

Use of Semiempirical Models for Calculation of B Terms in MCD Spectra. I. General Results and the Pariser-Parr-Pople (PPP) Model for Nonalternant Hydrocarbons^{1a}

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Abstract: Use of semiempirical models and of the usual perturbation expression for calculation of B terms of molecules of general symmetry are examined. It is pointed out that the results are origin independent for the exact solution of the model (full configuration interaction), provided that the proper commutation relation between the position and Hamiltonian operators holds in the model. The standard Pariser-Parr-Pople model is used to calculate B terms for ten nonalternant hydrocarbons. The magnitudes, but usually not signs, of the B terms of the several lowest energy transitions depend on the details of calculation such as choice of parameters and extent of configuration interaction. The signs of calculated B terms agree with experiment. Magnitudes are often too large, as are calculated oscillator strengths. Results of limited configuration interaction calculations are not significantly affected when the origin is moved inside the molecule. The convergence of the results of limited configuration interaction calculations to the exact results is investigated for the case of fulvene and is found to be quite rapid. Finally, a simple pictorial derivation of the signs of the contributions to the B term of a transition is given, permitting a rationalization of absolute signs in MCD spectra from properties of Hückel molecular orbitals.

Measurement of magnetic circular dichroism (MCD) of molecules has recently greatly increased in popularity.^{2,3} On the one hand, MCD spectroscopy is proving very useful for spectral assignments in inorganic complexes;³ on the other hand, it has been used as an additional means for characterizing organic compounds,⁴ holds promise as a source of structural information (in particular, for ketones⁵), and has even been proposed as a selective analytical method.⁶ Although MCD of organic molecules has been occasionally used to recognize and separate overlapping electronic transitions,⁷ more direct exploitation for spectral assignments has been slow in coming. This is a direct consequence of the generally low symmetry of organic molecules. In the absence of an axis of threefold or higher symmetry, the A terms and C terms, which are relatively easy to calculate and interpret and have proven very valuable in inorganic spectroscopy, are absent and only B terms remain.^{2,3} A terms of triphenylene,^{8a} coronene,^{8a} the tropylium cation,^{8b} the

pentacyanocyclopentadienide anion,^{7a} and some porphyrins,^{8c} as well as A and C terms of several hydrocarbon anions,^{8d} have been measured and calculated to varying degrees of sophistication.⁹⁻¹¹ A term of hexachlorobenzene has been located,¹² but these molecules are all rather atypical.

Most of the published MCD spectra of organic molecules of low symmetry have never been interpreted in the sense that the sign and at least relative size of their B terms have never been shown to agree with existing models of molecular structure. Saturated ketones⁵ and substituted benzenes¹²⁻¹⁴ are outstanding exceptions. They have not been treated numerically, but general rules could be obtained for the lowest singlet-singlet transition using group theory, thanks to the relatively high symmetry and to zero-order forbiddenness of the transition. Again, these are rather exceptional circumstances. Numerical calculation of the B terms in the highly symmetrical porphyrins has not led to very satisfactory agreement with experiment.⁹ We are aware of only two other numerical attempts to obtain B terms. The first investigated the lowest singlet-singlet bands of four alternant hydrocarbons¹⁵ using the CNDO model (it is known¹⁴ that the PPP model gives vanishing B terms for alternant hy-

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drocarbons as a result of perfect pairing). The authors used the standard perturbation formula^{2,3} and found reasonable agreement with experiment but did not discuss the problem of origin dependence of their results for molecules of symmetry lower than D_{2h} . Their tentative assignment of the α band of anthracene appears to be in error.¹⁶ The other numerical study¹⁷ appeared while our work was in progress. B terms of several lowest transitions in three substituted benzenes were calculated using the PPP model, finite perturbation method, and gauge-invariant orbitals, which eliminate the problem of origin dependence which plagues the users of the perturbation formula. Good agreement with experiment was found where data were available.

The perturbation formula for the B terms of a transition from the ground state $|G\rangle$ to the excited singlet state $|F\rangle$ measured on an isotropic solution of molecules without degenerate states reads^{2,3}

$$B(G \rightarrow F) = \text{Im} \left\{ \sum_{I, I \neq G} (\langle I | \mathbf{u} | G \rangle \cdot \langle G | \mathbf{m} | F \rangle \times \langle F | \mathbf{m} | I \rangle) / (W_I - W_G) + \sum_{I, I \neq F} (\langle F | \mathbf{u} | I \rangle \cdot \langle G | \mathbf{m} | F \rangle \times \langle I | \mathbf{m} | G \rangle) / (W_I - W_F) \right\} \quad (1)$$

where W_I is the energy of state $|I\rangle$, \mathbf{m} is the electric and \mathbf{u} the magnetic dipole moment operator, and the summation index I runs over all molecular electronic states. For practical use, the sum is truncated, and the results then are origin dependent unless the molecule is of high symmetry.^{2a, 13, 18}

We are interested in the use of MCD spectroscopy for spectral assignments for organic molecules of low symmetry, particularly in detecting and characterizing the excited states, testing the currently accepted MO models, cross-checking results of polarization studies, finding correlations between excited states of structurally related molecules, and, if reasonably safe MCD-structure relations can be established, in using MCD as an additional tool for probing the structure and electronic states of species isolated in low-temperature glasses.¹⁹ Since conventional semiempirical models are well known to simulate correctly other properties of excited states of molecules, it appears possible that they will account for MCD spectra as well, in spite of the relative complexity of formula 1 and in spite of the fact that new, previously rarely tested, aspects of the models will come into play, such as magnetic transition moments. However, a fairly extensive and systematic study is called for before firm conclusions can be drawn.

Where general insight rather than numerical results alone are the prime objective, formula 1 may offer certain advantages and complement the otherwise more appealing finite perturbation approach,¹⁷ since it is easier to pinpoint a mechanism by which a given B term arises, namely as a result of contributions by other molecular states. It may then be possible to rationalize or even predict at least the sign of these contributions by inspection of molecular orbitals involved in transitions among such states and perhaps even draw parallels between the mixing mechanisms in different but related

molecules on the basis of similarities in their MO's. Of course, all of this may or may not be meaningful depending on the role played by the origin dependence of computed B terms which thus clearly needs to be investigated first. As shown in the following treatment, the problem with origin dependence turns out to be more of a philosophical than of a practical nature, and most of our further work involves use of formula 1, although comparisons with the finite perturbation results will be made as frequently as feasible.

In the present paper, we start with some general questions in semiempirical model calculations of MCD spectra. It is shown that (i) use of exact solutions of the model, such as obtained from full configuration interaction (FCI) calculations, leads to origin-independent B terms although both sums in eq 1 are finite, provided that the proper commutation relation between the Hamiltonian (H) and position (\mathbf{r}) operators holds in the model; (ii) approximate results such as those of less complete CI calculations are origin dependent for molecules of low symmetry, primarily for the same reason which makes dipole length and dipole velocity formulations for oscillator strength inequivalent in such calculations (for SCF-CI calculations with all singly excited configurations (SCI), only for this reason); (iii) the nature of formula 1 and the usual MO-CI description of low-lying excited states are such that only very few terms in the sums are likely to make substantial contributions to the B term, thus simplifying spectral interpretations.

