Studies in Optical Activity. I. Rotational Strengths of Twisted Ethylene, Nonplanar 1,3-Butadiene, and the Chiral Methylcyclohexanones from Molecular Orbital Wave Functions

Arvi Rauk,* John O. Jarvie, Hideo Ichimura, and Jose M. Barriel

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada. Received December 30, 1974

Abstract: Rotatory strengths of twisted ethylene, nonplanar 1,3-butadiene, and the chiral 2- and 3-methylcyclohexanones are computed directly from wave functions obtained by the following molecular orbital methods, CNDO/2, INDO, ODIN, and RHF-LCAO-MO-SCF. Several approaches, including limited single-excitation CI and the electron-hole potential method are used to improve the description of the excited states. It is found that where configurational mixing is small, ordinary ab initio SCF calculations yield the correct sign of rotation for all the systems studied. The semiempirical methods give unpredictable results but the nonempirical approximate method, ODIN, with improved virtual orbitals yields values which in most cases agree well with values obtained by the RHF-SCF method. In none of the systems studied is origin dependence of $\langle i|\mathbf{r}|j\rangle\langle j|\mathbf{m}|i\rangle$ a problem if it is evaluated from the nonempirically derived wave functions. (+)-2-Methylcyclohexanone is predicted to have the R absolute configuration contrary to the accepted assignment based on the octant rule.

In recent years, several authors have reported computation of rotational strengths of molecules directly from molecular orbital (MO) wave functions. Most of the workers have utilized wave functions derived from semiempirical MO methods: HMO,[1] EHMO,[2-4] CNDO,[4-8] extended PPP,[2,9,10] and INDO.[11,12] The most extensive investigations to date are those of Richardson and coworkers[7,11,12] who also use limited configuration interaction (CI) to improve the excited state wave functions. Two studies using nonempirical wave functions over a Gaussian basis set and augmented by CI have also been reported.[13,14] Another is in preparation.[15] The paucity of experimental data on chiral systems small enough to be amenable to MO calculations has rendered it difficult to properly assess the quality of the computed results. We think it fair to say that, for the most part, the results have been discouraging, the quality of the excited state wave functions taking the brunt of the blame.

A usually effective approach to the computation of chemical effects in large molecules involves the use of model (small) systems which incorporate the effects. However, such an approach may be particularly dangerous[12] in the study of natural optical activity which is a second-order phenomenon and presumably very sensitive to minor changes in the charge distributions. The problem is compounded by the fact that the phenomenon involves a transition between two electronic states and therefore one requires a good description of both states. In addition, several of the investigations have shown that the results are sensitive to conformational effects, not only in the gross sense (staggered vs. gauche, syn vs. anti, etc.) but in the detailed values of bond lengths[7] and bond angles.[5,7]

In view of the number of reports in this area that have appeared in recent years, a systematic study of the effect of wave function quality on the computed values of the rotatory strengths is long overdue. We here submit such a study involving nonplanar ethylene and 1,3-butadiene, and the chiral methylcyclohexanones. All three systems have received previous attention in the present context. For each system, wave functions were generated by the following molecular orbital methods, listed in order of increasing mathematical rigor: the two common semiempirical schemes, CNDO/2 and INDO; a recently developed nonempirical approximate scheme, ODIN; and the ab initio RHF-LCAO-MO-SCF method using a minimal Slater orbital basis. Results are reported for various schemes to improve

the description of the excited states, short of extensive CI calculations.

We ignore for the moment questions involving the detailed effects of geometry variation and the suitability of twisted ethylene and nonplanar butadiene as models for actual chiral alkenes and dienes and concentrate on searching for conditions under which reliable values for rotatory strengths may be obtained for a given nuclear framework.

Theory

A quantum mechanical theory of natural optical activity was first presented by Rosenfeld in 1928.[16,17] The fundamental quantity for an electronic transition from a lower state Ψ_0 to an upper state Ψ_n is the rotational strength R_{0n}

$$R_{0n} = \text{Im}\{\langle\Psi_0|\boldsymbol{\mu}|\Psi_n\rangle\cdot\langle\Psi_n|\mathbf{m}|\Psi_0\rangle\} \qquad (1)$$

where $\boldsymbol{\mu}$ and $\mathbf{m}$ are the electric and magnetic dipole moment vectors, respectively, and Im means the "imaginary part of". The operators $\boldsymbol{\mu}$ and $\mathbf{m}$ are sums of one-electron operators,

$$\boldsymbol{\mu} = \sum_k \boldsymbol{\mu}_k = e\sum_k \mathbf{r}_k \qquad (2)$$

$$\mathbf{m} = \sum_k \mathbf{m}_k = \frac{e\hbar}{2mci}\sum_k \mathbf{r}_k \times \nabla_k \qquad (3)$$

where the sums extend over all electrons in the molecule and e is negative.

For each of the calculations reported we adopt as our ground state wave function Ψ_0 a single Slater determinant (an antisymmetrized product of one electron spin orbitals $\phi_i S_i$ where S is the spin eigenfunction, α or β, and ϕ is the spacial part).

$$\Psi_0 \simeq \Phi_0 = \left(\frac{1}{N!}\right)^{1/2} \times$$

$$\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1)\ldots & \phi_{N/2}(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_{N/2}(2)\beta(2) \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ \phi_1(N)\alpha(N) & \phi_1(N)\beta(N)\ldots & \phi_{N/2}(N)\beta(N) \end{vmatrix}$$

$$= |\phi_1\alpha\bar{\phi}_1\beta\ldots\phi_{N/2}\beta| \qquad (4)$$

Singlet excited state wave functions Φ^{iv} are constructed from the ground state configuration Φ_0 by replacing one of the occupied spin orbitals, i, by a spin orbital, v, from the set of virtual orbitals.

$$\Phi^{iv} = \frac{1}{\sqrt{2}} \ (|\phi_1\alpha\phi_1\beta \ldots \phi_i\alpha\phi_v\beta \ldots \phi_{N/2}\beta| -$$
$$|\phi_1\alpha\phi_1\beta \ldots \phi_i\beta\phi_v\alpha \ldots \phi_{N/2}\beta|) \quad (5)$$

Substitution of (4) and (5) into (1) and using (2) and (3) one obtains

$$R_{0n} \equiv R_{iv} = \frac{e^2\hbar}{mc} \ \text{Im} \ \left\{\langle\phi_i|\mathbf{r}|\phi_v\rangle\langle\phi_v|\frac{\mathbf{r}\times\nabla}{i}|\phi_i\rangle\right\} \quad (6)$$

where the extra factor of 2 arises from the normalization in eq 5.

Evaluation of the matrix elements of the electric dipole operator $\langle\Psi_0|\mu|\Psi_n\rangle$ using the length form of the operator (eq 2) has been shown to lead to rotational strengths which depend on the choice of the origin of coordinates.[13,18,19] The commutator relationship $[H,\mathbf{r}] = -\hbar^2\vec{\nabla}/m$ allows one to effect the following transformation for exact wave functions:

$$e\langle\Psi_0|\sum_k \mathbf{r}_k|\Psi_n\rangle = \frac{e\hbar^2}{m(E_n - E_0)} \langle\Psi_0|\sum_k \nabla_k|\Psi_n\rangle \quad (7)$$

Use of the velocity form of the electric dipole operator leads to calculated rotational strengths which are origin independent for arbitrary wave functions.[18] However, one is then left with errors inherent in the computation of the excitation energy $(E_n - E_0)$.

