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Use of Semiempirical Models for Calculation of B Terms in Magnetic Circular Dichroic Spectra. IV.^{1a} Substituted Benzenes in the Pariser–Parr–Pople Model

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Abstract: B terms in MCD spectra of the benzyl cation and anion are calculated in several approximations with the simple PPP model. Definite predictions are reached for signs of B terms of low energy transitions. The calculated signs of the first two B terms are easily understood in terms of a simple argument based on the well-known nodal properties of benzyl Hückel orbitals. A similar argument can be made for benzenes with a general conjugative substituent and suggests extrapolation of the calculated signs from the benzyl ions to isoelectronic substituted benzenes. This extrapolation is justified by numerical calculations and is in good agreement with experimental data, thus providing a simple intuitive rationalization of the well-known trends in MCD spectra of substituted benzenes. Unlike mesomeric effects of substituents, their inductive effects are calculated to have only very small influence on the lowest B terms. Finally, it is pointed out that the existence of these trends (in particular, of opposite effects of π -electron-donating and -withdrawing substitution) is related to general theorems concerning alternant pairing properties and that similar trends are to be expected for derivatives of other alternant hydrocarbons containing conjugative substituents.

At an early stage in the present surge of interest in MCD (magnetic circular dichroic) spectroscopy of organic compounds, it was noted that signs of bands in the MCD spectra of benzenes carrying ortho and para directing substituents are opposite to those found with meta directing substituents and a correlation between the maximum molar MCD of the first band and the Hammett σ_p constant was reported.^{1b} Other investigations followed,²⁻⁴ and it is now firmly established that substituted benzenes in which the substitu-

ent is electron donating have a positive lowest B term (the first transition corresponds to benzene $^1B_{2u}$ state) and a negative second B term (the second transition is believed to correspond to benzene $^1B_{1u}$ state), while the opposite is true for benzene with an electron-withdrawing substituent. Mesomeric substituent effect appears to be more important than inductive effect, since halobenzenes have a positive first B term.

A rationalization of these opposite trends in general

terms has been provided by Seamans² and by Eyring and collaborators^{3,4} starting with benzene and treating the presence of substituents as a perturbation on the benzene spectrum. It was shown that the dichotomy in substituent effects is a direct consequence of the well-known fact that the signs of "spectroscopic moments"⁵ of the substituents are opposite for the two classes of substituents. Correct absolute signs of the two B terms were obtained in a numerical calculation by Seamans and Linderberg,⁶ which also resulted in good agreement with numerical values. These authors used the PPP (Pariser-Parr-Pople) model with gauge-invariant orbitals and finite perturbation technique in both time-dependent Hartree-Fock and SCI (all singly excited configurations) approximations. Their procedure offers the great advantage that calculated B terms are origin independent.

Similar numerical results were recently obtained by Miles and Eyring⁷ using a different version of the PPP model (explicitly orthogonalized AO's), the usual perturbation formula,^{8,9} and the SCI approximation. It was stated without proof that the results are origin independent, but it is not immediately obvious why this should be so.

The use of the ordinary perturbation formula has the advantage that the mechanism by which the B terms arise is easily analyzed in terms of mixing of states by the magnetic field. As a result, it is easier to find relations between MCD spectra of structurally related molecules and to understand them in simple terms.¹⁰

We have recently discussed¹⁰ in detail some of the problems encountered with the use of semiempirical models and the usual perturbation formula for calculation and analysis of MCD spectra of π -electron systems, in particular the possible origin dependence of results for molecules of low symmetry. It was shown that already the ordinary version of the PPP model predicts correct signs of the first few B terms of about a dozen nonalternant hydrocarbons and that the results can often be understood in simple pictorial terms on the basis of nodal properties of Hückel MO's. Elsewhere,¹¹ we have shown that the simple PPP model predicts the existence of a mirror-image relationship between the MCD spectra of two species related by the alternant pairing symmetry, such as benzyl cation and benzyl anion.

In this paper, we use the simple PPP model to calculate the so far unknown MCD spectra of benzyl cation (**1a**) and benzyl anion (**1b**) and show that results for the lowest B terms are not sensitive to details of the calculation and that their signs can be understood easily from simple considerations of the shape of benzyl orbitals. Further, we find that calculated inductive effects of substituents on benzene are extremely small, while their mesomeric effects are large and are well modeled by the benzyl anion or cation, so that simple pictorial understanding of the MCD spectra of substituted benzenes results. While emphasis is placed on the use of the PPP model to examine general trends, concrete examples of results for specific substituted benzenes are also given. We believe that our work complements previously available analyses of the spectra of substituted benzenes²⁻⁴ in that it uses a different reference point (benzyl rather than benzene) and points out the importance of the mesomeric effect of the substituent.

