Table III. Single Ion Heats of Solvation in HMPA and Heats of Solvation of Separated Ions in THF to Form Solvated Ions

substance	solvent	heat of solvation, kcal/mol	ref
Li^+	HMPA	−141	23
Na^+	HMPA	−108	23
K^+	HMPA	−93	23, 24
AN^-	HMPA	−72	this work
$Na^+ + AN^-$	THF	−186[a]	this work

[a] This is the heat of solvation of the gas-phase ion assuming that the heat of ion-pair dissociation in THF is about −7 kcal/mol.

TATB assumption.[24] With this assumption it is assumed that the enthalpy of solvation of Ph_4As^+ is the same as that of Ph_4B^-. Even though the validity of this assumption has been questioned, it is probably of use here where the effects are large.

In view of the fact that anion radicals are thought to remain practically unsolvated in HMPA,[4,5,23] this enthalpy is much more exothermic than was expected. The steric hindrance around the electropositive phosphorus center in HMPA does not prevent strong anion solvation. In fact, the heat of solvation of the anthracene anion radical in HMPA is about 86% of that for the sodium cation, Table III.

From this study, single ion heats of solvation of the cation and anthracene anion radical in THF are not possible to determine. This is the case, since $AN^-\cdot$ and the alkali metal cation are always associated (tightly ion paired) with each other in THF.[25] However, from the work of Hirota[25] and others it is clear that the ion association enthalpy for the Na^+ cation with $AN^-\cdot$ is no larger than 10 kcal/mol and is probably close to 7 kcal/mol. From this we conclude that the sum of the solvation enthalpies of Na^+ and $AN^-\cdot$ together must be about $-179 - 7 = -186$ kcal/mol. Thus the solvation enthalpies estimated via the calculations of Hush and Blackledge[3] are not nearly exothermic enough.

Other than our preliminary communication, this represents the first report of anion radical solvation enthalpies.[26]

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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Graph-Theoretical Formulation of London Diamagnetism

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Abstract: A graph-theoretical method is presented for estimating the London diamagnetism, i.e., the diamagnetic susceptibility arising from a cyclic conjugated system of an organic compound. This method is based on the generalized version of Sachs' graph-theoretical theorem, and enables one to save much labor which would otherwise be needed. Moreover, the present approach enables one to analyze London diamagnetism to extract information about the susceptibility contributions of individual π rings in a polycyclic conjugated compound. An illustrative application to biphenylene is described in conjunction with its aromaticity.

Introduction

The diamagnetic anisotropy of a cyclic conjugated compound arises primarily from ring currents induced in its π-electron system. This picture, first proposed by Pauling,[1] was formulated in quantum-mechanical terms by London in 1937.[2] Diamagnetism due to ring currents is then termed London diamagnetism. His molecular orbital (MO) method for conjugated hydrocarbons placed in a uniform magnetic field was an extension of the simple Hückel MO model.[3] The diamagnetic susceptibility due to ring currents is hereafter called the diamagnetic susceptibility of a conjugated system. It is an important quantity because of its close correlation with aromaticity.[4,5]

0002-7863/79/1501-5913$01.00/0

However, it has never been easy to calculate the susceptibility of a large cyclic (or heterocyclic) conjugated system directly from London's field-dependent secular determinant.[6,7] A rather brute-force expansion of the determinant has often been practiced when some symmetry considerations[8] were not applicable. Fortunately, this problem can now be treated by means of graph theory. As pointed out by McWeeny et al.,[9-11] the London theory of diamagnetism has various topological or graph-theoretical aspects. Mallion emphasized that some graph-theoretical ideas—notably those concerning circuits and spanning trees[12]—specifically underlie the ring-current concept.[11]

We recently found that a generalized version[13,14] of Sachs' graph-theoretical theorem[15] can be applied to London's secular determinant for any kind of conjugated system.[5] The determinant can now readily be expanded into a corresponding characteristic polynomial. In this paper, I would like to present a much simpler formula for calculating the susceptibility of a conjugated system by appropriately rearranging such a field-dependent characteristic polynomial. For the first time, this formula enables us to analytically estimate the susceptibility contributions of individual π rings in a polycyclic conjugated system.