In the present study we report values for rotational strengths computed using both the length and velocity formulations of the electric dipole moment operator over a variety of wave functions. Since the molecular orbitals ϕ_i are expanded as linear combinations of exponential-type functions, χ_k (STO),

$$\phi_i = \sum_k \chi_k C_{ki} \quad (8)$$

the electric and magnetic dipole transition moments are ultimately over the STO basis. General expressions for the electric moment integrals in the length formulation and for the magnetic moment integrals have been reported.[20,21] General expressions for matrix elements of the gradient operator, ∇, have been reported by Fraga.[22]

It has been pointed out (see, for example, ref 23 and 24) that the virtual orbitals which arise from solution of the Fock equations are ill suited for the construction of excited state wave functions according to eq 5. Huzinaga and Arnau[23] have presented a projection operator formalism for the improvement of virtual orbitals toward construction of a wave function for a specific excited state, Φ^{kv}, by an appropriate modification to the usual Fock operator, F. Consider the matrix representation of the modified Fock operator, F', defined by

$$F_{ij}' = \langle\chi_i|F + (1 - P)\Omega_k(1 - P)|\chi_j\rangle \quad (9)$$

where P is a projection operator for the occupied MO's,

$$P = \sum_l^{occ} |\phi_l\rangle\langle\phi_l| \quad (10)$$

and the operator Ω_k is specifically chosen so as to effectively remove an electron from the k'th MO:

$$\Omega_k = -J_k + 2K_k \quad (11)$$

J_k and K_k are the usual coulomb and exchange operators.[25] Diagonalization of F' (eq 9) leaves the occupied MO's unchanged but causes mixing among the virtual orbitals,

$$\phi_v' = \sum_w^{vir} C_{vw}\phi_w \quad (12)$$

Using the improved virtual orbitals, the excited state wave function becomes

$$\Phi^{kv'} = \frac{1}{\sqrt{2}} \ (|\phi_1\alpha\phi_1\beta \ldots \phi_k\alpha\phi_v'\beta \ldots \phi_{N/2}\beta| -$$
$$|\phi_1\alpha\phi_1\beta \ldots \phi_k\beta\phi_v'\alpha \ldots \phi_{N/2}\beta|) \quad (13)$$

Substitution of (12) into (13) leads to a multi-configurational form for $\Phi^{kv'}$,

$$\Phi^{kv'} = \sum_w^{vir} C_{vw}\Phi^{kw} \quad (14)$$

For Ω_k defined by eq 11, the coefficients, C_{vw} are exactly the same as those obtained by diagonalization of the CI Hamiltonian matrix over all configurations obtained by a single excitation out of the particular orbital, Φ_k. It has been shown[23] that the excitation energy is given by

$$E(\Phi^{kv'}) - E(\Phi_0) = \langle\phi_v'|F'|\phi_v'\rangle - \langle\phi_k|F'|\phi_k\rangle \quad (15)$$

where F' is defined in eq 9. We refer to this procedure later as the IVO procedure.

Morokuma and Iwata[26] have extended this idea to the occupied manifold. Thus, diagonalization of the matrix representation of the modified Fock operator, F'', which is defined by

$$F_{ij}'' = \langle\chi_i|F + P\omega_vP|\chi_j\rangle \quad (16)$$

where

$$\omega_v = J_v - 2K_v \quad (17)$$

yields a set of occupied ground state MO's which are improved for the description of singlet excited states arising from excitation of an electron to ϕ_v. The projection operator, P, forces the improved ground state MO's, ϕ_i', to be related to the regular SCF occupied orbitals by a unitary transformation, thus leaving the ground state unchanged.

$$\phi_i' = \sum_l^{occ} C_{il}\phi_l \quad 1 \leq i \leq N/2 \quad (18)$$

The resulting improved excited state wave function becomes

$$\Phi^{k'v} = \frac{1}{\sqrt{2}} \ (|\phi_1'\alpha\phi_1'\beta \ldots \phi_k'\alpha\phi_v\beta \ldots \phi_{N/2}'\beta| -$$
$$|\phi_1'\alpha\phi_1'\beta \ldots \phi_k'\beta\phi_v\alpha \ldots \phi_{N/2}'\beta|) \quad (19)$$

Substitution of (18) into (19) leads to a multi-configurational form for $\Phi^{k'v}$:

$$\Phi^{k'v} = \sum_l^{occ} C_{kl}\Phi^{lv} \quad (20)$$

As with the improved virtual orbital treatment, the coefficients, C_{kl}, are the same as those obtained by a CI calculation that includes only configurations obtained by a single excitation to a particular orbital, ϕ_v. The excitation energy is given by

$$E(\Phi^{k'v}) - E(\Phi_0) = \langle\phi_v|F''|\phi_v\rangle - \langle\phi_k'|F''|\phi_k'\rangle \quad (21)$$

where F'' is defined in eq 17. We later refer to this procedure as the IGO procedure.

Morokuma and Iwata[26] have also shown that the excited state can be further improved by simultaneous application of eq 9 and 14. In this case one solves a secular equation based on the modified Fock operator,

$$F''' = F + (1 - P)\Omega_k(1 - P) + P\omega_vP \quad (22)$$

This results in a pair of MO's ϕ_k' and ϕ_v', which are improved for the particular excited state represented by $\Phi^{k'v'}$ and which are given by eq 18 and 12, respectively. The appropriate expression for the excitation energy is
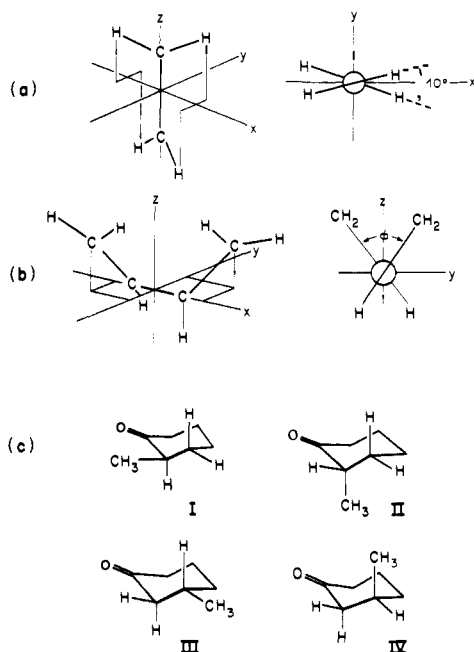
Figure 1. The absolute configurations of twisted ethylene (a), nonplanar 1,3-butadiene (b), and the chiral methylcyclohexanones (c).

$$E(\Phi^{k'\,v'}) - E(\Phi_0) = \langle \phi_v' | F | \phi_v' \rangle -$$
$$\langle \phi_k' | F | \phi_k' \rangle - J_{k'\,v'} + 2K_{k'\,v'} \quad (23)$$

where F is the self-consistent ground state Fock operator and $J_{k'v'}$ and $K_{k'v'}$ are the usual coulomb and exchange integrals[25] over the improved orbitals.

