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Author's Review

Ab Initio Calculations and Mechanistic Analyses of Optical Activity of Organic Molecules with Extended Chromophores

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Molecular orbital calculation of electronic transition energies and oscillator and rotatory strengths in the random phase approximation (RPA) is reviewed, and it is outlined how the three mechanisms contained in Kirkwood's theory of optical rotatory power and other features of the excitations may be extracted from such calculations. The method is applied to the chiroptical properties of *cis,trans*-(1,3)-cyclooctadiene and bicyclo[2.2.1]hept-5-en-2-one, both of which contain an extended chromophoric system. The results for the diene support Sandström's assignment of *P* helicity to the (—)-enantiomer despite the prediction of simple Diene Rule, and structural and spectral similarities to (—)-*trans*-cyclooctene are strong. The enone calculations confirm the model assumptions about the predominance of a $\vec{\mu}$—**m** rotatory strength mechanism whereas the analysis of the bond contributions and of the transition moment direction differs significantly from the assumptions governing the chirality rule of Schippers and Dekkers and other models.

INTRODUCTION

Despite over 60 years of theoretical development, the elucidation of the relationship between molecular structure and optical rotatory power has continued to proceed along two largely disjoint lines. In the first of these, approximate models have been formulated,[1,2,3] making extensive use of empirical data and parameters and avoiding or minimizing actual calculations of molecular wave functions.[4,5] The second line of approach, namely the explicit computation of electronic wave functions as basis for direct calculations of chiroptical properties, was initiated much later[2,6] with the advent of digital computers.

The most general formulation of the model approaches was given by Kirkwood,[4] who formally assumed a division of a given molecule into non-overlapping parts with no electron exchange between the individual parts.

Rewritten in terms of the rotatory strength for the 0 → q'th electronic transition in a chiral molecule,[1] the Kirkwood formulation can be expressed in the form

$$R_q \equiv \langle 0 | \vec{\mu} | q \rangle \cdot \langle q | \mathbf{m} | 0 \rangle \tag{1a}$$

$$= \sum_{a} R^q (\vec{\mu}_a, \mathbf{m}_a) + \sum_{a \neq b} R^q (\vec{\mu}_a, \mathbf{m}_b) + \sum_{a \neq b} R^q (\vec{\mu}_a, \vec{\mu}_b) \tag{1b}$$

where $\langle 0 | \vec{\mu} | q \rangle$ and $\langle q | \mathbf{m} | 0 \rangle$ are the electric and magnetic dipole transition moments for this excitation,[7] and where a and b label the individual parts of the molecule so that $\vec{\mu}_a$ and $\mathbf{m}_a$ designate local electric and magnetic transition moments. The individual contributions to the total rotatory strength are excitation specific, as indicated by the superscript q.

Eq. (1b) displays three characteristic contributions or mechanisms.[1,3] The first term is a sum of local rotatory strengths which we refer to as intrinsic contributions. The assumption that a single one of these contributions dominates the entire rotatory strength forms the basis of the one-electron or static-perturbation model of Condon, Altar and Eyring.[5] The second term, the $\mu - m$ mechanism,[3] contains couplings between local electric and magnetic transition moments in different parts of the molecule, and the third term, the $\mu - \mu$ mechanism, contains couplings between local electric dipole transition moments. The third term, taken alone, leads to the polarizability models,[4,8,9,10] and the last two terms, which are also referred to as dynamic couplings, are the mechanisms of exciton and independent system approaches.[1,3,11] Specific expressions for the various terms in eq. (1) within our own approach are given in Section III.

Practically speaking, the models are attractive because they can rationalize experimental data and, in many cases, provide concrete structural assignments with little or no computational effort, even for molecular systems of a size well beyond the systems tractable by the *ab initio* methods discussed below. Even ignoring theoretical misgivings about the rather drastic assumptions behind the models, however, the weakness of these approaches is that the individual models tend to focus solely on either the intrinsic contribution or on one or both of the dynamic coupling contributions. Since the different terms are not treated on the same footing, it is difficult to improve these approaches in a systematic way or to assess the range of their validity and the actual importance of the various mechanisms for any given transition in a given molecule.

