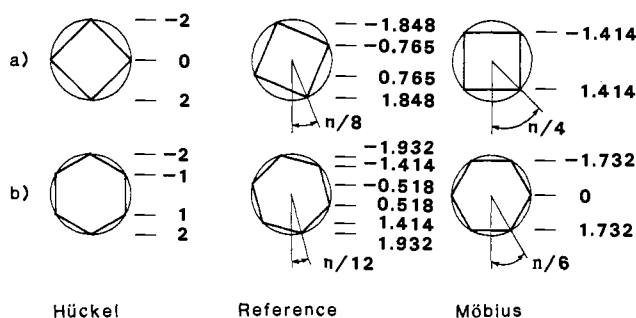


Figure 3. Mnemonic device for obtaining molecular orbital energies for Hückel, "reference", and Möbius $[N]$ annulenes (in units of β): (a) $[4]$ -annulene, (b) $[6]$ annulene.

Equation 5 shows that the difference between $P_{G_1'}(X)$ and $R_{G_1'}(X)$ is the sum of the contributions of two cycles associated with a circuit C in G_1 and dependent on only the value of V_C . If $V_C = \pi/2$, then the two cyclic components in Sachs graphs cancel in pairs. Hence the characteristic polynomial of G_1' with V_C equal to $\pi/2$ is identical with the reference polynomial of G_1 :

$$P_{G_1'}(X) = R_{G_1}(X) \quad (7)$$

Accordingly, we have found that $A(G_1')$ with V_C equal to $\pi/2$ represents a "structure" corresponding to the reference polynomial of $[N]$ annulene.

Concentration of Phase Factors

By using a unitary transformation devised by McWeeny²⁵ and later generalized by Gayoso and Boucekkine,²⁶ we can transform $A(G_1')$ into the adjacency matrix of a graph, G_2' , in which all edges except only one edge in G_1 have the weight equal to unity:²⁷

$$a'_{jj+1} = 1 = (a'_{j+1})^* \quad (8a)$$

$$a'_{1N} = \exp(iV_C) = (a'_{N1})^* \quad (8b)$$

where a'_{rs} denotes the element of the adjacency matrix of G_2' and $j = 1, 2, \dots, N-1$. The set of eqs 8 shows that all the phase factors in G_1' are concentrated in only one edge $1-N$. Now we can obtain an interesting graph for the reference structure of $[N]$ -annulene. Graphs G_1' and G_2' have the same characteristic polynomial and so G_2' with V_C equal to $\pi/2$ is also the graph representing the "structure" corresponding to the reference polynomial of $[N]$ annulene. Thus we have a graph for "reference" $[N]$ annulene, G_3' , shown in Figure 2, in which $1-N$ is weighted i or $-i$, according to two opposite directions.

The Eigenvalues of the Adjacency Matrix $A(G_1')$

The analytical expressions for the eigenvalues of Hückel, Möbius, "reference" $[N]$ annulenes have already been reported.^{28,29}

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However, we will try to obtain the analytical expression for the eigenvalues of $A(G1')$ because the expression gives the eigenvalues of the three systems by substituting appropriate values into parameter V_C in the expression. The expression may enable us to discuss from a unified point of view the correlation of individual energy levels for the three systems. However, we cannot obtain the eigenvalue of the adjacency matrix $A(G1')$ in an analytical form because it has no periodicity.

Let us consider a graph $G4'$ in which all the edges have the same parameter v . If $v = V_C/N$, then $A(G4')$ and $A(G1')$ have the same eigenvalues. Since $A(G4')$ has periodicity, we can obtain the eigenvalue of $A(G4')$ in an analytical form. The eigenvalues are easily obtained as follows:

$$x_J(v) = 2 \cos \{v + (2J \pi / N)\} \quad (9)$$

where $J = 0, \pm 1, \pm 2, \dots$. Here we wish to emphasize that the eigenvalue of $A(G4')$, $X_J(v)$, is a function of one parameter v and that by instituting the values $0, \pi/2N$, and π/N into v one can obtain the orbital energies for Hückel, "reference", and Möbius $[N]$ annulenes (in units of the resonance integral, β). Further, if

$$V_C = (e/\hbar c)SH \quad (10)$$

where S is the area $[N]$ annulene, then eq 9 gives the eigenvalues for $[N]$ annulene in the presence of the magnetic field H .