Numerical results have been obtained for ten non-alternant hydrocarbons using several standard versions of the simple PPP model. These show that (iv) already for SCI and particularly for more complete CI the degree of origin dependence of the calculated B terms is insignificant compared to the variation in the results due to parameter uncertainties and changes in the extent of CI, as long as the origin is kept somewhere inside the molecule, and moreover, the rate at which the calculated B terms approach their FCI values as one increases the extent of CI appears to be quite rapid, comparable to that found elsewhere²⁰ for oscillator strengths; (v) the sign of those B terms of the lowest few transitions which are calculated to be large in magnitude in the SCI or somewhat more extensive CI calculations most likely agree with those which would result from exact solution of the model, but this is not true for B terms calculated to be small nor for those describing higher energy transitions; (vi) for many transitions the physical origin of their calculated B term can be meaningfully visualized upon inspection of the form of appropriate molecular orbitals; (vii) already the simple PPP model appears useful since the calculated signs and even relative orders of magnitude for at least one and usually several lowest transitions agree with experimental data obtained for all hydrocarbons tested. Some of our results have appeared in a short communication.²¹

It should be emphasized here that all of our results pertain to pure electronic transitions and no vibronic effects such as those treated in ref 11 are included in the calculation. Our comparisons of experimental with

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calculated signs are based on the observed signs of the B terms of 0–0 transitions, while comparisons of numerical values of B terms are based on the method of moments.³

The agreement is poorest in the case of fulvene which will be discussed presently. More detailed discussion of the MCD spectra of the hydrocarbons studied will be relegated to papers dealing with their polarized electronic spectra, and only a general survey will be presented here in order to document the overall agreement of calculated with experimental signs claimed.

Results and Discussion

A. General. 1. Use of Formula 1. In common semiempirical models, expressions for state energies W and matrix elements of the electric dipole moment operator \mathbf{m} are well known, while elements of the magnetic dipole moment operator \mathbf{u} are needed much less frequently. As all operators in the model, \mathbf{u} is defined in terms of its AO representation and since $\mathbf{u} = i(\mathbf{r} \times \nabla)$ in units of Bohr magneton β_e , the problem is usually reduced to finding suitable expressions for the matrix elements of the operator ∇ . In our work we shall use the approach of Linderberg²² who defines them in such a way that the linear momentum operator $\mathbf{p} = -i\hbar\nabla$ and the semiempirical Hamiltonian H satisfy the proper commutation relation $[\mathbf{r}, H] = i\hbar\mathbf{p}/m$, where m is electron mass. This permits the elements of ∇ to be expressed in terms of the resonance integrals β and of elements of the operator \mathbf{r} , already present in the model, and it is not necessary to assume an explicit form for the radial dependence of the AO's.

2. Origin Independence of Exact Results for Semiempirical Models. Let $\Delta B(\mathbf{R})$ be the change in B calculated from (1) caused by shifting the origin by \mathbf{R} . It is well known^{13,18} that

$$\Delta B(\mathbf{R}) = (1/2c\hbar)(\mathbf{R} \times \langle G|\mathbf{m}|F \rangle) \sum_I \langle G|\mathbf{m}|I \rangle \times \langle I|\mathbf{m}|F \rangle \quad (2)$$

provided that one can assume

$$\langle I|\mathbf{p}|J \rangle = -(im/e\hbar)(W_I - W_J)\langle I|\mathbf{m}|J \rangle \quad (3)$$

where e is the (positive) magnitude of electron charge. Equation 3 follows from the commutation relation of \mathbf{r} and H if $|I\rangle$ and $|J\rangle$ are exact eigenfunctions of the model Hamiltonian²² (FCI solutions). The commutation relation in turn holds in the model because of the way in which matrix elements of ∇ were obtained. Moreover, the sum on the right-hand-side of eq 2 vanishes and thus $B(\mathbf{R}) = 0$ for any \mathbf{R}

$$\sum_I \langle G|\mathbf{m}|I \rangle \times \langle I|\mathbf{m}|F \rangle = \langle G|\mathbf{m} \times \mathbf{m}|F \rangle = 0 \quad (4)$$

The closure relation can be used since the elements $|I\rangle$ in the sum span completely the many-electron space of the semiempirical model, and action of operator \mathbf{m} , as defined in the model, clearly does not take any element $|I\rangle$ outside of this space. *E.g.*, in a PPP calculation, \mathbf{m} is a sum of one-electron operators \mathbf{m}_i acting on AO's according to the recipe $\mathbf{m}_i|\lambda\rangle = -e\mathbf{R}_\lambda|\lambda\rangle$, where \mathbf{R}_λ is the position vector of AO $|\lambda\rangle$.

The ability to use exact closure relations with finite sums is an advantage found with finite-space semiempirical models. It is purchased at the cost of having an only "approximate" operator \mathbf{m} , but at any rate,

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that bill has been paid as soon as the semiempirical model was adopted, with its recipe for calculation of dipole moments and other \mathbf{m} -dependent observables.

In an *ab initio* calculation, matrix elements of the corresponding operator \mathbf{m} are calculated using a different recipe (exact quadrature), and its action on an AO converts it into a linear combination of other AO's, some of which in general are not in the original basis set, and this clearly requires infinite sums in closure relations. Use of any finite AO basis set, FCI, and formula 1 will then still lead to origin-dependent B 's. The difference can best be summarized by saying that exact solutions of molecular systems are in general possible in finite time only for model Hamiltonians.

The origin independence of FCI results within a semiempirical model is probably of greater philosophical than practical importance, at least at present, since for most molecules of interest finding the exact (FCI) solutions is prohibitively expensive. It establishes that for a given semiempirical model there is an origin-independent "exact" B value for each transition defined by formula 1, which can be calculated in a finite number of steps. Depending on how realistic the model is, this value deviates more or less from the experimental value of B .

In practice, we must usually satisfy ourselves with an approximate solution of the model; formula 1 then provides us with an approximation to the "exact" B value and this approximate value will depend on the choice of origin unless the molecule is of high symmetry. To assess the importance of the origin dependence as a practical matter, it is necessary to explore numerically how large it is for various sizes of CI and how the uncertainty which it causes as the origin is allowed to move around in the molecule compares with other uncertainties inherent in the model or introduced by the approximations in solving the model. There are reasonable physical arguments¹³ suggesting that the best approximation to the exact result ought to be obtained with the origin located close to the center of the molecular charge density.

In a way, origin dependence is a similar nuisance to that found when oscillator strength is calculated from limited CI wave functions using a semiempirical model. The results for oscillator strength do not depend on the choice of origin, but they depend on the choice of formulas each of which would give the same result if the exact FCI solution of the model were used (dipole length, dipole velocity, dipole acceleration).

3. Origin Dependence of Approximate Semiempirical Results. There are two contributions to the origin dependence of B terms calculated from (1) when using approximate eigenfunctions of the model Hamiltonian to represent the states of the molecule (*e.g.*, in limited CI calculations). First, the states $|I\rangle$ which diagonalize the Hamiltonian in the many-electron subspace spanned by configurations used in the calculation are different from the exact eigenstates, so that eq 3 does not hold. Second, the sum on the right-hand-side of eq 2 is no longer complete, the closure relation cannot be used, and $\Delta B(\mathbf{R})$ need not vanish even if (3) did hold.

It is interesting to note that in the simple case of SCF–SCI approximation to the exact solution of the model (ground and all singly excited configurations) the sum in eq 2 does vanish although the summation over I clearly

spans only a small part of the total many-electron space. To see this, choose the following complete basis set. The first element, $|0\rangle$, is the SCF ground configuration. According to Brillouin's theorem, it also represents the ground state $|G\rangle$ and does not enter into any of the excited states $|I\rangle$ as given by the SCF-SCI approximation. The elements $|1\rangle$ through $|S\rangle$ are chosen to be the linear combinations of singly excited configurations as obtained from the SCI calculation, and they are thus identified with the excited states $|I\rangle$. Finally, the elements $|S+1\rangle$ through $|T\rangle$, which complete the basis set, are successively all of the doubly, triply, and more highly excited configurations. For this basis set, complete in the model, the closure relation holds.

$$\sum_{I=0}^S \langle G|\mathbf{m}|I\rangle \times \langle I|\mathbf{m}|F\rangle + \sum_{I=S+1}^T \langle G|\mathbf{m}|I\rangle \times \langle I|\mathbf{m}|F\rangle = 0$$

$$F = 1, 2, \dots, S \quad (5)$$

Now, the second sum in (5) vanishes since \mathbf{m} is a sum of one-electron operators and $|G\rangle$ differs in at least two spin orbitals from $|I\rangle$ if $I > S$. Consequently, the first sum must vanish also.