Theory

Let us consider a polycyclic conjugated hydrocarbon with N sp^2-carbon atoms. A geometry of its conjugated system is a kind of molecular graph, and is denoted by G. London's secular determinant for a conjugated system G can be expanded into the following characteristic polynomial:[5]

$$P_G(X,H) = X^N + \sum_{k=1}^{N} a_k(H)X^{N-k} \tag{1}$$

where H is the magnitude of the component of the external magnetic field perpendicular to the molecular plane, and

$$a_k(H) = \sum_{t\in T_k} (-1)^{n(t)} \prod_{r_i} [2\cos(\Theta_{r_i}H)] \tag{2}$$

Here, T_k is a set of all possible Sachs graphs of G,[15] each containing k vertices (i.e., k atoms), and $n(t)$ is the number of components of a Sachs graph t; Θ_{r_i} is $(2\pi eS_{r_i}/hc)$, in which S_{r_i} is the area enclosed by the ith π ring of G, and e, h, and c are the standard constants with these symbols; r_i runs over all π rings found in the Sachs graph t.

Equation 1 can be rearranged, by analogy with Hosoya's way of expanding a Hückel secular determinant,[16] as follows:

$$\begin{aligned} P_G(X,H) &= R_G(X) - 2\sum_{i}^{G} R_{G-r_i}(X)\cos(\Theta_{r_i}H) \\ &\quad + 2^2 \sum_{i>j}^{G} R_{G-r_i-r_j}(X)\cos(\Theta_{r_i}H)\cos(\Theta_{r_j}H) - \ldots \end{aligned} \tag{3}$$

where $R_G(X)$ is a reference polynomial for G in our terminology,[5,17] $G - r_i$ is a subgraph of G obtained by deleting the ith π ring r_i and all the edges (i.e., π bonds) incident to r_i, and $G - r_i - r_j$ is a subgraph of G obtained by deleting a pair of disjoint π rings r_i and r_j and all the edges adjacent to r_i and/or r_j; the first summation is practiced over all π rings in G, and the second summation over all possible pairs of disjoint π rings in G. A reference polynomial for a conjugated hydrocarbon can be expressed simply as[17]

$$R_G(X) = X^N + \sum_{k=1}^{[N/2]} (-1)^k p(k) X^{N-2k} \tag{4}$$

where $p(k)$ is the number of ways of choosing k disjoint π bonds from G[16,18] and $[N/2]$ is the maximum integer not larger than $N/2$.

Since the applied magnetic field can be treated as a small perturbation,

$$\cos(\Theta_{r_i}H) \approx 1 - \frac{1}{2}\Theta_{r_i}{}^2H^2 \tag{5}$$

By applying this approximation to eq 3, the following expression can be deduced:

$$\begin{aligned} P_G(X,H) &= R_G(X) - 2\sum_{i}^{G} R_{G-r_i}(X)\left(1 - \frac{1}{2}\Theta_{r_i}{}^2H^2\right) \\ &\quad + 2^2 \sum_{i>j}^{G} R_{G-r_i-r_j}(X)\left(1 - \frac{1}{2}\Theta_{r_i}{}^2H^2\right)\left(1 - \frac{1}{2}\Theta_{r_j}{}^2H^2\right) \\ &\quad - \ldots \end{aligned} \tag{6}$$

Note here that[16]

$$\begin{aligned} P_G(X,0) &= R_G(X) - 2\sum_{i}^{G} R_{G-r_i}(X) \\ &\quad + 2^2 \sum_{i>j}^{G} R_{G-r_i-r_j}(X) - \ldots \end{aligned} \tag{7}$$

With this expression in mind, eq 6 can be reduced to a much simpler form:

$$P_G(X,H) = P_G(X,0) + H^2 \sum_{i}^{G} P_{G-r_i}(X,0)\Theta_{r_i}{}^2 \tag{8}$$

A field-dependent characteristic polynomial of a conjugated system G can thus be expressed in terms of field-free characteristic polynomials of its subsystems $P_{G-r_i}(X,0)$. As long as the magnetic field is weak, $P_G(X,H)$ is linear both in every $\Theta_{r_i}{}^2$ and in the field strength squared.