Method of Calculation

The calculations were done as described in ref 10 and used the simple PPP model:¹² idealized geometry (regular hexagon, all bonds 1.40 Å), resonance integrals β only between neighbors (all equal to -2.318 eV), one-center electron-repulsion integral for carbon $\gamma_C = I_C - A_C = 10.84$ eV (values for heteroatoms as indicated in the text), two-center electron-repulsion integrals both according to Nishi-

moto and Mataga¹³ (N-M) or Ohno¹⁴ and Klopman¹⁵ (O-K) as indicated, one-center core integral for carbon $I_C = 11.42$ eV (values for heteroatoms as indicated in the text), no penetration integrals. Ground state determinant derived by the usual SCF procedure plus all singly excited configurations (SCI) or all singly and all doubly excited configurations (SDCI) were included in the configuration interaction procedure using the formulas given by Harris.¹⁶ Expressions for the matrix elements of the Hartree-Fock operator \hat{f} , one-electron electric moment operator \hat{m} and one-electron magnetic moment operator $\hat{\mu}$ in the AO representation were

$$\langle \kappa | \hat{f} | \kappa \rangle = -I_\kappa + \frac{1}{2} q_\kappa \gamma_{\kappa\kappa} + \sum_{\sigma (\neq \kappa)} (q_\sigma - Z_\sigma) \gamma_{\kappa\sigma}$$

$$\langle \kappa | \hat{f} | \lambda \rangle = \beta_{\kappa\lambda} - \frac{1}{2} p_{\kappa\lambda} \gamma_{\kappa\lambda}$$

$$\langle \kappa | \hat{m} | \lambda \rangle = -e r_{\kappa\lambda} \delta_{\kappa\lambda}$$

$$\langle \kappa | \hat{\mu} | \lambda \rangle = i(m/\hbar^2) \beta_{\kappa\lambda} (\mathbf{r}_\lambda \times \mathbf{r}_\kappa) \text{ Bohr magneton}$$

where Z_σ is the core charge of atom σ , q_κ and $p_{\kappa\lambda}$ are the elements of the charge-bond order matrix, \mathbf{r}_σ is the position vector of AO σ , and e and m stand for the magnitude of electron charge and mass, respectively. The expression for $\langle \kappa | \hat{\mu} | \lambda \rangle$ follows from the requirement that the proper commutation relation between the position operator \hat{r} and the Hamiltonian operator \hat{H} be fulfilled in the PPP model^{10,17,18} ($[\hat{r}, \hat{H}] = i \hbar \hat{\mathbf{p}}/m$), where $\hat{\mathbf{p}}$ is the linear momentum operator, and its use guarantees origin-independence of the B terms obtained from exact (full CI) PPP wave functions for π -electron systems of arbitrary symmetry.¹⁰

The usual^{8,9} perturbation formula for the B term of a transition from ground state G to excited state F was used:

$$B(G \rightarrow F) = Im \left\{ \sum_{I, I \neq G} \langle I | \hat{m} | G \rangle \langle G | \hat{M} | F \rangle \times \langle F | \hat{M} | I \rangle / (W_I - W_G) + \sum_{I, I \neq F} \langle F | \hat{m} | I \rangle \langle G | \hat{M} | F \rangle \times \langle I | \hat{M} | G \rangle / (W_I - W_F) \right\}$$

where W_A is the energy of state A . \hat{M} and \hat{m} are the electric and magnetic dipole operator, respectively, and the summation index I runs over all molecular electronic states obtained in the calculation.

Since the PPP model was solved only approximately (SCI or SDCI, but not full CI), and since the molecules investigated were of low symmetry (C_{2v}), the calculated B terms change when the origin of coordinates is moved along the twofold symmetry axis.

All calculations were therefore repeated twice, with origin at the two extremities of the molecules (top and bottom in formula **1**). Similarly as found for nonalternant hydrocarbons,¹⁰ the differences in the B values calculated with the two choices of origin were well within other uncertainties of the calculation. Only when the calculated B terms were almost exactly zero did the origin dependence become significant. This happened in particular for benzenes with an inductive substituent. However, signs of such very small terms are unreliable anyway because of the numerous approximations present in the PPP model. Thus, all numerical results quoted can be considered origin independent for practical purposes as long as the origin is kept inside the molecules.