It seems reasonable that the potentials, Ω_k and ω_v, would be improved by basing them on ϕ_k' and ϕ_v' instead of ϕ_k and ϕ_v. Thus, by successively updating Ω_k and ω_v, eq 22 can be iterated to self-consistency. The self-consistent improved MO's have been called "extended Hartree–Fock" MO's.[26]

Method

Wave functions used in the present work are derived from the semiempirical CNDO/2 and INDO schemes in the Pople–Segal parametrization,[27-30] from the ODIN (a nonempirical INDO) scheme,[31-33] and from the ab initio RHF-Roothaan LCAO-MO-SCF method (referred to in tables as RHF).[25] In each case a minimal STO basis set is used. Slater exponents are used in all cases except for the ODIN calculations where Clementi-Raimondi exponents were adopted.[34] The ab initio calculations on twisted ethylene and nonplanar 1,3-butadiene were carried out using a program[35] in which all one- and two-center integrals are computed exactly over exponential-type functions and in which all three- and four-center integrals are computed using Pople's[36] STO-3G Gaussian expansion of the STO's.[37] For ab initio calculations involving the larger methylcyclohexanones, all integrals are approximated by the STO-3G Gaussian expansion of the STO's[38] with optimized exponents. The wave functions derived from the approximate methods, CNDO, INDO, and ODIN, were subjected to deorthogonalization as described by Giessner-Prettre and Pullman[39] and used by Richardson[7,11] and Imamura[8] for calculating rotatory strengths. Where single excitation configuration interaction (CI) calculations within the CNDO method were performed, the CI coefficients and the required two-electron integrals, molecular orbitals, and molecular eigenvalues are those obtained using orthogonal orbitals rather than deorthogonalized orbitals. This procedure is more in keeping with the spirit of the CNDO approximations and is less likely to involve readjustment of empirical parameters.

Details of the geometry and absolute configurations of all molecules are shown in Figure 1. For twisted ethylene, the geometry is the same as used by Robin and coworkers.[14] One end is twisted out of planarity with the other end by 10° in the sense illustrated in Figure 1a. Three nonplanar geometries of 1,3-butadiene were considered with values for the dihedral angle ϕ of 45, 90, and 135°, in the direction indicated in Figure 1b. Except for the dihedral angle ϕ, the geometric parameters are those of s-trans-1,3-butadiene.[40] For ease in comparing results, the geometries for the methylcyclohexanones are identical with those used in previous investigations.[2,6] The absolute configurations are shown in Figure 1c.

Results

In Table I are presented the computed rotatory strengths for ethylene twisted 10° in the sense illustrated in Figure 1a. For comparison, the SCF and CI results of Robin et al.[14] who used an atom-optimized Gaussian basis set of double ζ quality have been included. In this and in other tables the rotatory strengths calculated by using the length form of the electric dipole operator are in units of cgs × 10^{40} and are designated r·m. The expression Im $\{\langle \Psi_i | \nabla | \Psi_j \rangle,$ $\langle \Psi_j | \mathbf{m} | \Psi_i \rangle\}$ is also evaluated and designated ∇·m. The units

Table I. Rotatory Strengths of the B_1 States of Ethylene Twisted 10° out of a Plane[a]

Transition[b]	Property	CNDO/2[f]	CNDO/CI[e]	INDO	ODIN	ODIN-IVO	RHF MIN	RHF BADZ[c]	CI[d]
$A_g \to B_{1u}$	r·m	-188	-77.8	-177.0	-68.6	-69.2	-56.4		
($\pi \to \pi^*$)	∇·m	-28.3	-2,24	-26.54	-12.9	-13.0	-10.25	-13.5	-43.1
	ΔE			0.4310			0.438	0.338	0.328
$A_g \to B_{1g}$	r·m	315	155	327.6	98.2		114.4		
($1b_{2g} \to \pi^*$)	∇·m	64.7	9.05	70.0	24.9		32.3	33.6	59.7
	ΔE			0.489			0.391	0.358	0.363
$A_g \to B_{1g}$	r·m	-163	-83.5	-176.2	-33.4	-32.8	-41.6		
($\pi \to 2b_{3u}$)	∇·m	-58.2	-15.9	-60.1	-18.2	-18.1	-15.2	-11.2	-7.11
	ΔE			0.492			0.568	0.458	0.459
$A_g \to B_{1u}$	r·m	0.85	5.11	1.08	1.12		0.74		
($3a_g \to 3b_{1u}$)	∇·m	0.68	3.18	0.73	0.50		0.47	0.09	1.52
	ΔE			0.592			0.864	0.605	0.605

[a] The units of $\langle i|r|j\rangle \cdot \langle j|m|i\rangle$ (=r·m) are cgs × 10^{40}. The units of $\langle i|\nabla|j\rangle \cdot \langle j|m|i\rangle$ (=∇·m) are such that ∇·m/ΔE is in cgs × 10^{40} if ΔE is in hartree units. [b] The symmetry designations refer to planar ethylene. [c] Reference 14 where a best atom double ζ basis of Gaussian-type orbitals is used. [d] The CI results are from ref 14. [e] Complete single excitation CI using the Nishimoto–Mataga[48] approximation to the Coulomb repulsion integrals. [f] Obtained using the exact[27] two-electron integrals. The results differ little if the Nishimoto–Mataga approximation[48] is used for the repulsion integrals.

are such that if $\nabla \cdot \mathbf{m}$ is divided by the excitation energy ($E_j - E_i$) in atomic units, then the result is the rotational strength in cgs $\times 10^{40}$ units as is $\mathbf{r} \cdot \mathbf{m}$. The data of Robin and coworkers presented in Table I have been treated accordingly.[41]

The computed rotatory strengths for two $\pi \to \pi^*$ transitions of nonplanar 1,3-butadiene (Figure 1) are presented in Table III and Figure 2.

The rotational strengths of the n $\to \pi^*$ (290 nm) transition in the four chiral methylcyclohexanones are given in Tables IV and V.