Since the sum vanishes at SCI level and FCI level, one might suspect that it does not become very large at levels intermediate between the two, at least for reasonable ways of selecting configurations, and this is indeed confirmed by our numerical results for the case of the PPP model. The main villain thus turns out to be condition 3, which is generally not satisfied at the SCI level, so that satisfying (2) does not guarantee origin independence of calculated B 's. It is also well known that condition 3 is necessary and sufficient for both dipole length and dipole velocity formulas for oscillator strength to give the same answer. The results obtained from the two formulas for oscillator strength have been investigated as a function of the size of CI for the PPP model.²⁰ The discrepancy is striking at the SCI level, but introduction of relatively few selected doubly and triply excited configurations removes it almost completely. Thus, there is already hope that a relatively moderate increase in the size of CI will yield a rapid improvement in the approximate validity of (3) and thus decrease the degree of origin dependence of B (e.g., SECI-2 type calculation of ref 20).

4. Dissection of the B Term of a Transition into Contributions from Individual Excited States. In the following, we shall assume that we are dealing with an exact FCI solution of the model for a molecule of low symmetry. Formula 1 indicates a way of dissecting the value $B(G \rightarrow F)$ into the contributions B_{I,G^F} ($I \neq F$) due to mixing by the magnetic field of excited states $|I\rangle$ other than $|F\rangle$ into the ground state $|G\rangle$

$$B_{I,G^F} = \text{Im}\{(\langle I|\mathbf{u}|G\rangle \cdot \langle G|\mathbf{m}|F\rangle \times \langle F|\mathbf{m}|I\rangle) / (W_I - W_G)\} \quad I \neq F, G$$

contributions B_{I,F^F} ($F \neq I$) due to mixing of excited states $|I\rangle$ other than $|F\rangle$ into the F th excited state

$$B_{I,F^F} = \text{Im}\{(\langle F|\mathbf{u}|I\rangle \cdot \langle G|\mathbf{m}|F\rangle \times \langle I|\mathbf{m}|G\rangle) / (W_I - W_F)\} \quad I \neq G, F$$

a contribution B_{F,G^F} due to mixing of excited state $|F\rangle$ into the ground state $|G\rangle$, and a contribution B_{G,F^F} due to mixing of the ground state $|G\rangle$ into the excited state

$|F\rangle$. The last two contributions are conveniently lumped together to give

$$B_{F,G^F} + B_{G,F^F} = \text{Im}\{(\langle F|\mathbf{u}|G\rangle \cdot \langle G|\mathbf{m}|F\rangle \times (\langle F|\mathbf{m}|F\rangle - \langle G|\mathbf{m}|G\rangle) / (W_F - W_G))\}$$

Each of these contributions, B_{I,G^F} , B_{I,F^F} , and $B_{F,G^F} + B_{G,F^F}$, may change its value when the origin is shifted by \mathbf{R} , since they all contain matrix elements of \mathbf{u} which are origin dependent, but the sum total, B , remains unchanged. Per cent change of contribution B_{I,G^F} is given by $100(\mathbf{R} \times \langle I|\mathbf{p}|G\rangle)_z / \langle I|\mathbf{r} \times \mathbf{p}|G\rangle_z$ which clearly can be made as large as desired by suitable choice of \mathbf{R} , and similarly for other contributions.

Physical intuition and more elaborate arguments¹³ suggest a choice of origin somewhere inside the molecule. The values of \mathbf{R} we then need to worry about are of the order of a few ångströms, perhaps up to 10 Å. General statements about the per cent change in the individual contributions are hard to make in the absence of more detailed information about the wave functions involved, but numerical results for the PPP model indicate that they are relatively small. In such a case, it makes sense to talk about the "mechanism" by which the B term arises.

Inspection of the mathematical form of the contributions B_{I,G^F} , B_{I,F^F} , and $B_{F,G^F} + B_{G,F^F}$ indicates that a few of them have a good chance of being much bigger than all the others. If this should occur, one could assign the origin of a B term of a given transition specifically to mixing with one or a few other transitions, and perhaps even estimate the "experimental" magnetic dipole transition moments between excited states from experimental B values, once a calculation or theoretical analysis has established the "mechanism" of the mixing. A certain check of self-consistency is possible, since obviously $B_{I,F^F} = -B_{F,I^I}$.

B terms dominated by a single contribution, or just a few, clearly also stand the best chance of being calculated correctly, and it is thus of interest to summarize at least qualitative rules which would indicate which of the contributions B_{I,G^F} , B_{I,F^F} , and $B_{F,G^F} + B_{G,F^F}$ are likely to be large (cf. ref 3).

First, the energy difference involved should be small to make the denominator small. In most molecules this will discriminate against B_{I,G^F} and $B_{F,G^F} + B_{G,F^F}$ as well as many of the B_{I,F^F} 's. This consideration alone has led certain authors to perform calculations in which all mixing with the ground state was neglected,⁹ or even just mixing of two transitions considered.¹⁵

Second, since all contributions to $B(G \rightarrow F)$ contain $\langle G|\mathbf{m}|F\rangle$ as a multiplicative factor, weak transitions can in general be expected to have relatively small B terms (intensities depend on $|\langle G|\mathbf{m}|F\rangle|^2$). More significant, the important contributions B_{I,F^F} , which are likely to be favored by the energy term, also contain $\langle G|\mathbf{m}|I\rangle$, indicating that states which cause intense transitions in ordinary absorption spectra are apt to contribute more.

A third rule follows from the presence of $\langle F|\mathbf{u}|I\rangle$ in the expression for B_{I,F^F} , which indicates a need for a large magnetic dipole transition moment between the contributing state $|I\rangle$ and the final state $|F\rangle$. In numerous molecules many of the low-lying excited states are fairly well represented by singly excited configurations, such as $\Phi_{1 \rightarrow -1}$ (often the lowest excited state), $\Phi_{1 \rightarrow -2}$, etc.

Here orbitals occupied in the SCF ground state are labeled by positive integers in the order of decreasing energy; virtual orbitals are labeled by negative integers in the order of increasing energy. Since \mathbf{u} is a sum of one-electron operators, $\langle \Phi_{i \rightarrow j} | \mathbf{u} | \Phi_{k \rightarrow i} \rangle = 0$ unless either $i = k$ or $j = l$. Configuration mixing will generally relax the situation somewhat but it appears reasonable to conclude that if transitions $G \rightarrow I$ and $G \rightarrow F$ are well described as single electron jumps between SCF molecular orbitals, states $|I\rangle$ and $|F\rangle$ will not be mixed strongly by the magnetic field if the jumps neither start nor end in the same orbital. If the states $|F\rangle$ and $|I\rangle$ correspond to a complicated mixture of configurations, it is likely that the contributions from these configurations will not all add up with the same signs and mixing will still be relatively weak.