Trends due to inductive effects of substituents were examined by increasing or decreasing the one-center core integral I_C for one of the carbon atoms, keeping γ_C constant.

Table I. Calculated Spectra of Benzyl Ions^a

		Transition													
		1		2		3		4		5		6		7	
N-M	E^b pol ^c	21.9	X	33.9 ^d	Y	46.3	X	47.0	Y	53.4	Y	57.2	X		
SCI	$f_{T_i}^d f_{P_j}^e$	0.07	0.01	0.7	0.3	0.02	0.02	0.2	0.1	0.6	0.2	0.8	0.4		
	$B_{T_i}^f B_{P_j}^g$	1.4	1.8	-0.9	-0.9	-2.1	-2.4	0.4	0.9	1.3	1.7	0.5	-1.6		
O-K	E^b pol ^c	24.5	X	34.1 ^d	Y	47.5	Y	48.6	X	52.4	Y	59.3	X		
SCI	$f_{T_i}^d f_{P_j}^e$	0.08	0.01	0.4	0.2	0.8	0.4	0.01	0.01	0.07	0.02	0.8	0.4		
	$B_{T_i}^f B_{P_j}^g$	1.4	1.7	-1.1	-1.2	-4.0	-4.6	3.5	4.4	0.1	0.2	-0.9	-1.2		
N-M	E^b pol ^c	18.8	X	29.4 ^d	Y	39.5	Y	40.9	X	47.8	X	48.5	Y	53.0	Y
SDCI	$f_{T_i}^d f_{P_j}^e$	0.03	0.01	0.3	0.2	0.4	0.2	0.07	0.05	0.2	0.1	0.05	0.04	0.003	0.002
	$B_{T_i}^f B_{P_j}^g$	0.6	0.6	-0.2	-0.01	3.6	3.7	-4.0	-4.0	0.7	0.7	-1.4	-1.3	-0.3	-0.2
O-K	E^b pol ^c	20.3	X	29.9 ^d	Y	41.6	Y	42.5	Y	44.6	Y	49.7	X	54.0	Y
SDCI	$f_{T_i}^d f_{P_j}^e$	0.03	0.02	0.3	0.2	0.2	0.2	0.06	0.05	0.2	0.2	0.2	0.1	0.02	0.01
	$B_{T_i}^f B_{P_j}^g$	0.8	0.8	-0.4	-0.3	4.2	4.3	-7.3	-7.0	3.6	3.5	-1.3	-1.5	-1.0	-0.9

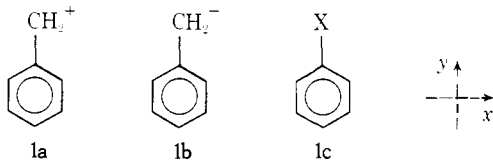
^a Results for anion and cation are identical except for the B terms. The B values given are those of the anion. Results for the cation can be obtained by inverting the sign. ^b Transition energy (10^3 cm^{-1}). ^c For definition of axes see formula 1. ^d Oscillator strength from the dipole length formula. ^e Oscillator strength from the dipole velocity formula. ^f B term in units of $10^{-3} \text{ D}^2 \beta_0 / \text{cm}^{-1}$. B_i is calculated with origin of coordinates at the top carbon atom in formula 1, B_b with origin at the bottom carbon. ^g The first observed absorption peak of the benzyl anion-cesium cation pair occurs at $28,000 \text{ cm}^{-1}$: F. J. Hopton, N. S. Hush, *Mol. Phys.*, **6**, 209 (1963). It probably corresponds to the second calculated transition. NOTE ADDED IN PROOF: Free benzyl anion has an absorption peak at $27,600 \text{ cm}^{-1}$ and a region of weaker absorption failing to at least $21,000 \text{ cm}^{-1}$; the absorption spectrum of benzyl cation is very similar [B. Bockrath and L. M. Dorfman, *J. Amer. Chem. Soc.*, **96**, 5708 (1974); R. L. Jones and L. M. Dorfman, *ibid.*, **96**, 5715 (1974)].