Frost and Musulin³⁰ have described a convenience device which allows one to write down quickly the orbital energies for Hückel annulene and Zimmerman^{31,32} that for Möbius annulene. The similar device for "reference" annulene can be obtained from eq 9. Figure 3 shows the example for [4]- and [6]annulenes.

From eq 9 we can also obtain the energy level correlation diagram for Hückel, "reference", and Möbius annulenes, which is very useful for the prediction on the allowedness of pericyclic reactions.^{33,34}

Concluding Remarks

In the previous sections we have discussed the connection (through variation of a single bond parameter) between the adjacency matrices (and the eigenvalue systems) for different types of $[N]$ annulene, namely, Hückel, "reference", Möbius and field-perturbed $[N]$ annulenes. The results are summarized as follows: the characteristic polynomial of the directed edge-weighted graph $G1'$ is dependent on only the value of V_C and the different choices of V_C lead to the different types of $[N]$ annulenes, that is, (a) if $V_C = 0$, then $A(G1')$ is the adjacency matrix of Hückel $[N]$ annulene; (b) if $V_C = (e/\hbar c)SH (<1)$, then $A(G1')$ is the adja-

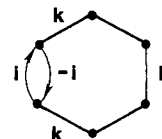


Figure 4. Directed edge-weighted graph for the reference structure for [6]annulene with bond alternation.

gency matrix of the field-perturbed $[N]$ annulene; (c) if $V_C = \pi/2$, then $A(G1')$ is the adjacency matrix of "reference" $[N]$ annulene; and (d) if $V_C = \pi$, then $A(G1')$ is the adjacency matrix of Möbius $[N]$ annulene.

The above results show that "reference" annulene, namely, the reference structure for annulene, is an intermediate system between Hückel and Möbius annulenes. This is true also for the eigenvalue systems of these systems (see eq 9). Moreover, it is seen that the external magnetic field brings Hückel annulene close to "reference" annulene.⁷

By using the Coulson's integral expression for TRE^{3,35} and eq 5 it is seen that the TRE value of $[N]$ annulene (the degree of the contribution of the circuit in $G1'$ to its stability) is a monotonical function of V_C ($0 < V_C < \pi$) with the maximum (or minimum) at $V_C = 0$ (or $V_C = \pi$). This leads to a unified understanding of Hückel^{36,37} and anti-Hückel rules^{4,19,20,31} for Hückel and Möbius annulenes.³⁸

It is desirable that the graph-theoretical reference structure has chemical reality. The directed edge-weighted graph, $G1'$, with the v_r parameters given by eq 2 itself is not unrealistic because one can obtain the graph with such parameters by applying the magnetic field to Hückel $[N]$ annulene. However, our graph for the reference structure for annulenes, $G3'$, does not have chemical reality. Another graph for the reference structure for annulene obtained by Herndon and Parkanyi³⁹ has chemical reality. Our approach naturally leads to a unified understanding of Hückel and anti-Hückel rules for monocyclic Hückel and Möbius annulenes, but their graph does not have a clear relationship with Möbius annulene.

It will be evident that our approach can be applied to monocyclic systems even with "acyclic" fragments and/or with bond alternations.⁴⁰ For example, Figure 4 shows a graph representing a reference structure for [6]annulene with bond alternation which also represents the homoconjugated system for *cis,cis,cis*-1,4,7-cyclonatriene in the crown form.⁴ However, the method in the present paper could not be applied to polycyclic systems except symmetrical bicyclic systems such as $[N]$ annuleno $[N]$ annulene.^{12,13}

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