Fourth, many contributions will be eliminated if the molecule has at least some symmetry. The three vectors, $\text{Im}\{\langle F | \mathbf{u} | I \rangle\}$, $\langle G | \mathbf{m} | F \rangle$, and $\langle I | \mathbf{m} | G \rangle$ should be mutually perpendicular for most efficient mixing. For instance, for $\pi\pi^*$ states, the former is out-of-plane, while the latter two are in-plane and they must not be collinear if there is to be a contribution. In many molecules of at least C_{2v} symmetry, excited states alternate in symmetry as one goes higher in energy and as a result, the nearest neighbors of transition $G \rightarrow F$ on the energy scale will tend to contribute strongly to $B(G \rightarrow F)$, but the next nearest neighbors will not, because they are of the wrong symmetry, while those any farther may already be too far in energy for efficient mixing.

All these factors are likely to cut down the number of really significant contributions and provide hope that simple interpretations of MCD spectra may be possible.

B. The PPP Model. In order to explore the problems of origin dependence and required size of CI, we have selected a very simple semiempirical model, PPP, and at first limited our attention to hydrocarbons, for which problems with parameters should be minimized. As already pointed out, nonalternant hydrocarbons had to be chosen. The MCD spectra of alternant hydrocarbons essentially measure deviations from perfect orbital pairing,¹⁴ which are believed to be small, vanish in the simple PPP model, and most likely will be harder to calculate than the first-order effects in nonalternants. It will be seen in the following that already the simple PPP model gives a surprisingly good account of low-energy portions of experimental MCD spectra. Some justification of the use of the π -electron approximation can be found in the fact that transitions involving σ electrons are generally weaker than $\pi\pi^*$ transitions and occur at relatively high energies while our calculations will concentrate on the lowest few transitions. Nevertheless, it is clear that further refinements should be investigated later (experimental B terms of alternants certainly do not vanish).

1. Method. The usual version of the PPP model was used throughout.²³ Wave functions for use with formula 1 were obtained from a CI procedure based on SCF molecular orbitals. The number of states $|I\rangle$ in the summations in formula 1 was always equal to the number of singlet spin-projected configurations used in the calculation. The parameters were $I_C = 11.42$

eV and $\gamma_C = 10.84$ eV, Ohno-Klopman²⁴ or Mataga-Nishimoto²⁵ formulas were used for two-center electron repulsion integrals as specified by labels OK and MN. Resonance integrals between nonneighbors were zero. In calculations on molecules other than fulvene I, all bond lengths were 1.40 Å and all nearest-neighbor resonance integrals were $\beta = -2.318$ eV. Unless otherwise specified, calculations on fulvene used the "self-consistent" procedure for determination of bond lengths as outlined in ref 26. The iterative procedure started with all bond lengths equal to 1.40 Å (regular pentagon). Values of β 's and γ 's between neighbors were then repeatedly adjusted using $r_{\mu\nu} = 1.517 - 0.18 p_{\mu\nu}$ (Å) and $\beta_{\mu\nu} = -2.318 \exp[0.335(p_{\mu\nu} - 2/3)]$ (eV). In calculations labeled X, the bond lengths were assumed to be 1.36 and 1.46 Å for classically double and single bonds, respectively, and nearest neighbor β 's were obtained from Linderberg's formula²² using carbon orbital exponents equal to 3.25 (-2.42 and -1.95 eV, respectively).

Bond angles were regular where possible. Matrix elements of \mathbf{m} and $\mathbf{r} \times \nabla$ between atomic orbitals μ and ν were obtained as

$$\langle \mu | \mathbf{m} | \nu \rangle = -eR_{\mu} \delta_{\mu\nu}$$

$$\langle \mu | \mathbf{r} \times \nabla | \nu \rangle = (m/\hbar^2) \beta_{\mu\nu} (\mathbf{R}_{\nu} \times \mathbf{R}_{\mu})$$

where \mathbf{R}_k is the position vector of the center of orbital k . Extent of CI varied. The ground configuration was always included. Abbreviations used are: SCI (all singly excited configurations), SDCI (singly and doubly), SDTCI (singly, doubly, triply), FCI (all), SECI-1, (selected singly and doubly excited using cut-off parameters $\epsilon = 0.1$, $\delta = 8$ eV, see ref 20), SECI-2 (selected singly, doubly, and triply excited using cut-off parameters $\epsilon = 0.1$, $\delta = 8$ eV, see ref 20), and "SECI-2" (same as SECI-2 but with $P_{cx} = P_{cy} = 0$, see ref 20).

SCI and TDHF (time-dependent Hartree-Fock) calculations using the finite perturbation method were performed exactly as in ref 17, using a program kindly provided by Dr. Seamans. These calculations are labeled SL.

2. General Results. Before proceeding to a comparison of results with those of other authors and with experiments, we shall briefly discuss the physical meaningfulness of the numbers obtained. This is always desirable in semiempirical procedures, but appears particularly important here, since formula 1 for B terms involves all excited states possible in the model, including those of relatively high energy. We need to consider the sensitivity of the results (a) to minor modifications of the model (choice of parameters), (b) to the accuracy with which the model is solved (extent of CI), (c) to the choice of origin.

(a) Dependence on Choice of Parameters. Choice of different functions for two-center repulsion integrals can significantly affect the order of states as well as their CI wave functions.²⁷ Variations in other parameters often only scale the energy of calculated transitions. Thus, it is no surprise that results of calculations using

(24) K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964); G. Klopman, *J. Amer. Chem. Soc.*, **86**, 4550 (1964).

(25) N. Mataga and K. Nishimoto, *Z. Phys. Chem. (Frankfurt am Main)*, **13**, 140 (1957).

(26) P. Hochmann, R. Zahradnik, and V. Kvasnička, *Collect. Czech. Chem. Commun.*, **33**, 3478 (1968).

(27) J. Koutecký, *J. Chem. Phys.*, **47**, 1501 (1967).

(23) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

the Mataga–Nishimoto formula differ significantly from those using the Ohno–Klopman formula, while reasonable changes in other parameters such as choice of resonance integrals have relatively little effect. This is shown in Table I for the case of fulvene (I). In general,

Table I. Comparison of Calculations of Fulvene B Terms^a

Energy, cm ⁻¹	Calcd ^b Exptl ^c	Transition	
		1 24,100–27,400 27,000	2 38,800–40,900 37,000
10 ³ B , D ² β_e /cm ⁻¹			
Calcd SECI-1-OK		-0.18	-0.19
Calcd SCI-OK		-0.72	+0.15
Calcd SCI-MN		-0.66	-0.20
Calcd X-SCI-OK		-0.74	+0.18
Calcd X-SL-SCI-OK		-0.242	-0.026
Calcd X-SL-TDHF-OK		-0.540	+0.025
Exptl ^c		ca. -0.05	ca. +0.05

^a OK, Ohno–Klopman integrals; MN, Mataga–Nishimoto integrals, SL, Seamans–Linderberg method, X, resonance integrals from gradient of overlap. For details see text, section B1. Location of origin for all calculations as shown in formula 1. ^b Range of values indicates differences between the various methods used. ^c Values for glc-purified 6,6-dimethylfulvene (solution in spectral quality cyclohexane), measured and evaluated by the method of moments as in ref 12. Details will be published elsewhere.

we find that results of the two formulas usually agree on the sign and order of magnitude of the B term of the lowest few transitions (only one in the case of fulvene) and disagree for the higher ones. Until the superiority of one or the other formula is clearly established, we shall only assign significance to the signs and orders of magnitude of B terms for which the two methods agree, *i.e.*, the few lowest ones. For this reason, Table II, which summarizes results for nonalternant hydrocarbons, only contains B terms for a few lowest transitions in each molecule.