Variation of γ_C had virtually no effect. Mesomeric substituent effects were simulated by varying the effective electronegativity of the substituent atom X in formula 1c. Again, changes in the one-center electron-repulsion integral of the substituent did not affect the calculated signs of B terms although they affected magnitudes somewhat. To simulate the effect of a π -electron-donating substituent X, $Z_X = 2$ and $\gamma_{X+} = 17 \text{ eV}$, while A_{X+} was varied; for an electron-withdrawing substituent X, $Z_X = 0$ and $\gamma_{X-} = 9 \text{ eV}$, while I_{X-} was varied. Concrete examples of specific substituents were also calculated using parameter values suggested in the literature: phenylborane,¹⁹ aniline,²⁰ phenol.²¹

It should be noted that for molecules of low symmetry, such as those considered here, the peak of transition $G \rightarrow F$ in the MCD spectrum is related to its B term by

$$[\theta]_M = -21.3458 f_2 B$$

where f_2 is a shape function. Thus, a positive B term implies a negative peak in the MCD spectrum. Since vibronic effects are not considered in our treatment, comparison of signs should strictly speaking be done with the 0-0 component of a transition or with B values obtained by the method of moments.⁸



Results and Discussion

Benzyl Cation (1a) and Benzyl Anion (1b). A well-known theorem states that the calculated absorption spectra of **1a** and **1b** are identical in the simple PPP model.^{22,23} We have shown recently that their calculated MCD spectra will be in mirror image relationship.¹¹ Numerical results for **1b** are shown in Table I, while those for **1a** can be easily derived by reversing the signs of all calculated B terms. It will be noted that the signs of the first two calculated B terms and, to a large degree, even their magnitudes are independent of the details of the calculation and thus ought to be quite reliable. The experimental MCD spectra are unknown, so that the results represent an *a priori* prediction.

Independently of the details of the calculation, the two lowest energy transitions are well represented as one-electron

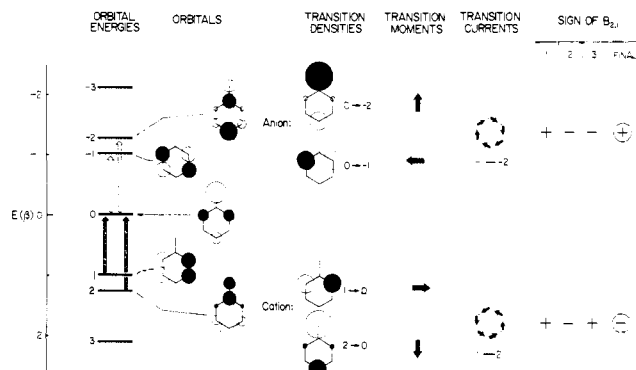


Figure 1. Derivation of the signs of the first two B terms of benzyl ions by inspection of Hückel molecular orbitals. See text.

tron jumps between SCF orbitals $1 \rightarrow 0$ and $2 \rightarrow 0$ in **1a**, and between SCF orbitals $0 \rightarrow -1$ and $0 \rightarrow -2$ in **1b** (bonding MO's are labeled by positive integers in the order of decreasing energy, antibonding MO's by negative integers in the order of increasing energy, the "nonbonding" orbital is labeled 0). Although there are some other minor but nonvanishing contributions, particularly, to the second B term, the B terms of both transitions are determined predominantly by the effect of their mutual mixing by the magnetic field. Conditions are thus right for application of a simple three-sign rule derived elsewhere,¹⁰ which relates the signs of the B terms to nodal properties of MO's involved in the two transitions. The nodal properties are essentially identical for SCF MO's and Hückel MO's, and we shall briefly show how the negative sign of the lowest B term and the positive sign of the second B term of the cation **1a**, and the opposite signs for the anion **1b**, simply follow from these nodal properties (Figure 1).

Inspection of the formula for B shows that it is sufficient to derive the B term of the lowest transition since the contribution of the mixing to the B term of the second transition will necessarily be equal in magnitude and opposite in signs. Using the nomenclature of ref 10, we need to derive the sign of $B^1_{2,1}$, and this will be a product of three signs. The first of these is positive both in the case of the cation **1a** and of the anion **1b** since $W_2 - W_1 > 0$ (the transition whose term we are deriving is lower in energy than the one with which mixing occurs). To derive the second signs, it is necessary to inspect the HMO orbitals 2, 1, 0, -1, and -2.