Discussion

Ethylene. Twisted ethylene is one of only two chiral systems for which rigorous extended basis set ab initio calculations have been reported and for which the rotational strength has been determined.[13,14] It is an inherently dissymmetric chromophore[42] and has been considered[9,14,43] to serve as a model compound in explaining the strong optical rotatory strengths observed in *trans*-cyclooctene and other twisted alkenes.[9,43,44] Although considerable discussion has taken place in recent years regarding the Rydberg vs. valence character of the lower lying states of simple mono-olefins (see, for example, ref 9, 14, 45, and 46), recent opinion[14,45,46] favors the view that the transition which gives rise to the observed sign of rotation in twisted olefins is the *valence shell* electric-dipole allowed, $\pi \to \pi^*$ transition which becomes magnetic-dipole allowed upon twisting. From Table I, it is evident that all of the methods here considered give the same signs as obtained from the most rigorous ab initio study[14] for all transitions. The magnitudes of the computed rotational strengths and $\nabla \cdot \mathbf{m}$ products obtained from ODIN and RHF with minimum basis agree well with the magnitudes obtained with the RHF calculation (non-CI) which employed a basis set of double ζ quality. However, magnitudes shift to a large extent upon configurational mixing. We notice that the semiempirical CNDO and INDO schemes also yield the correct signs in this case whereas an extended Pariser–Parr–Pople scheme gave the opposite sign for the $\pi \to \pi^*$ transition of *trans*-cyclooctene.[9]

A number of CI calculations were performed on twisted ethylene within the CNDO[47] approximation. A complete single excitation CI calculation, using the Nishimoto–Mataga approximation to the coulomb repulsion integrals,[48,49] yielded values of rotatory strengths which agree in sign to values obtained from the usual SCF procedure. However, whereas the SCF (non-CI) results differed little whether one used the approximate[48] or exact[27] (within the CNDO approximations) integrals, the CI results with two-electron integrals computed over s-type Slater orbitals often disagreed in sign with the SCF results, either in $\mathbf{r} \cdot \mathbf{m}$, or $\nabla \cdot \mathbf{m}$, or both. For brevity these results are not included in Table I. In fact, comparison of the results in columns three and four of Table I leads us to believe that the agreement in sign between SCF and CI results with the approximated integrals[48] is fortuitous. All configurations with B_1 symmetry contribute strongly to the rotatory strength, including several which are intuitively unreasonable, for example, one derived from an excitation of an electron from the lowest occupied valence orbital to the highest unoccupied MO. The zero-differential-overlap approximation does not allow the higher virtual orbitals to become sufficiently repulsive or the lower occupied MO's to become sufficiently attractive. For this reason, we regard CI results involving configurations constructed from these MO's within the semiempirical scheme with some skepticism.

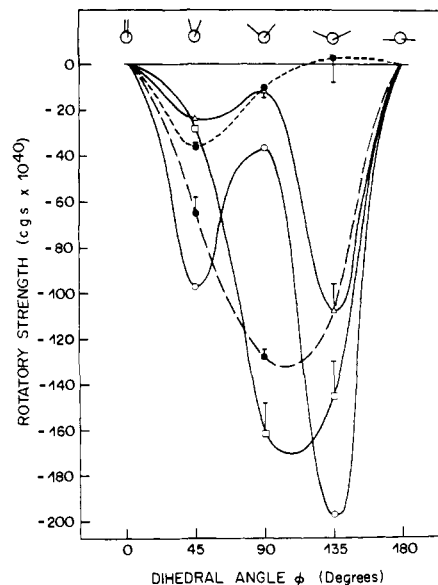Due to the high symmetry (point group D_2) and small

Figure 2. Rotational strengths for the $\pi \to \pi^*$ transition in 1,3-butadiene as a function of dihedral angle computed from ab initio RHF-SCF wave functions: (- - -) SCF result for R_{8a8b}; (- - -) SCF result for R_{7b9a}; ($\square$) IGO-IVO; ($\triangle$) SCF-CI; ($\bigcirc$) IGO-IVO-CI. The horizontal dashes connected to points on the curves represent the corresponding results obtained when the STO-3G approximation is applied to all integrals.

Table II. The z Components of the $A_g \to B_{1u}$ ($\pi \to \pi^*$) Transition in Twisted Ethylene

Method	$\langle A_g|z|B_{1u}\rangle^a$	$\langle A_g|\nabla_z|B_{1u}\rangle^a$	$\langle B_{1u}|m_z|A_g\rangle^b$
CNDO	0.9859	0.1481	-0.8115
CNDO-CI	0.3059	0.0088	-1.0785
INDO	1.0964	0.1653	-0.6848
ODIN	1.8408	0.3441	-0.1583
ODIN-IVO	1.8413	0.3444	-0.1594
RHF(MIN)	1.8140	0.3301	-0.1321
RHF(BADZ)^c		0.385	-0.149
RHF(BADZ)-CI^c		0.240	-0.762

^{a} In atomic units. ^{b} In units of bohr magnetons. ^{c} Reference 14.

basis set used for the calculations on ethylene, little variational flexibility exists for improvement of the occupied and virtual orbitals by the procedures outlined in eq 9–23. The greatest effect is experienced using the ODIN method.[33] As a result, the only IVO results cited in Table I are those obtained by the ODIN method.

An important consequence of the high symmetry of twisted ethylene is that the length and velocity forms of the electric dipole transition moment vector are exactly parallel and in the same direction as the magnetic dipole transition moment. For example, the moments of the $A \to B_1$ transitions in ethylene, oriented as shown in Figure 1a, are in the z direction. Therefore, the quantity $\mathbf{r} \cdot \mathbf{m}$ is *not* origin dependent. Accordingly, for this particular case, a direct comparison of $\mathbf{r} \cdot \mathbf{m}$ with $\nabla \cdot \mathbf{m}/\Delta E$ should serve as a better indication of the relative qualities of the nonempirically and semiempirically derived wave functions than in cases where the origin dependence is present. Assuming the experimental energy for the $\pi \to \pi^*$ transition, $\Delta E = 0.28$,[14,50] the following ratios of $\mathbf{r} \cdot \mathbf{m}$ and $\nabla \cdot \mathbf{m}/\Delta E$ may be derived from the data in Table I: CNDO/2, 1.86; CNDO-CI, 9.73; INDO, 1.87; ODIN, 1.49; ODIN-IVO, 1.49; RHF(MIN), 1.54. In as much as a deviation of the ratio from unity is a reflection of wave function quality, it is immediately apparent that the CNDO-CI wave function is anomalous. An examination of the vector components, $\langle A_g|z|B_{1u}\rangle$, $\langle A_g|\nabla_z|B_{1u}\rangle$ and $\langle B_{1u}|m_z|A_g\rangle$, given in Table II, reveals a considerable dis-

Table III. Rotatory Strengths for Two $\pi \to \pi^*$ Transitions in Twisted 1,3-Butadiene[a]