Consequently, London's secular equation for G can be written as

$$P_G(X,0) = -H^2 \sum_{i}^{G} P_{G-r_i}(X,0)\Theta_{r_i}{}^2 \tag{9}$$

When the unperturbed system does not have degenerate eigenvalues, the mth field-dependent eigenvalue (i.e., the mth root of eq 9) is expressible, to order H^2, in the form[2,6,9,19]

$$X_m = X_m{}^0 - H^2 \sum_{i}^{G} Q_{G-r_i}(X_m{}^0)\Theta_{r_i}{}^2 \tag{10}$$

where $X_m{}^0$ is the mth largest root of the field-free secular equation $P_G(X,0) = 0$, and

$$Q_{G-r_i}(X) = \frac{P_{G-r_i}(X,0)}{P_G'(X,0)} \tag{11}$$

Here, $P_G'(X,0)$ is the first derivative of $P_G(X,0)$ with respect to X. The total π-electron energy of a conjugated system is then

$$\begin{aligned} E_\pi(H) &= N\alpha + 2\beta \sum_{m=1}^{N/2} X_m \\ &= N\alpha + 2\beta \sum_{m=1}^{N/2} \left\{X_m{}^0 - H^2 \sum_{i}^{G} Q_{G-r_i}(X_m{}^0)\Theta_{r_i}{}^2\right\} \end{aligned} \tag{12}$$

where α is the Coulomb integral for a sp^2 carbon atom and β is the resonance integral between two bonded sp^2 carbon atoms.

Diamagnetic susceptibility of a conjugated system, χ_G, is given as the second derivative of the total π-electron energy with respect to H, i.e.,

$$\chi_G = \left[\frac{\partial^2 E_\pi(H)}{\partial H^2}\right]_{H=0} = -4\beta \sum_{m=1}^{N/2} \sum_{i}^{G} Q_{G-r_i}(X_m{}^0)\Theta_{r_i}{}^2 \tag{13}$$

It is now easy to evaluate the susceptibility of any conjugated system with this expression. Every $P_{G-r_i}(X_m{}^0,0)$ in eq 11 can readily be evaluated by constructing a secular determinant for a subgraph $G - r_i$. It is noteworthy that this final expression for χ_G is applicable not only to conjugated hydrocarbons but also to any heterocyclic systems.

In 1957, Hazato explicitly stated that the diamagnetic susceptibility of a polycyclic conjugated system is an additive function of its constituent π rings.[20] In accord with this, eq 13 can be written as

$$\chi_G = \sum_i^G \chi_{r_i} \tag{14}$$

where χ_{r_i} is the ith ring susceptibility defined by

$$\chi_{r_i} = -4\beta\Theta_{r_i}^2 \sum_{m=1}^{N/2} Q_{G-r_i}(X_m{}^0) \tag{15}$$

The quantity χ_{r_i} can reasonably be interpreted as the susceptibility contribution of the ith π ring. This aspect of χ_G indicates that a current induced in each π ring does not interfere with that in any other π ring at the limit of zero magnetic field even if both π rings share one or more π bonds.

From another point of view, the susceptibility χ_G can be regarded as an additive function of all the occupied molecular orbitals, namely

$$\chi_G = 2\sum_{m=1}^{N/2} \chi_{X_m} \tag{16}$$

where χ_{X_m} is the mth orbital susceptibility defined by

$$\chi_{X_m} = -2\beta \sum_i^G Q_{G-r_i}(X_m{}^0)\Theta_{r_i}^2 \tag{17}$$

The quantity χ_{X_m} can be interpreted as the susceptibility contribution of the mth molecular orbital.

When the unperturbed conjugated system has degenerate eigenvalues $X_{m^*}{}^0$, the characteristic polynomial is rewritten as

$$P_G(X,0) = U(X)(X - X_{m^*}{}^0)^2 \tag{18}$$

The field-dependent secular equation is then

$$U(X)(X - X_{m^*}{}^0)^2 = -H^2 \sum_i^G P_{G-r_i}(X,0)\Theta_{r_i}^2 \tag{19}$$

After a simple treatment of this equation, analogous to that of Pullman and Pullman,[6] the following eigenvalues can be obtained:

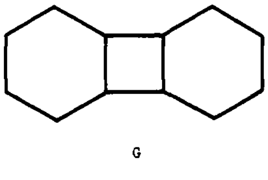
$$X_{m^*} = X_{m^*}{}^0 \pm \sqrt{-\frac{V(X_{m^*}{}^0)}{U(X_{m^*}{}^0)}}\,H + \frac{U'(X_{m^*}{}^0)\,V(X_{m^*}{}^0) - U(X_{m^*}{}^0)\,V'(X_{m^*}{}^0)}{2U(X_{m^*}{}^0)^2}H^2 \tag{20}$$

where

$$V(X) = \sum_i^G P_{G-r_i}(X)\Theta_{r_i}^2 \tag{21}$$

The field dependence of the other eigenvalues can be expressed in the form of eq 10, as before. The overall susceptibility χ_G of any conjugated system is given by twice differentiating the total π-electron energy with respect to H.