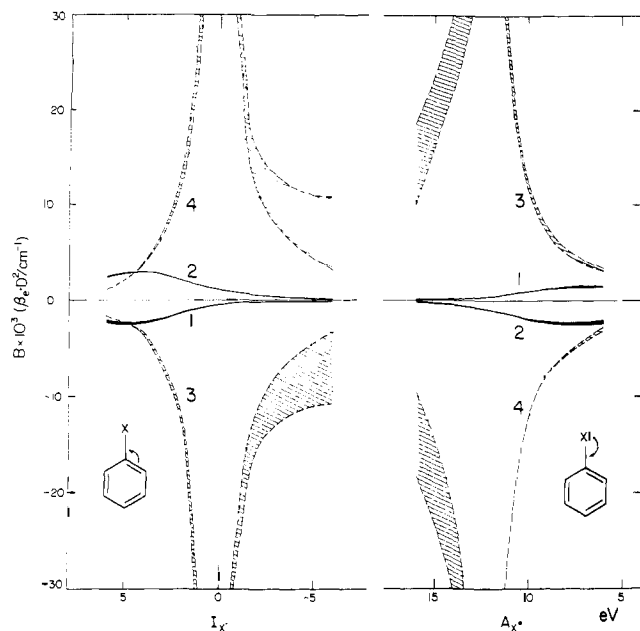


Figure 2. The first four B terms of benzene with a mesomeric substituent as a function of its electronegativity (SCI approximation). Thickness of lines indicates uncertainty due to origin dependence.

whose form is shown in Figure 1. Transition densities between orbitals are easily constructed by multiplication of the MO expansion coefficients on identical atoms in the two orbitals and are shown in Figure 1 for the transitions $0 \rightarrow -1$, $0 \rightarrow -2$, $1 \rightarrow 0$, and $2 \rightarrow 0$. Electric dipoles of the transition densities are also indicated. Their directions are obvious already from inspection of the starting HMO's. Following the rule derived in ref 10, the second sign is negative both for **1a** and **1b** (with orbital phases as chosen), since in each case the head of the arrow representing the moment of the second transition ($2 \rightarrow 0$ in **1a**, $0 \rightarrow -2$ in **1b**), *i.e.*, the one with which mixing occurs, is displaced clockwise from the head of the arrow representing the moment of the first transition ($1 \rightarrow 0$ in **1a**, $0 \rightarrow -1$ in **1b**), *i.e.*, the one whose B term we are calculating.

The third signs can be derived from the sense of the circulation of the "transition current" between orbitals by whose occupancy the two excited states differ and is positive for the cation **1a** (counterclockwise circulation) and negative for the anion **1b** (clockwise circulation), as shown in Figure 1. This follows from the nodal properties of ordered pairs of orbitals, 1 and 2 in the cation and -1 and -2 in the anion, using the simple recipe of ref 10: the arrow assigned to each bond is directed from atom κ to atom λ , where the labels κ and λ are chosen in such a way that $C_{f\lambda}C_{i\lambda} - C_{f\lambda}C_{i\kappa} > 0$. Here, $C_{f\kappa}$ is the MO coefficient of the κ th AO in the first MO of the pair (the one involved in the transition whose B term we are determining), while $C_{i\lambda}$ is the MO coefficient of the λ th AO in the second MO of the pair (the one involved in the transition with which mixing occurs).

Multiplying the three signs, we obtain an overall negative sign for the cation and a positive sign for the anion, in agreement with the numerical calculation. Because of the pairing of the MO's 0, 1, and 2 of the cation with MO's, 0, -1 , and -2 of the anion, which holds not only for HMO's but also for SCF MO's,²² it is obvious from Figure 1 why **1a** and **1b** give just the opposite results.

This derivation of the signs of the lowest two B terms by inspection singles out the essential ingredients which determine the sign. If the electronic structure of the species **1a** or **1b** is now perturbed, *e.g.*, by introduction of a heteroatom,

one can expect the sign of the B term to remain unchanged as long as these factors remain unaffected or affected but little. To summarize, these are (i) the B terms of the lowest two transitions originate from the magnetic mixing of the lowest two states, (ii) the transitions are well described as one-electron jumps $1 \rightarrow 0$, $2 \rightarrow 0$ in **1a** and $0 \rightarrow -1$, $0 \rightarrow -2$ in **1b**, (iii) the nodal properties and approximate size of coefficients of the MO's 2, 1, 0, -1 , and -2 are the same as in **1a** and **1b**. Clearly, these conditions will be fulfilled when the perturbation is only small. Numerical results to be discussed in the next section indicate that they are fulfilled even for quite large perturbations, such as going from the benzyl anion to phenol. Thus, the simple derivation of the signs of B terms of **1a** and **1b** given above essentially accounts for known effects of conjugative substituents on benzene.