(b) **Dependence on the Extent of CI.** At present, exact FCI solutions cannot be obtained for large molecules and one must be satisfied with approximate solutions. This is unfortunate since it is then impossible to determine whether disagreements with experiment are due to basic flaws in the model or to approximations made while solving it. The presently most popular approximation is the SCI procedure, and the common values of parameters were chosen by most authors so as to make the SCI results agree with experiment. Thus, it is sometimes argued that it is unnecessary and indeed incorrect to include multiply excited configurations in the calculation. However, it is also well known^{19, 20, 27, 28} that introduction of multiply excited configurations into the calculation can often introduce new low-lying states and change the order of others. The experimental evidence is still insufficient to clearly distinguish whether one or the other approach is better from a practical point of view (*cf.* the notorious problem with E_{2g} state of benzene²⁹), but we feel that the need for considera-

(28) E. M. Evleth, *Theor. Chim. Acta*, **11**, 145 (1968); T. W. Stuart and N. L. Allinger, *ibid.*, **10**, 247 (1968); K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972); J. Downing, V. Dvořák, J. Kolc, A. Manžara, and J. Michl, *ibid.*, **17**, 70 (1972); J. Karwowski, *ibid.*, **18**, 47 (1973). For a longer list of references, see J. Michl and J. Downing in "Energy, Structure and Reactivity," D. W. Smith and W. B. McRae, Ed., Wiley, New York, N. Y., 1973, p 299.

(29) A. M. Taleb, I. H. Munro, and J. B. Birks, *Chem. Phys. Lett.*, **21**, 454 (1973); P. J. Hay and I. Shavitt, *ibid.*, **22**, 33 (1973).

Table II. Experimental and Calculated Signs of B Terms^a

No.		Transition					
		1	2	3	4	5	6
I ^b	Exptl En	27	37				
	B	-	+				
II ^c	Exptl En	14	28	34	35		
	B	+	-	+	+		
III ^d	Exptl En	21	29	31	37	42	
	B	-	-	+	+	-	
IV ^e	Exptl En	18	26	29			
	B	+	+	-			
V ^f	Exptl En	25	28	31	35		
	B	-	-	+	+		
VI ^g	Exptl En	20	24	28	30	34	
	B	0	-	+	-	+	
VII ^h	Exptl En	13	22				
	B	+	-				
VIII ^e	Exptl En	24	28	29	34		
	B	-	-	+	-		
IX ^e	Exptl En	14	20	26	27	32	35
	B	0	+	+	-	+	-
X ⁱ	Exptl En	23	27	29	32		
	B	+	+	-	-		
	Calcd B	+	+	-	-		

^a Observed electronic transitions are identified by the position of their origin (units of 1000 cm⁻¹). All assignments to calculated transitions are based on matching not only energies and intensities but also polarization directions. Details of the experimental work will appear elsewhere (*cf.* footnotes in the first column on the left). ^b Data for 6,6-dimethylfulvene. Table I and unpublished results. ^c Reference 30. ^d M. R. Whipple and J. Michl, unpublished results. ^e J. Kolc and J. Michl, unpublished results. ^f J. Kolc, E. W. Thulstrup, and J. Michl, *J. Amer. Chem. Soc.*, in press. ^g V. Kratochvíl and J. Michl, unpublished results. ^h E. W. Thulstrup, C. Jutz, and J. Michl, submitted for publication. ⁱ J. F. Muller, D. Cagniant, O. Chalvet, D. Lavalette, J. Kolc, and J. Michl, *J. Amer. Chem. Soc.*, **96**, 5038 (1974).

tion of multiply excited configurations certainly cannot be dismissed out of hand.

Figure 1 shows the rapid convergence of results obtained for the various extent of CI to the exact FCI result. It is seen that there is some difference between SCI and FCI even for the lowest two states, which are described by similar wave functions in the SCI and FCI solutions, namely essentially $1 \rightarrow -1$ excitation for the first one and $2 \rightarrow -1$ for the second one. These are the only two transitions accessible to us experimentally. Higher transitions have very dissimilar wave functions in the SCI and FCI descriptions which cannot even be correlated. However, it is not necessary to go much beyond the SCI approximation in order to get results almost identical with those of FCI. In particular, the SECI-1 and SECI-2 selection procedures described in detail elsewhere²⁰ seem to provide fair approximations to FCI. While we realize that it is hazardous to extrapolate from 6π -electron systems to larger ones, we feel encouraged by the overall agreement between the SCI and particularly SECI-1 results with FCI results shown in Figure 1. Again, we shall only assign significance to calculated signs and orders of magnitude of B terms for which SCI and SECI-1 results agree, and only such results are shown in Table II.

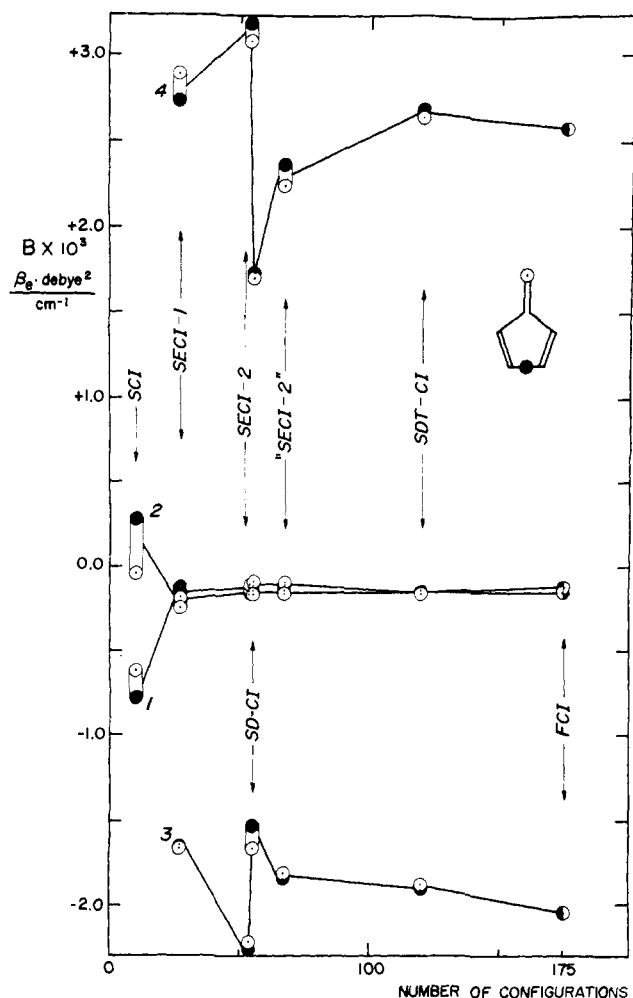


Figure 1. Calculated B terms of fulvene transitions 1-4 as a function of the extent of CI (Ohno-Klopman integrals). Black and white dots refer to the two choices of origin shown in the formula on the right.

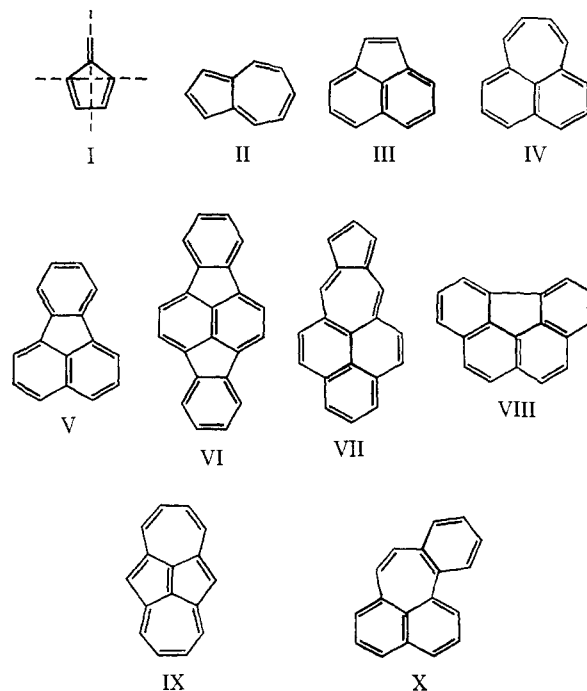
(c) **Origin Dependence.** Since for molecules of low symmetry results of our calculations other than FCI depend on the choice of origin, it is crucial to find out how strong this dependence is. Numerical results for nonalternant hydrocarbons listed in Table II show that moving the origin anywhere within the carbon skeleton of the molecule affects the calculated B terms to a degree which is negligible compared with the uncertainties considered in the preceding two sections. This is true already at the SCI level of approximation, and even more so at the SECI-1 level and is illustrated in Figure 1 in the case of fulvene. In practice, we always repeat each calculation with different locations for the origin and consider as significant only those results whose sign and order of magnitude are not affected as the origin is moved within the carbon skeleton of the molecule. So far, only very rarely have we found a result which would pass the preceding two criteria (a and b) but fail the origin-dependence criterion, even in a molecule as large as VII.