Reliable quantum-mechanical calculation of the relevant transition moments in eq. (1), on the other hand, depends upon the adequate solution of a number of problems. In the first place, the effects of electron correlation (in the sense of going beyond a simple orbital description) intrude already in a first-order treatment,[12] whereas ground state expectation values of one-electron operators are sensitive to correlation only in second order.[14] This can be readily seen for the case of a two-electron, two-orbital system, in which a Hartree-Fock ground-state single determinant $|\Delta\rangle$ is built from one doubly-occupied orbital. An improved wave function is $|0\rangle = |\Delta\rangle + \lambda |DE\rangle$, where $|DE\rangle$ is the doubly-excited configuration, and λ is a mixing parameter, while an excited state $|q\rangle$ can be described approximately as equal to $|SE\rangle$, the spin-adapted singly-excited configuration. A transition moment $\langle 0 | f | q \rangle$

of a one-electron operator f is then given by $\langle \Delta | f | \mathrm{SE} \rangle + \lambda \langle \mathrm{DE} | f | \mathrm{SE} \rangle + \mathrm{O}(\lambda^2)$. The corresponding ground-state expectation value $\langle 0 | f | 0 \rangle$ is simply $\langle \Delta | f | \Delta \rangle + \mathrm{O}(\lambda^2)$, since the one-electron nature of f guarantees that terms linear in λ must vanish. This suggests, and experience indicates, that a configuration interaction (CI) calculation involving only single excitations would not be expected to be adequate for calculations of optical activity except in semiempirical methods where the parameters incorporate correlation effects.

Besides the general problem of accuracy just described, calculations of optical activity, like other magnetic properties, are subject to the inherent origin-dependence of the angular momentum operator, so that the magnetic dipole transition moment depends upon an arbitrary displacement $\mathbf{d}$ through $\langle 0 | (\mathbf{r} - \mathbf{d}) \times \vec{\nabla} | \mathrm{q} \rangle = \langle 0 | \mathbf{r} \times \vec{\nabla} | \mathrm{q} \rangle - \mathbf{d} \times \langle 0 | \vec{\nabla} | \mathrm{q} \rangle$. The dipole velocity expression in eq. (2) below ensures origin independence of the rotatory strength, but numerical results calculated with length (eq. (1a') below) and velocity expressions often do not agree.[1] Again, proper treatment of electron correlation turns out to be necessary to ensure that the two versions of the electric dipole transition moment are equivalent, as they must be for exact wave functions.

The status of *ab initio* all-electron computational methods for chiroptical properties is now that quite satisfactory results can be obtained for medium-sized molecules (see *e. g.* references in Section II). In Section II we outline the particular method we have found effective in addressing the problems outlined above.

The results of all-electron full-molecule calculations show little or no immediate kinship with the mechanisms visualized in the models. Each molecule becomes a case by itself, and meaningful analyses into contributions from individual parts of the molecules are thwarted by the use of delocalized molecular orbitals (MO's), often expanded in bases containing very diffuse atomic arbitals, and by extensive configuration interaction masking the individual orbital contributions. Previous atom and bond decomposition schemes for computed rotatory strengths (see references in[14,15]) either lack generality in terms of arbitrary basis sets or have not actually established a connection to the mechanisms in the Kirkwood theory. However, as outlined in Section III the use of localized MO's allows us to express the resulting intensities in contributions of the same form as the terms in eq. (1b).[14–17] In this formulation, which requires no approximations beyond those entering the general computational scheme, the local electric and magnetic transition moments $\vec{\mu}_{\mathrm{a}}$ and $\mathbf{m}_{\mathrm{a}}$ are well-defined and refer to excitations out of the individual localized orbitals. This approach therefore provides a consistent extraction and comparison of individual Kirkwood mechanisms, and by the same token a well-defined analysis of the computed intensities into structural terms is expressed as bond and bond-bond coupling contributions.