Dihedral angle ϕ,[b] deg	Transition	Property	HMO[c]	PPP[d]	CNDO	INDO	ODIN	ODIN-IVO	RHF
45	A → B	r·m	−75		10.23	4.74	−42.2	−40.6	−35.9
	($\pi_2 \to \pi_3$)	∇·m	−167.7	0.74	2.70	1.93	−6.64	−6.39	−5.12
		∆E	0.223		0.409	0.409			0.3448
	A → A	r·m	70		88.4	98.4	28.9	69.3	50.7
	($\pi_2 \to \pi_4$)	∇·m			15.95	18.0	5.35	13.5	9.47
		∆E			0.482	0.468			0.4464
90	A → B	r·m	−95		−212.5	−192.2	−113.8	−119.9	−128.1
	($\pi_2 \to \pi_3$)	∇·m	−26.3	−2.9	−43.9	−40.8	−21.9	−22.7	−24.7
		∆E	0.277		0.441	0.441			0.3935
	A → A	r·m	95		64.5	71.4	32.1	80.9	82.6
	($\pi_2 \to \pi_4$)	∇·m	26.3		16.8	19.2	5.03	16.3	16.2
		∆E	0.277		0.457	0.457			0.4154
135	A → B	r·m	−75		−162.5	−148.1	−100.4	−103.0	−107.8
	($\pi_2 \to \pi_3$)	∇·m	−16.3	−8.5	−26.3	−24.1	−17.3	−17.8	−17.2
		∆E	0.223		0.416	0.416			0.3529
	A → A	r·m	70		48.2	43.6	63.4	53.2	57.5
	($\pi_2 \to \pi_4$)	∇·m			19.4	21.1	14.5	10.9	13.0
		∆E			0.474	0.451			0.442

[a] The units of $\langle i|\mathbf{r}|j\rangle \cdot \langle j|\mathbf{m}|i\rangle$ (=r·m) are cgs $\times 10^{40}$. The units of $\langle i|\nabla|j\rangle \cdot \langle j|\mathbf{m}|i\rangle$ (=∇·m) are such that ∇·m/∆E is in cgs $\times 10^{40}$ if ∆E is in hartree units. [b] Refer to Figure 1b for geometry. [c] Interpolated from the results of ref 1. [d] Estimated from the results of ref 2; includes some CI.
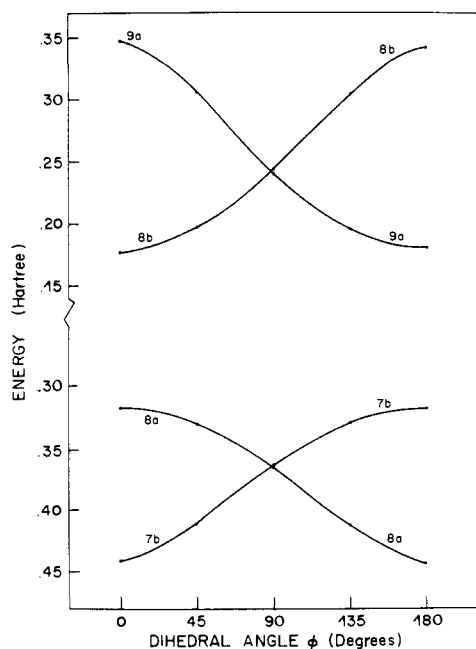

Figure 3. Correlation diagram for the π molecular orbitals of 1,3-butadiene as a function of dihedral angle.

crepancy between the semiempirical and nonempirical wave functions. In planar ethylene, the $\pi \to \pi^*$ transition is electric-dipole allowed, magnetic-dipole forbidden. In the moments computed from the nonempirically derived SCF wave functions, for a small twist, the selection rules are reflected in the fact that the magnetic dipole moment is much smaller than the electric dipole moment. The electric and magnetic dipole moments derived from the CNDO and INDO methods are approximately the same magnitude.

Butadiene. Nonplanar 1,3-butadiene is another example of an intrinsically dissymmetric chromophore.[42] Although this molecule has been the subject of intensive theoretical investigation, particularly in connection with the mode of its ring closure to cyclobutene (see, for example, ref 51 and 52), we are aware of only four studies (by the HMO,[1] EHMO,[2] PPP,[2,10] and RHF (Gaussian basis set)[15] methods) of its chiroptical properties. A comparison of rotatory strengths, calculated by various methods, of two transitions in twisted 1,3-butadiene is given in Table III,[53] as a func-

tion of dihedral angle, ϕ (Figure 1b). Comparison of the results obtained by the different methods reveals that the ab initio RHF method and ODIN with improved virtual orbitals give very similar results both for the rotatory strength (r·m) and for the scalar product ∇·m. The results obtained by the approximate schemes CNDO, INDO, and ODIN are substantially different, however, when the normal Hartree–Fock virtual orbitals are used. At $\phi = 45°$, the CNDO and INDO methods give the incorrect sign compared with that predicted by the empirically derived diene rule.[55]

The results of a more extensive study, within the ab initio RHF framework, are shown in Figure 2. The correlation diagram for the four π orbitals of 1,3-butadiene is shown in Figure 3. The symmetries are designated according to the point group C_2. The occupied π orbitals, 7b and 8a, cross at a dihedral angle slightly less than 90°, as do the virtual π orbitals, 8b and 9a. Loosely speaking, the lowest energy excitation at dihedral angles less than 90° is 8a → 8b, whereas at 90° and above, the lowest transition is 7b → 9a. Both transitions lead to configurations of the same symmetry, B, and considerable configurational mixing will occur in the vicinity of $\phi = 90°$. In Figure 2, the dashed lines show the calculated angular dependence of the rotational strengths, $R_{8a,8b}$ and $R_{7b,9a}$ (eq 6). $R_{8a,8b}$ is largest in the vicinity of $\phi = 45°$ and is small for $\phi > 90°$. On the other hand, $R_{7b,9a}$ is maximum near $\phi = 100°$ and large at other dihedral angles. A CI calculation (SCF-CI) involving the two lowest configurations of B symmetry, constructed from the SCF orbitals, yields an improved wave function for the lowest B state reached by a $\pi \to \pi^*$ ($\pi_2 \to \pi_3$) transition. The rotatory strength of the transition to this two-configuration CI-improved state is traced by the solid line connecting triangular points in Figure 2. The curve has a minimum near $\phi = 90°$ but does not change sign as expected from similar CI results using a PPP wave function.[2] Improvement of the virtual and ground state occupied orbitals (IVO-IGO) toward the same $\pi_2 \to \pi_3$ transition according to the procedure outlined in the Theory section leads to the angular dependence shown by the solid line connecting square points in Figure 2. The quantitative features differ significantly, a maximum being predicted near $\phi = 90°$. After a two-configuration CI calculation using configurations constructed from the *improved* orbitals (IVO-IGO-CI), however, the rotational strength of the $\pi_2 \to \pi_3$ transition is again predicted to have a lower value at $\phi \simeq 90°$ than at $\phi = 45°$ or $\phi = 135°$. The last result is shown in Figure 2 by the solid
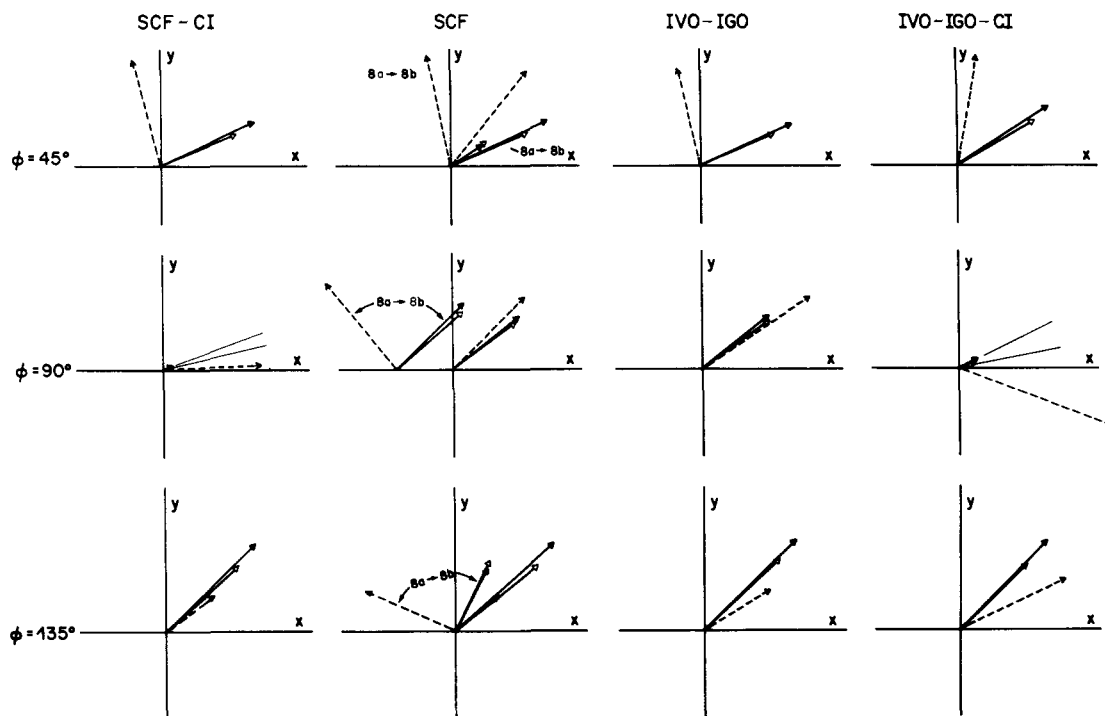
Figure 4. Component transition moments of the rotational strengths of the $\pi \rightarrow \pi^*$ transitions of 1,3-butadiene illustrated in Figure 2: $(\rightarrow)$ $\langle i|\mathbf{r}|j\rangle$; $(\rightarrow)$ $\langle i|\nabla|j\rangle$; $(\rightarrow)$ $\langle i|\mathbf{m}|j\rangle$. In atomic units, $\langle i|\nabla|j\rangle$ and $\langle j|\mathbf{m}|i\rangle$ are illustrated to scale and the length of $\langle i|\mathbf{r}|j\rangle$ has been reduced by a factor of 5. In the SCF column, the unmarked vectors correspond to the 7b $\rightarrow$ 9a transition.