3. Comparison with the Seamans-Linderberg Method. In Table I, our results for fulvene are compared with results obtained by the procedure described by Seamans and Linderberg¹⁷ using identical parameters and SCI and TDHF approximations (SL). The SL procedure is based on use of gauge-invariant atomic orbitals

and finite perturbation theory. The authors also avoid the use of the dipole length operator and base the calculations strictly on the use of the dipole velocity operator instead. The results of the two methods are similar, but our B terms appear to be somewhat larger. This might be related to our use of dipole length matrix elements which are also known to give exaggerated values for oscillator strengths. We have also performed a similar comparison for azulene.³⁰ In this instance, the SL-TDHF results agree in sign with those obtained by use of formula 1 regardless of details of calculation, and with experiment, while the SL-SCI results give an incorrect sign for the first two transitions.

It appears premature to attempt an evaluation of the relative merits of the two methods at this time. The order-of-magnitude agreement of the two procedures is encouraging and we plan to continue with systematic comparisons.

4. Comparison with Experiments. Table II shows the calculated signs of B terms for ten nonalternant hydrocarbons for those transitions where the above-mentioned tests for physical meaningfulness were passed, *i.e.*, the several lowest transitions. The agreement with experimental signs appears to be excellent, indicating that the use of the simple PPP model is quite reasonable. Quantitative agreement is poor (see the case of fulvene in Table I), but rough orders of magnitude as well as relative magnitudes for several transitions in the same molecule are generally correct. It is not surprising that the calculated magnitudes are often too large considering that the dipole length matrix elements which enter the calculation also predict oscillator strengths which are too large. Some relief can be obtained if only the ratio of B to dipole strength is compared with experiment and this possibility will be considered in papers describing the detailed spectroscopy of the hydrocarbons I-X.



5. Derivation of Signs of Contributions to B Terms by Inspection of HMO's.

In view of the good agree-

(30) E. W. Thulstrup, P. L. Case, and J. Michl, submitted for publication.

ment of calculated signs of B terms with experiment, it appears reasonable to analyze the process in which they were obtained in more detail. Units of $10^{-3} \beta_e \text{D}^2/\text{cm}^{-1}$ will be used throughout.

Our numerical results show that the origin dependence of the individual terms in the sums on the right-hand side of eq 1 is mostly very small. This will then permit us to discuss individually the contributions B_{I,G^F} , B_{I,F^F} , and $B_{F,G^F} + B_{G,F^F}$ to the B value of the F th transition. Moreover, only very few of these contributions are significant, at least in the case of the low-lying transitions which interest us here. In the FCI calculation of the B term of the first transition in fulvene, in which a total of 175 states are considered ($B = -0.15$), only six out of the total 347 contributions have absolute value above 0.01, while 314 have absolute value of less than 10^{-5} . This calculation gives $B = -0.13$ for the second transition, and again only six terms exceed 0.01 in absolute value. The same conditions are found in general.

Even in the SCI calculations on the largest hydrocarbons examined, VI and VII, this situation prevails. Among the 241 contributions to the B term of the second transition in VI ($B = -8.82$; the first transition is symmetry forbidden), the largest contributions are -4.48 , -2.56 , -1.72 , and -0.88 , eight others have absolute magnitude 0.1 or more, while most of the rest are totally negligible. The B term of the third transition in VI is $+1.86$, the largest contributions are $+1.72$, -0.32 , then three more above 0.1 in absolute value, and most of the rest are again insignificant. Among the 199 contributions to the B term of the first transition in VII, which is equal to 3.90, those largest in absolute value are $+3.68$, $+0.27$, five more above 0.1, and most of the rest are again very small. The B term of the second transition in VII is -4.77 , the leading contribution is -3.68 , the next most important ones are -0.76 , $+0.50$, -0.49 , -0.47 , and there are only seven others above 0.1.

The selection of just a few important terms among many is easily understood as outlined in part A of this paper. Energy difference in the denominator, dipole moment of the contributing transition, matching of configurations, and symmetry combine their requirements in a way which is clear once a complete calculation is inspected. However, for the time being, we do not feel confident enough to limit the number of terms to be considered before the calculation is performed. For instance, mixing of intermediate states into the ground state often contributes significantly to the final value of B , although it does not provide the leading term.

Clearly, however, the fact that only extremely few of the terms in formula 1 are significant is responsible for the relative success of its application. If the resultant B terms reflected a delicate balance of a great number of positive and negative contributions, they would undoubtedly be very sensitive to minor details of the model and much less likely to agree with experiment. Such a situation apparently obtains for the higher transitions, which indicates that it will be very hard to calculate their B terms correctly.

Inspection of our results also shows that the lack of sensitivity of the B terms of low-lying transitions to details of the calculation already mentioned above is caused by relative lack of sensitivity of the individual leading contributions to such details. It is thus possi-

ble to ascribe a degree of physical reality to the calculated individual contributions.

In most instances, contributions of the type B_{I,F^F} , originating in the mixing between excited states $|I\rangle$ and $|F\rangle$ by the effect of the magnetic field, are dominant. If the I th as well as F th excited state can be described reasonably well by means of a single spin-projected configuration, it is possible to derive the sign of the B_{I,F^F} contribution from simple consideration of nodal properties of the SCF molecular orbitals involved in the excitation. Since these are the same as the nodal properties of Hückel MO's available in standard tables, it then becomes easy to rationalize low-energy parts of MCD spectra on the basis of very simple concepts. This procedure will be illustrated in the following in the case of the B term of the first transition of fulvene, $B(G \rightarrow 1)$.

As already mentioned above, only very few contributions to this B term are significant. The four largest are $B_{1,G^1} + B_{G,1^1}$, $B_{2,1^1}$, $B_{3,1^1}$, and $B_{5,1^1}$. They are similar in magnitude but all are negative so that it is safe to expect the sum to be negative and this agrees with experiment. This situation holds for all the calculations with the various extent of CI listed in Figure 1 except SCI, in which the excited states are probably described rather poorly. The reason why the SCI B value for the first transition is so much more negative than the others such as SECI-1 (Figure 1) is that in SCI both $B_{1,G^1} + B_{G,1^1}$ and $B_{2,1^1}$ are substantially more negative.

For the sake of illustration, we shall now show how one can understand in easy pictorial terms the origin of the minus sign of $B_{2,1^1}$, using SCI wave functions for simplicity. The resulting recipe has been found useful for interpretation of MCD spectra in general.