In Section IV the approach is illustrated by computation and analysis of the chiroptical properties of two chiral systems with extended chromophores of long-standing interest, namely a twisted diene chromophore in the form of *cis,trans*-(1,3)-cyclooctadiene and a coupled-chromophore model system, bicyclo[2.2.1]hept-5-en-2-one. Section V contains concluding remarks.

II. CALCULATION OF ROTATORY STRENGTHS

In this and the following section, we shall present the theoretical expressions necessary to establish our notation. For the present purpose we shall evaluate the rotatory strength, eq. (1), in the so-called »velocity« form[1,7]

$$R_q^{\nabla} = (2c\,\omega_q)^{-1} \langle 0 | \vec{\nabla} | q \rangle \cdot \langle 0 | \mathbf{r} \times \vec{\nabla} | q \rangle \tag{2}$$

(in atomic units), and for the oscillator strength we shall use the »mixed« expression[1,7]

$$f_q = (2/3)\, \langle 0 | \vec{\nabla} | q \rangle \cdot \langle 0 | \mathbf{r} | q \rangle \tag{3}$$

Here $\langle 0 | \mathbf{r} | q \rangle$ and $\langle 0 | \vec{\nabla} | q \rangle$ are the length and velocity versions of the electric dipole transition moment,[7] and ω_q is the transition energy. Other theoretical expressions are available for the intensities,[1] including eq. (1a) which can be written in the »length« form[7]

$$R_q^{r} = (2c)^{-1} \langle 0 | \mathbf{r} | q \rangle \cdot \langle 0 | \mathbf{r} \times \vec{\nabla} | q \rangle . \tag{1a'}$$

For exact wave functions, all of them give identical results; addressing the problems mentioned in the Introduction for approximate calculations was a major motivation in selecting the particular approach described below. For purposes of analysis into individual mechanistic terms, eqs. (2) and (3) turn out to be more suitable than their formally equivalent alternative forms.[14]

We limit ourselves here to molecules for which an MO description in the form of a Hartree-Fock wave function for the ground state is an adequate starting point. Singly, doubly, *etc.* excited configurations with respect to the ground state are denoted $|\alpha \rightarrow m\rangle$, $|\alpha \rightarrow m, \beta \rightarrow n\rangle$ *etc.*, where α and β label the occupied and m and n label the unoccupied (virtual) orbitals. As indicated in the Introduction, CI including only singly excited configurations omits first-order correlation effects on the calculation of electronic intensities.[18,19] Including doubly and higher excited configurations within conventional CI methods, *cf. e. g.* ref. 20—23 and references therein, is one way of dealing with these effects, but these methods optimize the wave functions for the individual electronic states, whereas the method we prefer for the calculation of transition energies and intensities, namely the Random Phase Approximation (RPA),[1] directly optimizes the description of the excitation process.

The RPA method is often presented within the more general framework of linear response theory.[24-26] However it can be considered a non-variational CI approach[1,27] which includes the effect of doubly excited configurations in such a way that the transition energies and transition dipole moments are correct to first order in electron correlation. Indeed, the method can be derived by imposing the equivalence of the various intensity expressions and the fulfilment of, *e. g.*, the Condon sum rule for rotatory strengths, as conditions on the CI coefficients.[27] The RPA method describes transition properties at the same general level of accuracy as the Hartree-Fock method describes the ground state.