line connecting open circular points. The present ab initio results support previously obtained semiempirical results[2,10] in establishing the importance of configurational mixing near $\phi = 90°$ and the large effect of cross terms which arise in the use of CI wave functions on the computed values for the rotatory strengths. However, the ab initio results differ both quantitatively and qualitatively from the two sets of semiempirical results.

Clearly, the calculated value of the rotatory strength of a transition is very sensitive to the method of construction of the excited state. Information on the origin of this sensitivity may be obtained by examining the magnitudes and directions of the electric and magnetic dipole moment vectors, which are shown for the $\pi_2 \rightarrow \pi_3$ transition in Figure 4. For geometries $\phi = 45°$ and $\phi = 135°$ where configurational mixing is weak, the directions of the vectors are determined by the dominant transition. It is clear from consideration of the $\phi = 90°$ results that the CI expansion implicit in the IVO-IGO procedure (eq 14 and 20) does not have a significant contribution from the other important configuration, $\Phi^{8a,8b}$, and yields an inadequate description of the desired excited state. It is noteworthy that where configurational mixing should be small, the directions and the magnitudes of the electric dipole vector are not sensitive to the types of configurations used. This is not the case for the magnetic dipole moment where the direction ($\phi = 45°$) or magnitude ($\phi = 135°$) may vary in a seemingly unpredictable fashion. The effect of configurational mixing on both vectors is quite complex where such mixing is strong ($\phi = 90°$). Although it is appropriate at this point to raise the question of origin dependence of the magnetic dipole vector and of the rotatory strength computed using the length form of the electric dipole moment operator, this is deferred in favor of a more detailed discussion after the next section.

Methylcyclohexanones. The chiral methylcyclohexanones are examples of inherently symmetric chromophores,[42] the optical rotational strength being produced by a dissymmetric intramolecular perturbation. An experimentally deduced and theoretically supported *octant rule* successfully
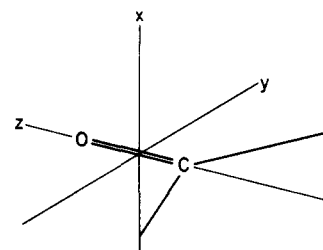

Figure 5. Axes convention for octant rule for carbonyl compounds.

(in most cases) correlates the sign of the contribution to the rotational strength of a perturbing group (in the saturated part of the molecule) with its spacial orientation relative to the carbonyl group.[56-58] According to the rule, the sign is given by the sign of the product *xyz* of the coordinates of the perturbing group when the carbonyl group is oriented as in Figure 5. A fluorine substituent is known to contribute in a sense opposite to that contributed by a carbon or hydrogen substituent[56] and other limitations have been discovered.[59] An extension of the *octant rule* to accommodate unsaturated substituents has also been proposed.[60] Calculations of rotatory strengths of methylcyclopentanones[11] and methylcyclohexanones[2,6,8] from semiempirical wave functions have been presented.

In Table IV is given a comparison of rotatory strengths of the n $\rightarrow$ π^* transition calculated from CNDO, INDO, ODIN, ODIN-IVO, and RHF wave functions for (R)-2-methylcyclohexanone (I), (S)-2-methylcyclohexanone (II), (S)-3-methylcyclohexanone (III), and (R)-3-methylcyclohexanone (IV) in the conformations illustrated in Figure 1c. For compounds I, II, III, and IV, application of the *octant rule*[56] would lead one to expect the signs $\simeq 0$, +, −, and − respectively, for the rotational strength of the n $\rightarrow$ π^* transition. Inspection of Table IV reveals that the computed results are widely scattered. The agreement between results obtained by the approximate method ODIN with improved virtual orbitals (ODIN-IVO) and by the ab initio RHF

Table IV. Rotatory Strengths for the n → π* Transitions in the Chiral Methylcyclohexanones[a]

Compd[b]	Method	ΔE, hartree[c]	$\nabla \cdot m$	$r \cdot m$
1	CNDO	0.257	−0.593	−0.631
	INDO	0.218	0.104	1.21
	ODIN		−6.20	−10.8
	ODIN-IVO		2.37	12.1
	RHF	0.197	1.97	9.00
II	CNDO	0.254	0.286	6.79
	INDO	0.216	0.416	7.31
	ODIN		−8.39	−0.63
	ODIN-IVO		15.83	76.2
	RHF	0.195	3.24	16.5
III	CNDO	0.260	−1.43	−4.75
	INDO	0.216	−2.21	−6.88
	ODIN		9.73	20.8
	ODIN-IVO		−2.06	−10.3
	RHF	0.193	−1.86	−8.54
IV	CNDO	0.256	2.88	14.8
	INDO	0.212	1.34	8.20
	ODIN		−1.85	−3.34
	ODIN-IVO		0.84	4.12
	RHF	0.192	0.81	4.41