The contribution to the B term of the transition $G \rightarrow F$ due to mixing the excited state $|I\rangle$ into the excited state $|F\rangle$ is defined as

$$B_{I,F^F} = 23.07 \frac{\langle F|\mathbf{r} \times \nabla|I\rangle}{W_I - W_F} \cdot \langle G|\mathbf{r}|F\rangle \times \langle I|\mathbf{r}|G\rangle$$

where W is in cm^{-1} , \mathbf{r} in \AA , ∇ in \AA^{-1} , and B_{I,F^F} in $\beta_e \text{D}^2/\text{cm}^{-1}$.

We shall assume that $|G\rangle = \Phi_0$ (ground SCF determinant), $|F\rangle = \Phi_{s \rightarrow t}$, and $|I\rangle = \Phi_{u \rightarrow v}$, where $\Phi_{a \rightarrow b}$ is a normalized singlet-projected singly excited configuration obtained from Φ_0 by exciting an electron from orbital a to orbital b . Then,

$$\langle G|\mathbf{r}|F\rangle = \sqrt{2} \langle t|\mathbf{r}|s\rangle$$

$$\langle G|\mathbf{r}|I\rangle = \sqrt{2} \langle v|\mathbf{r}|u\rangle$$

$$\langle F|\mathbf{r} \times \nabla|I\rangle = \langle t|\mathbf{r} \times \nabla|v\rangle \delta_{su} - \langle u|\mathbf{r} \times \nabla|s\rangle \delta_{tv}$$

Thus, $B_{I,F^F} = 0$ unless the one-electron excitations in $\Phi_{s \rightarrow t}$ and $\Phi_{u \rightarrow v}$ either start ($s = u$) or end ($t = v$) in the same orbital (this is simply a restatement of rule 3 of section A4). Let us label the common orbital k . Let the other MO involved in the transition $G \rightarrow F$ be labeled f , and let the other MO involved in the transition $G \rightarrow I$ be labeled i . Thus, if $B_{I,F^F} \neq 0$, either $|F\rangle = \Phi_{k \rightarrow f}$ and $|I\rangle = \Phi_{k \rightarrow i}$, or $|F\rangle = \Phi_{f \rightarrow k}$ and $|I\rangle = \Phi_{i \rightarrow k}$.

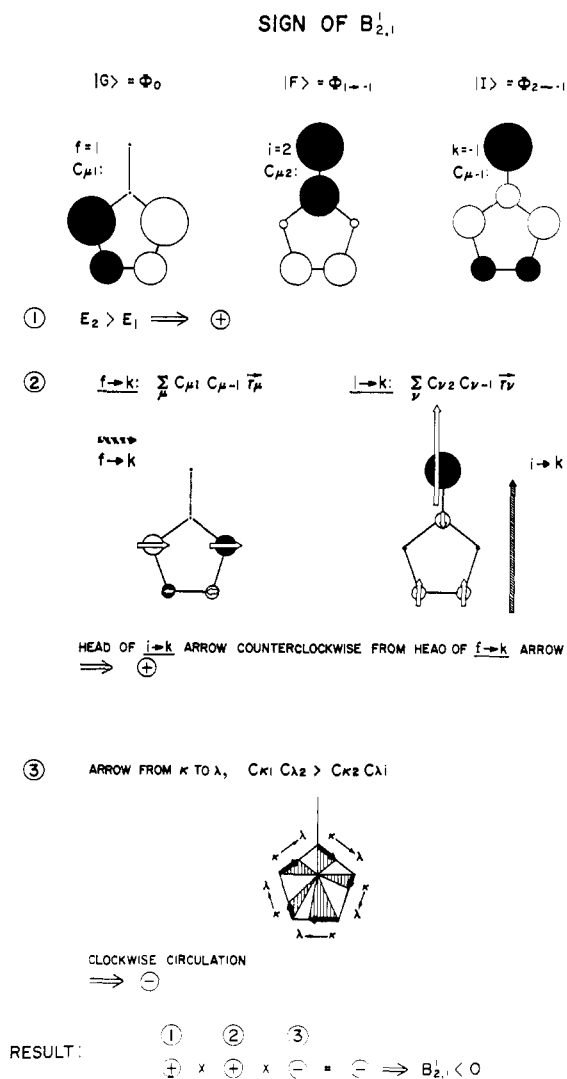


Figure 2. Determination of the sign of $B_{2,1}^1$ by inspection. The expansion coefficients of SCF-MO's 1, 2, and -1 are proportional to the diameter of circles shown in the formulas on top (black, positive; white, negative). The three signs whose product determines the sign of $B_{2,1}^1$ are derived below. Atomic transition densities (black, positive; white, negative, circle diameter indicates size) contribute to the only final nonvanishing components of the transition vectors $f \rightarrow k$ and $i \rightarrow k$ (hatched arrows), amounts represented as vectors located at atoms in the middle two formulas (white arrows). In the bottom formula, vectors located in bonds start in terminus κ and point toward terminus λ as defined by the condition that their length, $C_{\kappa 1} C_{\lambda 2} - C_{\kappa 2} C_{\lambda 1}$, be positive. The vector for bond 5-6 is equal to zero. Shaded triangles indicate contributions of the individual bonds to the prevailing sense of circulation (all contributions are clockwise).

Using the standard LCAO expansion $|a\rangle = \sum_{\kappa} C_{\kappa a} \cdot |\kappa\rangle$ and the usual expressions for matrix elements of \mathbf{r} and $\mathbf{r} \times \nabla$ in AO basis

$$\langle \kappa | \mathbf{r} | \lambda \rangle = \mathbf{R}_{\lambda} \delta_{\kappa \lambda}$$

$\langle \kappa | \mathbf{r} \times \nabla | \lambda \rangle = 0.131 \beta_{\kappa \lambda} (\mathbf{R}_{\lambda} \times \mathbf{R}_{\kappa})$ ($\beta_{\kappa \lambda}$ in eV, \mathbf{R} in Å) and taking advantage of the fact that $\langle \kappa | \mathbf{r} | \lambda \rangle$ lies in a molecular plane so that the only nonvanishing contribution comes from the z component of $\langle \kappa | \mathbf{r} \times \nabla | \lambda \rangle$ we get, in units of $10^{-3} \beta_e D^2 / \text{cm}^{-1}$

$$B_{I,F}^F = [6044 / (W_I - W_F)] [(\sum_{\mu} C_{\mu f} C_{\mu k} \mathbf{R}_{\mu}) \times (\sum_{\nu} C_{\nu i} C_{\nu k} \mathbf{R}_{\nu})]_z \cdot \left\{ \sum_{\substack{\text{bonds} \\ \kappa-\lambda}} C_{\kappa f} C_{\lambda i} \beta_{\kappa \lambda} (\mathbf{R}_{\lambda} \times \mathbf{R}_{\kappa})_z \right\}$$

where W is in cm^{-1} , β in eV, and \mathbf{R} in Å. Using $\beta_0 = -2.318$ eV and $\mathbf{R}_{\lambda} \times \mathbf{R}_{\kappa} = (\mathbf{R}_{\lambda} - \mathbf{R}_{\kappa}) \times \mathbf{R}_{\kappa}$, this can be converted into the final form

$$B_{I,F}^F = [14010 / (W_I - W_F)] \left\{ \left[\sum_{\mu} C_{\mu f} C_{\mu k} \mathbf{R}_{\mu} \right] \times \left[\sum_{\nu} C_{\nu i} C_{\nu k} \mathbf{R}_{\nu} \right]_z \cdot \left\{ \sum_{\substack{\text{bonds} \\ \kappa-\lambda}} [\mathbf{R}_{\kappa} \times (\beta / \beta_0) (C_{\kappa f} C_{\lambda i} - C_{\kappa i} C_{\lambda f}) (\mathbf{R}_{\lambda} - \mathbf{R}_{\kappa})]_z \right\} \right\}$$

Often, β can be considered constant for all bonds and β / β_0 can then be absorbed into the constant in front. In most of our calculations, $\beta / \beta_0 = 1$.