Application to Biphenylene



G

Table I. Subgraphs of G for Biphenylene

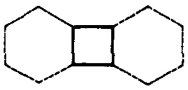
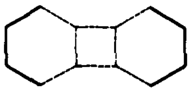
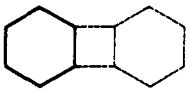
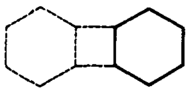
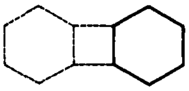
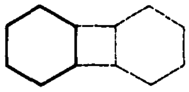
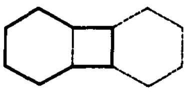
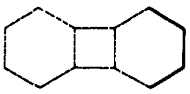
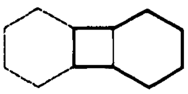
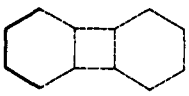
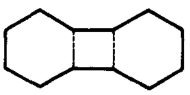
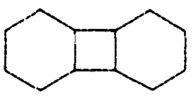
i	r_i	$G-r_i$	$P_{G-r_i}(X,0)$
1			$(X^4-3X^2+1)^2$
2			$X^6-6X^4+9X^2-4$
3			$X^6-6X^4+9X^2-4$
4			X^4-3X^2+1
5			X^4-3X^2+1
6			1

Table II. Orbital Susceptibilities and Orbital Resonance Energies of Biphenylene

m	X_m	χ_{X_m}/χ_0	RE_{X_m}, β
1	2.5321	0.224	0.144
2	1.8019	−0.237	−0.054
3	1.3473	−1.659	−0.256
4	1.2470	0.591	−0.037
5	0.8794	2.087	0.161
6	0.4450	−1.072	0.104

In order to see how the above formulation can be applied to polycyclic conjugated systems, let us calculate the susceptibility of a biphenylene conjugated system. A graph representing the conjugated system is here denoted by G. All the possible subgraphs needed for the χ_G calculation are listed in Table I, together with their characteristic polynomials. A field-free characteristic polynomial for an entire conjugated system of biphenylene is[16]

$$P_G(X,0) = X^{12} - 14X^{10} + 69X^8 - 154X^6 + 162X^4 - 72X^2 + 9 \tag{22}$$

The largest six eigenvalues, which correspond to the occupied molecular orbitals, are given in Table II. Since there are no degenerate energy levels in this compound, eq 9-13 are usable to calculate the susceptibility. The first derivative of eq 22 is

$$P_G'(X,0) = 12X^{11} - 140X^9 + 552X^7 - 924X^5 + 648X^3 - 144X \tag{23}$$

Using the numerical values for $Q_{G-r_i}(X_m{}^0)$ in Table III, the susceptibility of a biphenylene conjugated system G is evaluated in this manner:

$$\chi_G = -4\beta \sum_{i=1}^{6}\sum_{m=1}^{6} Q_{G-r_i}(X_m{}^0)\Theta_{r_i}^2 \tag{24}$$

Since the assumption has tacitly been made that there is no bond alternation in the conjugated system G, two hexagons and one tetragon in G are all assumed to be regular in shape. The ring areas are necessarily set in the ratio

Table III. A List of Numerical Values for $Q_{G-r_i}(X)$

X	$Q_{G-r_1}(X)$	$Q_{G-r_2}(X)$	$Q_{G-r_3}(X)$	$Q_{G-r_4}(X)$	$Q_{G-r_5}(X)$	$Q_{G-r_6}(X)$
X_1	0.0417	0.0056	0.0056	0.0018	0.0018	0.0001
X_2	−0.0156	0.0182	0.0182	−0.0086	−0.0086	−0.0048
X_3	0.1703	−0.1867	−0.1867	−0.1480	−0.1480	0.1286
X_4	−0.2749	0.1331	0.1331	0.2204	0.2204	−0.1768
X_5	0.0454	−0.0144	−0.0144	−0.0628	−0.0628	0.0870
X_6	−0.0093	0.1149	0.1149	−0.0209	−0.0209	−0.0470