[a] The units of $\langle i|r|j\rangle \cdot \langle j|m|i\rangle$ (=r·m) are cgs × 10⁴⁰. The units of $\langle i|\nabla|j\rangle \cdot \langle j|m|i\rangle$ (=∇·m) are such that ∇·m/ΔE is in cgs × 10⁴⁰ if ΔE is in hartree units. [b] Refer to Figure 1c. [c] 1 hartree = 27.2 eV.

method lends credence to the calculated signs of rotation. In all cases the semiempirical INDO method yields the same signs as are obtained from the nonempirical methods. The RHF and ODIN-IVO procedures yield a substantial value for the rotational strength of I, contrary to expectations based on the octant rule. The sign of the computed rotatory strength for compound IV does not agree with the prediction based on the octant rule but has been verified experimentally in related systems.[61]

It was anticipated that significant improvement should occur in the excited state wave function upon application of the procedures described by eq 9–23 for two reasons. First, since the methylcyclohexanones have no elements of symmetry, maximum optimization of the occupied and virtual orbitals is possible. Second, a single-excitation CI calculation (on IV) within the CNDO approximation suggests that the configurations which contribute most to the singlet n → π* excited state either are constructed by excitation from orbital n to the virtual orbitals or are constructed by excitation from the occupied orbitals to the π* orbital. Both of these kinds of configurations should be optimally included, the former in the RHF-IVO method, the latter in the RHF-IGO method. In Table V the RHF-IVO and RHF-IGO results for r·m and ∇·m are compared with the results obtained from the regular SCF wave function. The results

for simultaneous IVO-IGO are also included in Table V. The computed rotatory strengths for all compounds become smaller in the sequence SCF → IVO → IGO → IVO-IGO and in the last step ∇·m changes sign. We can offer only a partial explanation for this unexpected result. Inspection of the charge distribution of the "n" and "π*" orbitals reveals that both orbitals are highly localized to the carbonyl moiety. Both orbitals *become even more localized* upon "improvement" for the excited state. Although this increased localization is in the right direction,[62] we believe it is exaggerated, particularly by the IGO procedure.

Comparison of the computed rotatory strengths with experiment is hampered by the fact that at least two conformers are present in equilibrium.[63] If one denotes the enantiomeric forms by an asterisk (e.g. I*) then the following equilibria apply:

$$I \rightleftharpoons II*$$

$$III \rightleftharpoons IV*$$

Relative stabilities estimated by the RHF method indicate that I is 0.85 kcal/mol more stable than II* and that III is 3.32 kcal/mol more stable than IV*. With the tentative assumption that the RHF-IVO results (Table V) most closely approximate reality, (R)-2-methylcyclohexanone is predicted to have a rotatory strength of +3.2 × 10⁻⁴⁰ cgs and (S)-3-methylcyclohexanone is predicted to have a rotatory strength of −6.65 × 10⁻⁴⁰ cgs at 25°. Due to the unexpectedly large positive rotation of structure I, the prediction for (R)-2-methylcyclohexanone is not in accord with expectations based on the octant rule[64] which have led to the generally accepted configurational assignment.[64,65]

Origin Dependence of m and r·m. The spacial dependence of **m** and **r·m** may be expressed as $\langle j|\mathbf{r} \times \nabla|i\rangle$ and $\langle i|\mathbf{r}|j\rangle \langle j|\mathbf{r} \times \nabla|i\rangle$, respectively. A shift to a new origin,

$$\mathbf{r}' = \mathbf{r} + \mathbf{R}$$

leads to the new values

$$\mathbf{m}' = \langle j|\mathbf{r} \times \nabla|i\rangle + \mathbf{R} \times \langle j|\nabla|i\rangle =$$

$$\mathbf{m} + \mathbf{R} \times \langle j|\nabla|i\rangle \quad (24)$$

and

$$\mathbf{r}' \cdot \mathbf{m}' = \langle i|\mathbf{r}|j\rangle \cdot \langle j|\mathbf{r} \times \nabla|i\rangle + \langle i|\mathbf{r}|j\rangle \cdot \mathbf{R} \times$$

$$\langle j|\nabla|i\rangle = \mathbf{r} \cdot \mathbf{m} + \langle i|\mathbf{r}|j\rangle \cdot \mathbf{R} \times \langle j|\nabla|i\rangle \quad (25)$$

For optical transitions which are electric-dipole forbidden but magnetic-dipole allowed, as is the n → π* transition of carbonyl compounds, the rotatory strength, **r·m**, is virtually origin independent since both transition moments $\langle i|\mathbf{r}|j\rangle$ and $\langle j|\nabla|i\rangle$ will be much smaller than $\langle j|\mathbf{r} \times \nabla|i\rangle$. Thus, in practice, the computed values **m** and **r·m** for such transi-

Table V. Rotatory Strengths[a] of the n → π* Transition of the Methylcyclohexanones Using "Improved" Orbitals

Compd	Property	SCF	RHF-IVO	RHF-IGO	RHF-IVO-IGO
I[b]	r·m	9.00 (9.12)	7.47 (7.52)	1.85 (1.83)	0.98 (0.93)
	∇·m	1.97 (2.06)	1.31 (1.36)	0.28 (0.32)	−0.03 (−0.02)
	ΔE[c]	0.197 (0.197)	0.192 (0.192)	0.165 (0.164)	
II	r·m	16.5	14.3	3.07	1.31
	∇·m	3.24	2.24	0.46	−0.25
	ΔE[c]	0.195	0.190	0.164	
III	r·m	−8.54	−6.67	−1.39	−0.40
	∇·m	−1.86	−1.14	−0.24	0.09
	ΔE[c]	0.193	0.188	0.163	
IV	r·m	4.41	3.77	0.64	0.28
	∇·m	0.81	0.53	0.05	−0.09
	ΔE[c]	0.192	0.187	0.162	

[a] The units of $\langle i|r|j\rangle \cdot \langle j|m|i\rangle$ (=r·m) are cgs × 10⁴⁰. The units of $\langle i|\nabla|j\rangle \cdot \langle j|m|i\rangle$ (=∇·m) are such that ∇·m/ΔE is in cgs × 10⁴⁰ if ΔE is in hartree units. [b] The numbers in parentheses were obtained using the STO-4G expansion of the STO's. [c] ΔE is in units of hartrees. 1 hartree = 27.2 eV.
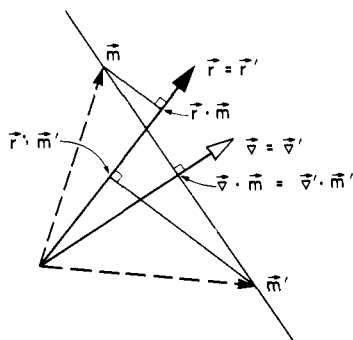
Figure 6. Hypothetical two-dimensional illustration of the variation of $\mathbf{m}$ $(=\langle j|\mathbf{m}|i\rangle)$, $\mathbf{r}$ $(=\langle i|\mathbf{r}|j\rangle)$, ∇ $(=\langle i|\nabla|j\rangle)$, $\nabla\cdot\mathbf{m}$, and $\mathbf{r}\cdot\mathbf{m}$ upon an arbitrary shift of origin from $\mathbf{r}$ to $\mathbf{r}'$. The terminus of the vector $\mathbf{m}$ is constrained (in three dimensions) to a plane perpendicular to ∇. The origin dependence of $\mathbf{r}\cdot\mathbf{m}$ arises from the noncollinearity of $\mathbf{r}$ and ∇.

tions will be relatively insensitive to all reasonable choices of the origin for the operators. In principle, such is not the case for optical transitions which are electric-dipole allowed.