Although the final expression may appear to be complex, each term has a simple pictorial representation and its sign is usually easily derived by inspection of the molecular orbitals f , i , and k . The sign of $B_{I,F}^F$ is determined as the product of three signs. The first is given by the sign of $W_I - W_F$: positive if $I > F$, negative if $I < F$. The second and third are given by the expressions within the first and second curly brackets, respectively. The second sign is positive if the head of the transition length vector of transition $G \rightarrow F$, i.e., $\sum_{\mu} C_{\mu f} C_{\mu k} \mathbf{R}_{\mu}$, is displaced less than 180° clockwise from the head of the transition length vector of the transition $G \rightarrow I$, i.e., $\sum_{\nu} C_{\nu i} C_{\nu k} \mathbf{R}_{\nu}$, and negative otherwise (if the vectors are parallel or antiparallel, $B_{I,F}^F = 0$). The third sign is positive if the "transition current circulation" proceeds counterclockwise and negative if it proceeds clockwise.

The direction of the arrows representing transition length vectors is easily derived from positions of atoms and atomic transition densities $C_{\mu s} C_{\mu t}$ and requires no further comment. To determine the sense of "transition current circulation" an arrow is first assigned to each bond: the two termini of the bond κ and λ are labeled in such a way that $C_{\kappa f} C_{\lambda i} - C_{\kappa i} C_{\lambda f}$ is positive, then an arrow is drawn starting at atom κ toward atom λ and its length is made proportional to $(\beta / \beta_0) (C_{\kappa f} C_{\lambda i} - C_{\kappa i} C_{\lambda f})$. Then, both ends of the arrow are connected to the origin of coordinates and the area of the resulting triangle is determined. It is counted positive if the arrow is pointed counterclockwise (directed left when viewed from the origin) and negative in the opposite case. All areas are added algebraically and if the sum is positive, the circulation is counterclockwise and the contributed sign positive. In the opposite case, it is negative. Often, all or most of the arrows are directed in the same sense and the contributed sign is obvious even without the somewhat lengthy determination of areas of triangles.

The quantity which determines the direction of the arrows is $C_{\kappa f} C_{\lambda i} - C_{\kappa i} C_{\lambda f}$ which provides an interesting measure of a relation between orbitals i and f and is fairly easily estimated by inspection from shapes and nodal properties of these orbitals. The sign of $B_{I,F}^F$ obtained from the "three sign recipe" is obviously independent of the choice of phase of orbitals f , i , and k . Multiplication of any of these by -1 changes two of the three signs and leaves the product intact.

Finally, the application to the determination of the sign of $B_{2,1}^1$ in fulvene is shown in Figure 2.

Summary

Both theoretical considerations and numerical results for simple π -electron systems indicate that calcu-

lations of signs of B terms of molecules of low symmetry using the standard perturbation formula^{2,3} are not as hopeless as has been believed (e.g., ref 3). In semiempirical model calculations, the exact (FCI) results are origin independent. Even the nonvanishing origin dependence of approximate results is insignificantly small if large enough CI is used, at least for the PPP model. Convergence of approximate to FCI results is quite fast. Simple pictorial rationalization of the signs of B terms is possible in terms of HMO's of the molecule. On the negative side, it must be emphasized that meaningful predictions are possible only for the few lowest energy electronic transitions. However, the signs of the B terms of these low-energy bands are correctly predicted already by the simple PPP model, at least for π -electron chromophores of nonalternant hydrocarbons. It appears likely that the model will also work for substituted derivatives and heterocyclic analogs of alternant as well as nonalternant hydrocarbons, since the exact pairing property is lost in all of these. This is now being tested.

After the completion of this manuscript it has come to our attention that a π -electron calculation on several heterocycles and their derivatives by a method similar to that used by us has just appeared.³¹ It was claimed that the calculated B terms are origin independent since all SCF singly excited configurations were used but no

(31) D. W. Miles and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, 70, 3754 (1973).

proof was given of this statement. According to the analysis presented here and in ref 21, this is not sufficient in itself to guarantee origin independence, since the proper commutation relation between \mathbf{r} and H and relation 3 also need to be satisfied.

Further improvement in the semiempirical model will be required for π -electron calculations on alternant hydrocarbons. Finally, for many chromophores, the π -electron approximation will have to be abandoned but the increased size of CI will then make it harder to examine origin dependence and convergence to exact solutions and we hope to obtain additional experience with π -electron models first.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work. The initial point of our programming work was an SCF-CI PPP program written by Mr. John Downing (ref 20), which in turn profited greatly from use of a subroutine using an algorithm of ref 32, kindly provided by Professor Frank E. Harris. We are grateful to Dr. Charles R. Flynn for preparation of 6,6-dimethylfulvene and to Professor Henry Eyring for kind permission to use his MCD instrument. The MCD spectra used in this paper were taken by Miss Patti L. Case and Mr. Michael R. Whipple. Finally, we are obliged to Dr. L. Seamans for a copy of his program and a fruitful discussion.

(32) F. E. Harris, *J. Chem. Phys.*, 46, 2769 (1967).

Mechanism of Halide Substitution in Dichloro- μ -tetrapropionato-dirhenium(III)^{1a}

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Abstract: Kinetic and equilibrium measurements are reported for the reaction $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{Cl}_2 + \text{Br}^- = \text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{ClBr} + \text{Cl}^-$ in acetonitrile. The reaction is reversible with $K = (1.1 \pm 0.1) \times 10^{-2}$ at 25.0° . The forward rate constant in the anhydrous solvent is given by the expression $k_t = A[\text{Br}^-]/([\text{Cl}^-] + B[\text{Br}^-])$ with $A = 3.4 \times 10^{-5} \text{ sec}^{-1}$ and $B = 4.1 \times 10^{-2}$ at 25° , which is interpreted in terms of a two-step mechanism involving loss of Cl^- prior to entry of Br^- . The reaction is subject to strong catalysis by traces of neutral donor molecules including water. The second stepwise replacement of Cl^- by Br^- has an equilibrium constant determined only approximately as $(4 \pm 2) \times 10^{-3}$.

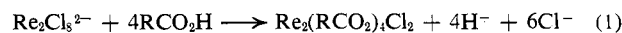
The structural and reaction chemistry of Re(III) complexes was elucidated several years ago largely through the efforts of Cotton and his coworkers. The dimeric Re(III) complex $\text{Re}_2\text{Cl}_8^{2-}$ was identified,² and it was noted³ that refluxing this ion in the carboxylic acid solvent readily converts it to the given carboxylato halide complex of Taha and Wilkinson.⁴

(1) (a) Based on the Ph.D. Thesis of T. R. W., Iowa State University, 1972; (b) National Science Foundation Trainee, 1968–1969; National Science Foundation Predoctoral Fellow, 1969–1972.

(2) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 4, 326 (1965).

(3) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, 6, 214 (1967).

(4) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).



At the time we began work on the problem of the mechanism of halide ion substitution in these dinuclear Re(III) complexes, a useful first study appeared to be the reactions of either $\text{Re}_2\text{Cl}_8^{2-}$ or $\text{Re}_2(\text{RCO}_2)_4\text{Cl}_2$ with another halide ion. The former reaction appeared too complex a system in which to make the first attempt at a meaningful resolution of the mechanism, not only because eight steps are involved in the conversion of $\text{Re}_2\text{Cl}_8^{2-}$ to, say, $\text{Re}_2\text{Br}_8^{2-}$ but also because the intermediate mixed ligand complexes can exist in a number of isomeric forms. Moreover, relatively high concentrations of halide ions are required to prevent loss of