SCI calculations (all singly excited configurations) on the benzyl ion predict two additional transitions and SDCI calculations (all singly and all doubly excited configurations) predict several additional transitions to lie in the experimentally accessible region. However, for these and other higher energy states, introduction of doubly excited configurations has a profound effect, and the nature of the wave functions, as well as calculated signs of B terms, are considerably changed (Table I). Experimental MCD results for this spectral region might help to assess the relative merits of omission *vs* inclusion of doubly excited configurations in PPP calculations.

Benzene with a Conjugative Substituent (1c). Inductive and conjugative effects of a substituent are easily separated in a model calculation. The effect of a purely conjugative substituent is mimicked by varying the effective electronegativity of X in formula **1c**. For an electron-donating substituent, X contributes two π -electrons ($Z_X = 2$), and its effective electronegativity is determined²⁰ primarily by the value of A_{X+} . A substituent with large A_{X+} is very weakly π -electron donating, one with small A_{X+} is strongly π -electron donating. In a calculation, A_X can be varied smoothly and the resulting picture (Figure 2) shows overall trends. Only certain values of A_{X+} correspond to experimentally attainable situations, *e.g.*, $A_{X+} \approx 9$ eV to an amine, $A_{X+} \approx 11$ eV to a phenol, $A_{X+} \approx 16$ eV to a fluoro derivative, etc. Of course, a real substituent will also have an inductive effect, which we are presently not considering.

Similarly, for an electron-withdrawing substituent, X contributes no π -electrons ($Z_X = 0$), and its effective electronegativity is determined²⁰ primarily by the value of I_{X-} . A substituent with large I_{X-} is strongly π -electron withdrawing, one with small I_{X-} is weakly π -electron withdrawing. Again, I_{X-} can be varied smoothly in a calculation, thus representing the effects of various electron-withdrawing substituents. Figure 2 shows that the trend is just the opposite of that found with electron-donating substituents. This is in agreement with the results of Koutecký²³ who showed that such species are approximately paired in the sense of alternant symmetry, if one recalls the theorem¹¹ about mirror-image relation between MCD spectra of paired species.

While Figure 2 clearly demonstrates the existence of general trends in agreement with those deduced by analogy to benzyl cation **1a** and anion **1b**, its simplifying feature, namely constant one-center electron-repulsion integral γ_X for all substituents X, is unrealistic for any actual substituent. Numerical tests showed, however, that the effect of this simplification is only minor, and that it does not affect the signs of the first two B terms. Results for several substituted benzenes obtained with literature values of parameters are given in Table II and demonstrate the validity of this statement. Agreement with experimental B terms³ (aniline,

Table II. Calculated Spectra of Substituted Benzenes^a

Compound		Transition							
		1		2		3		4	
Aniline	E_{ν}^b pol ^c	34.2	X	42.2	Y	49.8	X	52.2	Y
	f_{ν}^d, f_{ν}^e	0.06	0.02	0.4	0.2	0.4	0.2	0.9	0.4
	B_{ν}^f, B_b	1.0	1.0	-2.2	-2.2	7.8	8.4	-8.6	-8.8
Phenol	E_{ν}^b pol ^c	35.3	X	44.0	Y	51.1	X	52.8	Y
	f_{ν}^d, f_{ν}^e	0.05	0.02	0.3	0.1	0.6	0.3	1.0	0.5
	B_{ν}^f, B_b	0.7	0.7	-1.8	-1.9	10.4	11.0	-11.0	-10.9
Phenylborane	E_{ν}^b pol ^c	35.6	X	42.4	Y	51.2	X	52.0	Y
	f_{ν}^d, f_{ν}^e	0.04	0.01	0.4	0.2	0.6	0.3	0.8	0.4
	B_{ν}^f, B_b	-0.9	-0.9	1.8	1.9	-19.4	-20.7	20.2	21.2

^a N-M parameters, SCI. ^b Transition energy (10^3 cm^{-1}). ^c For definition of axes see formula 1. ^d Oscillator strength from the dipole length formula. ^e Oscillator strength from the dipole velocity formula. ^f B term in units of $10^{-3} \text{ D}^2 \beta_e / \text{cm}^{-1}$. B_{ν} is calculated with origin of coordinates at the top carbon atom in formula 1. B_b with origin at the bottom carbon.