From eq 24 it can be seen that the origin dependence of the magnetic moment vector $\langle j|\mathbf{r}\times\nabla|i\rangle$ is tied to the gradient vector, $\langle j|\nabla|i\rangle$, in the manner illustrated in Figure 6. If the two vectors are transferred to the same origin then the terminal point of $\mathbf{m}$ is restricted to a plane perpendicular to $\langle j|\nabla|i\rangle$. The origin dependence of $\mathbf{r}\cdot\mathbf{m}$ arises from the fact that for inexact wave functions, $\mathbf{r}$ $(=\langle i|\mathbf{r}|j\rangle)$ is not parallel to $\langle i|\nabla|j\rangle$ as shown in Figure 6. The extent of origin dependence, however, depends on the extent of the deviation from collinearity of the length and the gradient vectors. It can be seen from Figure 4 that the length and velocity forms of the electric dipole operator lead to moments which are collinear to within 3° in all cases except for the two CI results at $\phi = 90°$ where the angle between the short vectors was as great as 10°. Thus, *in practice*, origin dependence of $\mathbf{m}$ and $\mathbf{r}\cdot\mathbf{m}$ is not a serious consideration in any of the systems studied. It would appear that inaccuracies normally incurred in the computation of excitation energies could outweigh the advantages obtained by using the origin independent expression for the rotational strength. A more reliable test for the quality of the wave functions consists of computation and comparison (for collinearity) of both $\langle i|\mathbf{r}|j\rangle$ and $\langle i|\nabla|j\rangle$.

Conclusions

Within the standard parametrizations, the semiempirical CNDO/2 and INDO methods yield unreliable results for computed rotatory strengths, as does the nonempirical ODIN method. Of the methods tested, we feel the best results are obtained from the ab initio RHF-LCAO-MO-SCF method with improved virtual orbitals (IVO), if a single electronic configuration adequately describes the excited state. Where configurational mixing is expected to be large, as in the perpendicular geometry of butadiene, a limited CI calculation is necessary, to yield the correct qualitative behavior. Improvement of the ground state occupied orbitals (IGO) has a much more dramatic effect on the computed results than IVO, apparently leading to an over-correction in the case of the methylcyclohexanones.

The scattering of numbers that appears in the tables clearly implies that it is not yet meaningful to speak *quantitatively* about computed optical rotatory strengths. The data for ethylene (minimal STO basis vs. double ζ Gaussian basis) and for structure I (STO-3G vs. STO-4G minimal basis) suggest that the ground state wave function may be adequately described (for the computation of rotational

strengths) by nonempirical methods without having to use extended basis sets or to invoke CI. The satisfactory agreement between ODIN-IVO and RHF-SCF results supports this conclusion. However, results from all systems studied confirm previous conclusions in other contexts that the usual Hartree-Fock virtual orbitals are not adequate for construction of the excited states. The IVO and IGO procedures lead to general improvement. However, in some cases, as in the case of butadiene at $\phi = 90°$, important electronic configurations may be omitted or improperly included in the excited state description by these procedures.

Observation of the degree to which the computed vector $\langle i|\mathbf{r}|j\rangle$ is parallel to the vector $\langle i|\nabla|j\rangle$ may serve as a rough guide to the quality of the wave functions and the reliability of the computed rotatory strengths. Although collinearity is no guarantee that the vectors are pointed in the right direction or have the right magnitudes reason dictates that the results should be qualitatively better if the angle between the vectors is small then if it is large. For this reason we feel that rotatory strengths should be computed using both the length and velocity forms of the dipole moment operator.

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suggest that the computed ground state wave functions are similar to those obtained by the ab initio RHF method if one uses a minimal basis set. As yet unexplained anomalies exist in the calculated Hartree–Fock virtual orbitals and in the virtual orbital energies. As a result, it has not been possible to compute meaningful excitation energies by this method. Accordingly ODIN excitation energies are omitted from Tables I, III, and IV.

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Activity Coefficients of 2:1 Electrolytes in Structured Aqueous Solutions

Lowell W. Bahe* and David Parker[1]

Contribution from the Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201. Received October 22, 1974

Abstract: A model for an ion immersed in a dielectric medium as a spherical charge surrounded by a region of dielectric gradient has been introduced previously. The treatment of this model is extended to structured solutions of all types of strong, binary electrolytes. The Madelung constant method of calculating energies is analyzed in terms of a Guntelberg charging process. The activity coefficients of the alkaline earth halides and nitrates, and of $NiCl_2$ and $CoCl_2$, are examined on the basis of a loose fluorite structure in solution. The results show excellent agreement with experimental data up to concentrations as high as 2 or 3 M.

A model for ions in solution pictures each ion as a spherical charge surrounded by a sea of dielectric gradient. The dielectric gradient sea surrounding one ion interacts with the electric field from another ion to produce a repulsive force, in addition to the coulombic force, between that ion pair. As a result of this additional force, 1:1 electrolytes were shown to assume a loose face-centered-cubic lattice in solution. The partial molar electrical free energy of this structured solution was found via a Madelung-type calculation. This led to an expression for activity coefficients of 1:1 electrolytes which agreed with experimental data from the lowest concentrations at which measurements had been made up to concentrations as high as 4 M.[2] This model also led to an interpretation of heats of dilution for 1:1 electrolytes which agreed well with experimental data.[3]

In this paper the theory will be extended to strong binary electrolytes of all valence types and a generalized expression for partial molar free energies and activity coefficients

will be developed. For the binary salt $C_{\nu_+}A_{\nu_-}$ the type of electrolyte is designated by the ratio $z_+:z_-$. One formula unit of this salt exists in solution as ν_+ cations of charge z_+ and ν_- anions of charge z_-.

Theory

In carrying out the analysis of the specific ion–ion interactions in unsymmetrical electrolytes it became evident that the equations developed in the first paper[2] were valid for symmetrical 1:1 electrolytes in which one kind of ion (cation or anion) possessed a dielectric gradient sea while the other kind did not. The force generated by the field of one ion acting on the dielectric gradient surrounding the other was recognized, but the force generated by the field of the other acting on the gradient surrounding the one was neglected. The complete expression for the interaction force between two ions, i and j, in solution is given, to the degree of approximation in ref 2, by