Specifically, the RPA yields the following expressions for the three dipole transition moments required in eq. (2, 3)[1,28]

$$\langle 0 | \mathbf{r} | q \rangle = 2^{1/2} \sum_{\alpha} \sum_{m} \langle \alpha | \mathbf{r} | m \rangle\, S_{\alpha m,q} \tag{4}$$

$$\langle 0 \,|\, \vec{\nabla} \,|\, \mathrm{q} \rangle = 2^{1/2} \sum_{\alpha} \sum_{\mathrm{m}} \langle \alpha \,|\, \vec{\nabla} \,|\, \mathrm{m} \rangle \, T_{\alpha\mathrm{m,q}} \tag{5}$$

$$\langle 0 \,|\, \mathbf{r} \times \vec{\nabla} \,|\, \mathrm{q} \rangle = 2^{1/2} \sum_{\alpha} \sum_{\mathrm{m}} \langle \alpha \,|\, \mathbf{r} \times \vec{\nabla} \,|\, \mathrm{m} \rangle \, \mathrm{T}_{\alpha\mathrm{m,q}} \tag{6}$$

The right-hand-sides of these relations contain single-electron transition moments summed over all the orbital excitations $\alpha \rightarrow \mathrm{m}$. The coefficients $S_{\alpha\mathrm{m,q}}$ and $T_{\alpha\mathrm{m,q}}$ are determined together with the excitation energies ω_{q} from the RPA equations[1,28]

$$\sum_{\alpha} \sum_{\mathrm{m}} (A + B)_{\beta\mathrm{n},\alpha\mathrm{m}} \, S_{\alpha\mathrm{m,q}} = \omega_{\mathrm{q}} \, T_{\beta\mathrm{n,q}} \tag{7a}$$

$$\sum_{\alpha} \sum_{\mathrm{m}} (A - B)_{\beta\mathrm{n},\alpha\mathrm{m}} \, T_{\alpha\mathrm{m,q}} = \omega_{\mathrm{q}} \, S_{\beta\mathrm{n,q}} \tag{7b}$$

Here **A** is an energy matrix whose elements $A_{\beta\mathrm{n},\alpha\mathrm{m}}$ represent the interaction between singly excited configurations ($\beta \rightarrow \mathrm{n}$) and ($\alpha \rightarrow \mathrm{m}$), and the **B** matrix has elements $B_{\beta\mathrm{n},\alpha\mathrm{m}}$ representing the interaction between the Hartree-Fock ground state and doubly excited configurations ($\beta \rightarrow \mathrm{n}$, $\alpha \rightarrow \mathrm{m}$). The matrices $\mathbf{A} \pm \mathbf{B}$ can hence be labelled by indices referring to single excitations, even though the **B** matrix explicitly introduces electron correlation through the interaction with doubly excited configurations. Explicit expressions for the matrix elements are given in ref. 1. The coefficients fulfill the orthonormality relation

$$\sum_{\alpha} \sum_{\mathrm{m}} S_{\alpha\mathrm{m,q}} \, T_{\alpha\mathrm{m,p}} = \delta_{\mathrm{q,p}} \tag{8}$$

so that a single orbital excitation $\alpha \rightarrow \mathrm{m}$ contributes the amount

$$\mathrm{w}_{\alpha\mathrm{m,q}} = S_{\alpha\mathrm{m,q}} \, T_{\alpha\mathrm{m,q}} \tag{9}$$

to the normalization of the excitation $0 \rightarrow \mathrm{q}$. Similarly the quantity

$$W_{\alpha,\mathrm{q}} = \sum_{\mathrm{m}} \mathrm{w}_{\alpha,\mathrm{mq}} \tag{10}$$

measures the total contribution from all excitations out of occupied orbital α to the normalization of this transition. Neglect of the **B** matrix would make $S_{\alpha\mathrm{m,q}} = T_{\alpha\mathrm{m,q}}$, and the method would reduce to conventional singly excited CI. In RPA itself the difference between the S and T coefficients is usually small but important for the accuracy of the computed results.