+0.47; phenol, +0.16; in units $10^{-3} \text{ D}^2 \beta_e / \text{cm}^{-1}$ is fairly good.

Inspection of intermediate numerical results shows that the analogy to **1a** and **1b** is correct because all the conditions stated (i-iii) are fulfilled, particularly for strongly interacting substituents. Condition i remains fulfilled quite well since the first two transitions are drawn closer together in energy as the effective electronegativity of the substituent becomes different from that of carbon. At the same time, however, conditions ii and iii gradually become less well fulfilled as configuration interaction and form of MO's begin to approach that of benzene, for which calculated B 's vanish. Nevertheless, the transition is smooth and extrapolation from **1a** and **1b** thus remains admissible even for weakly interacting substituents.

The nodal properties of the critical orbitals 2, 1, 0, -1, and -2, which determine the signs of the B terms, are easily derived from a PMO-type²⁴ consideration of their origin: all five orbitals can be visualized as originating from the degenerate pairs of benzene HOMO's (highest occupied molecular orbitals) and LFMO's (lowest free molecular orbitals) and the "nonbonding" orbital on the substituent. One of the HOMO's and one of the LFMO's are antisymmetrical with respect to a plane containing the X-C bond and perpendicular to the molecular plane and remain essentially unaffected by the substitution since they have a zero coefficient at the carbon which carries the substituent. The other HOMO will mix with the substituent AO in a bonding fashion and will decrease in energy, becoming orbital 2; the other LFMO will mix with the substituent AO in an antibonding fashion and will become orbital -2, while the substituent AO, with admixtures from both the antisymmetric HOMO and the antisymmetric LFMO, becomes orbital 0. Similar arguments can be made if the isolated AO of the substituent is bonding or antibonding, rather than nonbonding, or if the substituent consists of several atoms with π -orbitals, and permit a pictorial rationalization of the nodal properties and thus the absolute sign of the lowest two B terms, from the most primitive quantum chemical notions. Signs of the B terms of higher transitions are harder to analyze, since the assignment of the states of benzene itself remains unclear.²⁵ For third and fourth B terms, SCI calculation gives large numerical values, and equal signs for first and third B term, and also equal signs for the second and fourth B term. Doubly excited configurations probably need to be included in the calculation, but choice of parameters affects results for the higher transitions strongly, and we prefer to leave this problem outside the framework of the present investigation. Fortunately, the inclusion of higher excited configurations has no effect on signs of the first B terms and on the mechanism by which they arise.

Benzene with an Inductive Substituent (1c). In all preceding comparisons with experiment it has been tacitly as-

sumed that the inductive effect can be neglected. This assumption will now be justified.

We have carried out a series of SCI calculations in which the inductive effect of the substituent was simulated by changing the effective electronegativity²⁰ $(A_C + I_C)/2$ of one of the carbons in the benzene ring and calculating the B terms. Even quite large changes result in only very small values of B terms, well below our estimated limit of significance (at least an order of magnitude less than values obtained with mesomeric substituents). Inductively electron-withdrawing substituents give small negative first B terms and small positive second B terms, inductively electron-donating substituents behave in just the opposite way as required by Koutecký's approximate pairing theorem²³ combined with the theorem about MCD spectra of paired systems.¹¹ Because of the small size of the calculated B terms, we do not attach much significance to these signs. However, it seems reasonable to predict that even quite strongly inductively perturbed benzenes, such as pyridinium and pyrylium cations, will have only small B terms of the first two transitions compared with conjugatively substituted benzenes, or with benzyl ions **1a** and **1b**. Because of the smallness of the inductive effects, we believe that the results obtained above with consideration of conjugative effects alone are directly comparable with experiment. Because of near degeneracy of the next two calculated excited states in inductively perturbed benzenes, their calculated B terms are somewhat larger. The sign of the third B term is the same as that of the first one and that of the fourth term the same as that of the second one. Again, uncertainties related to the effect of doubly excited configurations make SCI results for these higher states suspect.