Table IV. Ring Susceptibilities and Ring Resonance Energies of Biphenylene

i	χ_{r_i}/χ_0	RE_{r_i}, β
1	−0.113	−0.231
2	1.273	0.204
3	1.273	0.204
4	−0.625	−0.119
5	−0.625	−0.119
6	−1.316	−0.092

$$S_{r_1}:S_{r_2}:S_{r_3}:S_{r_4}:S_{r_5}:S_{r_6} = 0.3849:1.0000:1.0000:1.3849:1.3849:2.3849 \quad (25)$$

Accordingly,

$$\Theta_{r_1}{}^2:\Theta_{r_2}{}^2:\Theta_{r_3}{}^2:\Theta_{r_4}{}^2:\Theta_{r_5}{}^2:\Theta_{r_6}{}^2 = 0.1481:1.0000:1.0000:1.9179:1.9179:5.6877 \quad (26)$$

Let χ_G of benzene be denoted by χ_0, and the susceptibility χ_G thus calculated for biphenylene is $-0.1326\chi_0$. It is in good agreement with the value so far published for this compound ($-0.131\chi_0$).[6] For simplicity, χ_0 is taken as a unit of diamagnetic susceptibility in this paper; it is equal to $-0.2222\ \Theta_{r_2}{}^2\ \beta$, in which a factor $\Theta_{r_2}{}^2$ is the same as that for biphenylene.

On the other hand, Dewar-type resonance energies are $0.123\boldsymbol{\beta}$ for biphenylene and $0.273\boldsymbol{\beta}$ for benzene.[17,21,22] Here, $\boldsymbol{\beta}$ is the absolute value of β. These resonance energies are positive, indicating that these compounds are aromatic in Dewar's sense.[23] I previously pointed out that the sign of the susceptibility χ_G is an excellent indication of aromaticity.[5] However, this is not true for the present compound; the sign of χ_G for biphenylene is not identical with that of the resonance energy. Biphenylene is obviously one of the rare examples for which the sign of χ_G does not represent aromatic character.

The concept of partial resonance energy has once been introduced to estimate the aromaticity contribution of each π ring in a polycyclic conjugated system.[24] It is here termed the ith ring resonance energy (RE_{r_i}) when it is associated with the ith π ring. Ring resonance energies of biphenylene,[24] together with its ring susceptibilities, are reproduced in Table IV. It can therein be seen that the sign of every ring susceptibility exactly agrees with that of the corresponding ring resonance energy; both χ_{r_i} and RE_{r_i} obey Hückel's $(4n + 2)$ rule of aromaticity.[3] Although the overall resonance energy is not exactly an additive function of individual π rings,[24] the ring resonance energy is a good measure of aromaticity for each π ring.

However, it appears that susceptibilities of larger π rings are much more weighty than expected from the ring resonance energies. This is essentially due to the factor $\Theta_{r_i}{}^2$ imposed on χ_{r_i}. As shown in eq 26, this factor increases in proportion to the ring area squared. In contrast to χ_{r_i}, RE_{r_i} is free from any effect of the area of the ring concerned. Consequently, larger π rings contribute more to the susceptibilities, but less to the resonance energy. The magnitude of χ_{r_i} is necessarily in poor correlation with that of RE_{r_i}. The existence of two or more π rings in a conjugated system thus makes the overall susceptibility less correlative with aromaticity, although both quantities are directly related to the existence of the π rings. This constitutes the primary reason why the sign of χ_G for biphenylene is typically different from that of the overall resonance energy.

In this context, one attempt has so far been made to partition the susceptibility into individual contributions from its constituent π rings. Coulson et al. semiempirically estimated the π-electron contribution to the magnetic moment of each π ring and then the susceptibility assignable to each π ring.[25] In their model, constituent rings of biphenylene were one tetragonal and two hexagonal π rings only. However, the overall susceptibility somewhat deviated from a sum of the ring susceptibilities calculated by them. A deviation of 4.6% was found in the case of biphenylene.[25]

Orbital susceptibilities of biphenylene are presented in Table II. In parallel with the mth orbital susceptibility, the mth orbital resonance energy (RE_{X_m}) can be defined as the difference between the mth orbital energy of a conjugated system and the corresponding orbital energy of its reference structure.[26] For most compounds, RE_{X_m} is given as the difference between the mth orbital energies of a conjugated system and its reference structure. Therefore, the overall resonance energy can be expressed as a sum of the orbital resonance energies. However, as may be seen from Table II, correlation between χ_{X_m} and RE_{X_m} is not good; the sign of χ_{X_m} sometimes differs from that of RE_{X_m}. This is also due to the weights $\Theta_{r_i}{}^2$ imposed on the former quantity. If all the ring areas are set equal to some constant, the sign of χ_{X_m} can be adjusted to that of RE_{X_m} for all orbitals of biphenylene.