Recent applications include the chiroptical properties of thioketones,[29] *trans*-cyclooctene, methyl-cyclopentene and methyl-cyclobutene,[14] methyl-cyclopropanes,[30] adamantanones,[15] and α-substituted cyclohexanones.[31] In addition we have applied the RPA to the study of the ordinary electronic spectra of planar mono-olefins,[32] and the cyclohexadiene system.[33] Other applications of the RPA to calculating optical rotatory power have also been reported,[34,35] and a general survey of recent RPA calculations is given in ref. 26. In our own RPA calculations we have included up to about 2000 singly excited configurations, and hence indirectly through the **B** matrix, up to nearly 2,000,000 doubly excited configurations. The solution of eqs. (7) for this number of configurations requires the use of iterative methods.[28,36]

III. ANALYSIS OF ROTATORY STRENGTHS

The Hartree-Fock wave function for the ground state and the RPA formalism in eqs. (4—10) are invariant with respect to a transformation from delocalized to localized MO's.[37] We can thus assume that our occupied orbitals are localized, *e. g.* by the Foster-Boys method,[37,38] with centroids

$$\vec{\varrho}_\alpha = \langle \alpha \mid \mathbf{r} \mid \alpha \rangle. \tag{11}$$

Localizing the orbitals allows us to define the following bond transition moments:

$$\mathbf{r}_{\alpha,q} = 2^{1/2} \sum_{m} \langle \alpha \mid \mathbf{r} \mid m \rangle \, S_{\alpha m,q} \tag{12}$$

$$\mathbf{p}_{\alpha,q} = 2^{1/2} \sum_{m} \langle \alpha \mid \vec{\nabla} \mid m \rangle \, T_{\alpha m,q} \tag{13}$$

$$\begin{aligned} \mathbf{l}_{\alpha,q} &= 2^{1/2} \sum_{m} \langle \alpha \mid \mathbf{r} \times \vec{\nabla} \mid m \rangle \, T_{\alpha m,q} \\ &= \mathbf{l}'_{\alpha,q} + \vec{\varrho}_\alpha \times \vec{\nabla}_{\alpha,q} \end{aligned} \tag{14}$$

with

$$\mathbf{l}'_{\alpha,q} = 2^{1/2} \sum_{m} \langle \alpha \mid (\mathbf{r} - \vec{\varrho}_\alpha) \times \vec{\nabla} \mid m \rangle \, T_{\alpha m,q}. \tag{15}$$

The index m is again summed over all virtual orbitals. These bond moments therefore represent the contributions to a particular total transition moment due to excitations out of the individual localized bond orbitals. $\mathbf{l}'_{\alpha,q}$ of eq. (15) specifically represents the local magnetic dipole transition moment for excitations out of orbital α with the origin for the magnetic dipole moment operator at the centroid for this orbital. Within the present approach the local moments defined by eqs. (12, 13, 15) take the role of the $\vec{\mu}_a$ and $\mathbf{m}_a$ transition moments which were left undefined in the presentation of eq. (1). The summation over all virtual orbitals makes it immaterial for this purpose whether the virtual orbitals are localized.

These bond moments can be employed in eqs. (4—6) and subsequently in eqs. (2, 3) to yield

$$\begin{aligned} R_q = {} & (2c\,\omega_q)^{-1} \sum_{\alpha} \mathbf{p}_{\alpha,q} \cdot \mathbf{l}'_{\alpha,q} + (2c\,\omega_q)^{-1} \sum_{\alpha \neq \beta} \mathbf{p}_{\alpha,q} \cdot \mathbf{l}'_{\beta,q} + \\ & + (4c\,\omega_q)^{-1} \sum_{\alpha \neq \beta} (\vec{\varrho}_a - \vec{\varrho}_b) \cdot (\mathbf{p}_{\alpha,q} \times \mathbf{p}_{\beta,q}) \end{aligned} \tag{16a}$$