Conclusions

It has been possible to make *a priori* predictions of the signs of B terms in the MCD spectra of benzyl cation **1a** and benzyl anion **1b**. While results for the low-energy transitions are probably quite reliable, previous experience¹⁰ indicates that this will be progressively less so for higher energy regions in the spectrum. The absolute signs for the first two transitions are easily understood in intuitive terms based on the nodal properties of benzyl HMO's using a three-sign rule.¹⁰ Nodal properties of benzyl HMO's are in turn easily derived from the very simplest quantum chemical notions. The same notions apply to benzene with a conjugatively π -electron-donating or a π -electron-withdrawing substituent, which are isoelectronic with **1b** and **1a**, respectively, and lead one to an extrapolation from **1a** and **1b** to conjugatively substituted benzenes. Numerical results show that such an extrapolation is correct and agree with experimental signs. The opposite MCD signs found with π -electron-donating and π -electron-withdrawing substituents thus follow from the existence of approximate alternant pairing

properties between such π -electron systems as discussed by Koutecký²³ and from the theorem¹¹ about mirror-image relation between MCD spectra of paired systems. On the other hand, effects of purely inductive substituents on benzene MCD are predicted to be much smaller.

Because of the generality of the pairing theorems^{11,23} one can predict the existence of similar mirror-image relationships for other alternant hydrocarbons with substituents of the donor and acceptor types. Theoretical and experimental work on such compounds is presently under way.

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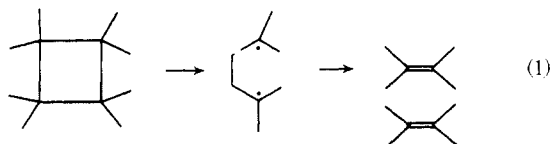
Organic Transition States. III.¹ An *ab Initio* Study of the Pyrolysis of Cyclobutane *via* the Tetramethylene Diradical

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Abstract: An *ab initio* calculation has been carried out for the potential energy surface of the pyrolysis of cyclobutane to form two ethylene molecules *via* a nonconcerted pathway. The computations involve SCF calculations at the STO-3G level followed by a 15-dimensional configuration interaction treatment. It is found that the tetramethylene diradical is a thermodynamically stable species represented by two energy wells corresponding to two conformations of the molecule. The first of these, a *gauche* geometry, presents a barrier to dissociation of 3.6 kcal/mol and a barrier to reclosure of ~ 2 kcal/mol. The energetics of dissociation *via* the other favored conformation, *trans*, are similar.

The thermal dissociation of cyclobutane to form two ethylene molecules has widely been held to be a nonconcerted process which proceeds by way of a transitory intermediate species, the tetramethylene diradical.



This reaction is one of the most elementary considered by Woodward and Hoffmann,⁴ who conclude that the $\sigma_{2s} + \sigma_{2s}$ concerted addition of two ethylenes to form cyclobutane is symmetry forbidden while the $\sigma_{2s} + \sigma_{2a}$ non-least-motion path is symmetry allowed. Examination of this latter path, however, reveals strong steric interactions which lead to a large energy of activation along such a reaction coordinate. Attempts to show that the reaction proceeds in a concerted but symmetry allowed fashion have proven negative⁵ and an *ab initio* calculation for the least-motion path reveals a large activation energy.⁶

If one then concludes that the dissociation takes place in a nonconcerted manner, a diradical intermediate is probably the simplest valence form that one can imagine for the result of breaking but one of the two bonds of cyclobutane.

It should be noted that the diradical structure in (1) implies nothing about whether the ground state of such a species is a singlet or triplet or about the nature of the orbitals that the unpaired electrons occupy, except that the concept is only useful if the orbitals are more or less nonbonding.⁷ As pointed out by Hoffmann, *et al.*,⁸ the oxygen molecule should not be considered to be a diradical in this sense.

There exists a persuasive body of indirect evidence⁹ for the participation of such diradical states in many nonconcerted reactions of which reaction 1 may be considered a prototype. Nevertheless, such a species has never been observed in a thermal reaction, although recent CIDNP experiments provide evidence for a nonconcerted diradical path in the *photolysis* of cyclic ketones.¹⁰

The tetramethylene diradical has, however, been predicted to be thermodynamically stable. The pyrolysis of cyclobutane is known to be a first-order reaction with an activation energy of 62.5 kcal/mol.¹¹ Benson¹² has carried out a thermodynamic estimation of the enthalpy of $\cdot\text{CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\cdot$ which he finds to lie at least 4 kcal/mol below the activation energy for the reaction. He thus argues that the tetramethylene diradical is thermodynamically stable and represents an energy well on the potential energy surface of reaction 1.

A key feature of this analysis is the assumption that the removal of two hydrogens from C_4H_{10} to give the tetra-