Finally, it goes without saying that, if actual bond alternation in biphenylene is taken into consideration, the overall susceptibility χ_G becomes positive in accord with the resonance energy.[27]

Concluding Remarks

An NMR criterion of aromaticity has widely been used according to which diamagnetic ring currents indicate aromaticity while paramagnetic ring currents indicate antiaromaticity.[28] However, no one had ever been able to explain why diamagnetism of a conjugated system is correlative with its aromaticity[29] until we recently demonstrated that the susceptibility of a conjugated system strongly reflects its conjugative stabilization.[5] The present study not only clarified the graph theoretical structure of London diamagnetism, but also showed that, at the level of constituent π rings (in Sachs' sense[15]), the magnetic criterion of aromaticity is identical with the energetic criterion. The overall susceptibility is exactly an additive function of constituent π rings. Since each ring susceptibility is proportional to the area of the π ring squared, the overall susceptibility is necessarily influenced by the areas of all the π rings concerned. Accordingly, the susceptibility-based criterion of aromaticity might be a bit less decisive for some polycyclic conjugated systems. It should be stressed that the simplicity and elegance of the Hückel MO model are mostly retained in the final expression of the susceptibility (eq 13).

Acknowledgment. The use of the facilities of the Hokkaido University Computing Center is gratefully acknowledged.

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Use of Configuration Selection Methods to Study the Sudden Polarization Effect

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Received April 4, 1979

Abstract: The variation of the dipole moment of twisted ethylene as a function of the angle of pyramidalization of one CH_2 group is determined for a variety of AO basis sets and levels of CI treatment. The results for moderate amounts of pyramidalization are seen to be strongly dependent on the choice of one-electron basis functions in the CI, although for still larger angles (20° and beyond) this effect becomes much less important. Configuration selection methods prove to be very effective in this investigation, making feasible the extension of such calculations to more chemically interesting systems than would otherwise be possible.

I. Introduction

The high polarizability of the lowest singlet excited states in hetero- and nonsymmetrical biradical systems is easily understandable from a physical point of view[2-5] and the possible experimental consequences of this phenomenon have received wide attention in recent years.[6-14] In discussing this effect it is obviously important to have quantitative information about the manner in which the electronic charge is redistributed as either the internuclear geometry of such biradicals is varied or the nature of their substituents is changed. It is therefore desirable that theoretical methods be developed which are capable of giving a reliable description of large charge displacements which occur as a result of a relatively small perturbation at one of the radical centers.

One of the simplest examples in which this "sudden polarization" effect can be studied is in the first two singlet excited states of twisted ethylene as one of its CH_2 groups is pyramidalized.[2b,5,15] The geometrical change in question is accompanied by a reduction in the molecular symmetry from D_{2d} to C_s,[5,15] and thus to describe the polarization effect properly it is necessary to achieve a smooth transition from the delocalized to the localized representation of a biradical (compare ref 16, 11, and 15). A proper description of the pyramidalization of ethylene places severe demands on the theoretical method employed since it requires an accurate determination of the balance between two highly polarizable centers which are at the same time only weakly interacting. In the framework of a general configuration interaction treatment these considerations imply that great care must be taken in the choice of the configuration space used in the calculations, including the one-electron basis from which the requisite determinantal functions are formed. On the other hand, if relatively flexible AO basis sets are to be used and more chemically interesting systems than ethylene are to be studied in future applications, it is clear that the extent of the CI must be kept as limited as possible, consistent with the above accuracy requirements. The present paper thus presents a series of truncated CI calculations using a variety of AO and MO (or NO) basis sets in order to describe the sudden polarization effect in the lowest two singlet excited states of ethylene, with the ultimate goal of being able to design practical theoretical treatments which are applicable to larger organic biradical systems.

II. Nonpyramidalized Twisted Ethylene Treated in C_s Symmetry

Because of the D_{2d} symmetry of 90° twisted ethylene none of the electronic states in this conformation can possess a

0002-7863/79/1501-5917$01.00/0