$$\equiv \sum_{\alpha,\beta} R^q{}_{\alpha,\beta} \tag{16b}$$

and

$$\begin{aligned} f_q = {} & (2/3) \sum_{\alpha} \mathbf{p}_{\alpha,q} \cdot \mathbf{r}_{\alpha,q} + \\ & + (1/3) \sum_{\alpha \neq \beta} (\mathbf{p}_{\alpha,q} \cdot \mathbf{r}_{\beta,q} + \mathbf{p}_{\beta,q} \cdot \mathbf{r}_{\alpha,q}) \equiv \sum_{\alpha,\beta} f^q{}_{\alpha,\beta} \end{aligned} \tag{17}$$

for the two intensities.[14] Eq (16a) has exactly the form of the Kirkwood expression of eq. (1), and eq. (17) provides a similar decomposition of the oscillator strength, where the bond-bond terms are symmetrized with respect to length and velocity contributions. Each individual term in the decomposition of the rotatory strength in eq. (16a) is independent of the choice of origin for the molecular coordinate system, because all the transition moments involved are purely local and the last term contains only distances between the centroids.

We thus have a computationally well-defined procedure for the extraction of terms mimicking the various mechanisms of optical rotatory power. The terms appear on an equal footing and are hence directly comparable. Moreover, the formalism does not invoke neglect of overlap and electron exchange since the local moments refer to localized MO's, which are born orthonormal, and electron exchange is explicitly included in the calculation through the evaluation of the elements of the matrices **A** and **B** of eq. (7)[1].

Besides the overall mechanistic information, the decomposition expressed in eqs. (16, 17) also provides analysis into structural terms, such as inherent bond contributions and bond-bond couplings, and allows identification of effective chromophores. For some purposes the analyses expressed by eqs. (16, 17) are too detailed to be useful and more coarse-grained pictures can be obtained by introducing effective bond contributions defined through

$$R^q = \sum_{\alpha} [R^q_{\alpha\alpha} + 1/2 \sum_{\beta}{}' (R^q_{\alpha\beta} + R^q_{\beta\alpha})] \equiv \sum_{\alpha} R^q_{\alpha,\mathrm{eff}} \tag{18}$$

$$f^q = \sum_{\alpha} [f^q_{\alpha\alpha} + 1/2 \sum_{\beta}{}' (f^q_{\alpha\beta} + f^q_{\beta\alpha})] \equiv \sum_{\alpha} f^q_{\alpha,\mathrm{eff}} \tag{19}$$

The summation over virtual orbitals in the definition of the local bond moments in eqs. (16—19) has obliterated a number of details in the description of the excitations, such as distinctions between local and charge-transfer excitations and between degenarate and non-degenerate exciton couplings. Some indication of these features can be gleaned from the normalization contributions $w_{\alpha m, q}$ of eq. (9), if the virtual orbitals are localized.[28] If desired, more informative representations of the nature of the excitations can be obtained from population analyses or contour plots of charge rearrangments and transition densities,[14] and from changes in the effective size of the electron distribution in the excitation.[32]

IV. APPLICATIONS

Conjugated Dienes

In non-planar, cisoid conjugated dienes, the twisted diene group can adopt either a right-handed (*P*) helicity or a left-handed (*M*) helicity. Experimental evidence supported by π-electron calculations led to an early diene rule,[39] according to which the lowest ($N \rightarrow V_1$) transition in a cisoid diene with P helicity will show a strong positive rotatory strength (*R*), while *M* helicity leads to negative *R*. The sign of the $N \rightarrow V_2$ transition is expected to be opposite. The rule accounted for the structure of a number of molecules, but systematic exceptions indicated that the so-called allylic axial bonds can contribute in a significant, often sign-determining way;[40,33] see ref. [33] for a survey of the history of the diene rule.

Notwithstanding the prediction of this rule, Sandström *et al.*[41] have proposed that (—)-*cis,trans*-1,3-cyclooctadiene (»CTCO«, Figure 1), for which they have observed a long-wavelength CD band at 230 nm with $R \approx -48 \times 10^{-40}$ cgs, has an absolute configuration with right-handed (P) helicity for the diene moiety. The CD spectrum also exhibits a second negative band at $\lambda < 190$ nm. The two bands correspond to allowed UV bands at the same locations.

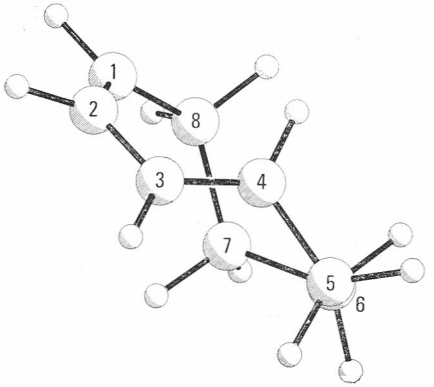

Figure 1. PLUTO plot of the geometry of *cis,trans*-1,3-cyclooctadiene (CTCO), viewed along an axis passing through the midpoint of the $C_3{=}C_4$ bond, showing the numbering of the carbon atoms.

In order to provide a theoretical assessment of this assignment, we performed an extended-basis set RPA calculation[42] on CTCO, using the MM2-optimized geometry.[41] The basis set we employed was a Dunning-Hay $[3s2p/2s]$ valence double-zeta basis[43] (with STO-5G on the non-chromophore H atoms), augmented with two sets of diffuse s and p-type single Gaussian functions ($\alpha_s = .0437, .0173$; $\alpha_p = .04, .016$) on each of the four carbons of the diene moiety, for a total of 120 basis functions. This same basis was used previously to good effect in a study of (—)-*trans*-cyclooctene.[14] SCF molecular orbitals were generated on the GAUSSIAN 80 program system,[44] yielding an SCF energy of —309.749514 hartrees. The full set of 1980 excitations out of valence occupied MO's was used in the subsequent RPA calculation.

TABLE I

Overall computed RPA results for cis,trans-*1,3-cyclooctadiene (CTCO). Experimental values are shown in parentheses*

Excitation	ΔE^{a}	$f^{r\nabla}$	$R^{(r)b,d}$	$R^{\nabla b,c}$	$\Delta\langle r^2\rangle^{e}$	Nature
1	5.97	.17	—35	—29	9.1	$\pi_2 \to \pi_3$ (70%)
	(5.4)	(.09)	(—48)			
2	6.32	.00	13	16	64.4	$\pi_2 \to$ Ryd.
3	6.63	.02	—12	10	62.9	$\pi_2 \to$ Ryd.
4	6.68	.02	—21	—22	81.4	$\pi_2 \to$ Ryd.
5	7.00	.02	—3	—3	89.2	$\pi_2 \to$ Ryd.
6	7.12	.12	—86	—71	31.2	$\pi_1 \to \pi_3$ (50%)
	(>6.5)		(—)			

[a] Excitation energy in eV. [b] Rotatory strength, in cgs $\times 10^{40}$. [c] Eq. (2). [d] Origin-independent part of R^{r}, eq. (1a′). See Ref. [1]. [e] Change in expectation value of r^2 during excitation, Ref. [32], in $(\text{a. u.})^2$.

Table I shows the results obtained for the lowest few singlet excitations. It is seen that the overall agreement with experiment is reasonable, and that the calculations support the assignment of P helicity to the (—) enantiomer of CTCO. Two intense bands are predicted, with an energy separation of 1.15 eV, in accord with the experimental band separations of at least 1.1 eV. The present calculations are comparable in quality to our earlier calculations on (—)-*trans*-cyclooctene,[14] and also show the same systematic overestimation of the individual excitation energies by 0.5 eV or so. This discrepancy is due in part to the fact that the basis set is not yet saturated as far as the RPA goes, and also to the neglect of higher-order effects in our method. On the basis of contributions to the normalization of the excitation eigenvector [eq. (9)], charge rearrangement populations, and changes in the expectation values of $\langle r^2 \rangle$ during the excitation,[32] the lowest excitation is assigned as a valence-like transition out of π_2 into an effective virtual orbital (EVO) made up of a linear combination of the canonical virtual orbitals dominated by the π_3^* MO. In a localized orbital picture in which a set of valence-like, antibonding localized virtual orbitals has been constructed to correspond to the valence localized occupied orbitals,[28] the transition is depicted as consisting largely of a local $\pi \rightarrow \pi^*$ excitation within $C_3{=}C_4$, with lesser contributions from $\pi\,(C_1{=}C_2) \rightarrow \pi^*\,(C_1{=}C_2)$ and $\pi\,(C_3{=}C_4) \rightarrow \pi^*\,(C_1{=}C_2)$. The next four singlet excitations are computed to be of Rydberg type, as evidenced by their large $\Delta\,\langle r^2 \rangle$ values.[32] The sixth excitation is again a valence-type transition, arising, in a delocalized picture, from the π_1 orbital, again into an EVO of about 50% π_3^* character. The $\Delta\,\langle r^2 \rangle$ value of 31.2 (a. u.)^2 suggests that the upper state is less compact than for $N \rightarrow V_1$ but still much less diffuse than the Rydberg excitations. The localized picture shows the largest contribution to be $\pi \rightarrow \pi^*$ within $C_1{=}C_2$, with lesser contributions from $\pi\,(C_1{=}C_2)$ and $\pi\,(C_3{=}C_4)$ into $\pi^*\,(C_3{=}C_4)$, but many other terms also appear. The two valence excitations determine the overall appearance of the CD spectrum, since computer simulations based upon assigning a Gaussian band shape to each computed rotatory intensity show that the contributions from the Rydberg excitations largely cancel.

TABLE II

Mechanistic analysis for rotatory strengths of $N \rightarrow V_1$ and $N \rightarrow V_2$ excitations in CTCO

Fragment	*R* (intr.)	*R* (μ—*m*)	*R* (μ—μ)	*R* (total)
$N \rightarrow V_1$				
entire	+22.7	—39.5	—11.7	—28.5
$\pi\,(C_3{=}C_4)$ only	+16.9	—22.5	+39.4	+34
C_1—C_4 chain	+22.6	—27.0	+7.5	+3
»butadiene«[a]	+22.6	—39.9	+4.9	—12.4
$N \rightarrow V_2$				
entire	+6.1	—32.9	—44.0	—70.8
$\pi\,(C_3{=}C_4)$ only	—1.8	—13.4	—42.6	—57.7
C_1—C_4 chain	+6.4	—38.9	—47.4	—79.9
»butadiene«[a]	+5.9	—37.0	—42.9	—76.7

[a] Includes all the sigma and pi bonds corresponding to a butadiene molecule, with C—C bonds replacing C—H bonds where appropriate for CTCO.

The oscillator strength of the $N \rightarrow V_1$ band is revealed by the decomposition in eq. (17) to consist primarily of a local $\pi \rightarrow \pi^*$ $(C_3{=}C_4)$ contribution of 0.23 and a local $\pi \rightarrow \pi^*$ $(C_1{=}C_2)$ contribution of 0.07, paralleling the weights of π ($C_3=C_4$) and π ($C_1=C_2$) in the normalization, together with a host of small couplings within the rest of the molecule that act to reduce the total oscillator strength to 0.17. For the $N \rightarrow V_2$ band, the total computed oscillator strength of 0.12 is dominated by local $\pi \rightarrow \pi^*$ contributions of 0.15 for $C_1=C_2$ and 0.04 for $C_3=C_4$, with smaller terms as above. Again, discrepancies of up to *ca.* 20% would be expected for the intensities at the RPA level, even for much larger basis sets, due to neglect of second-order terms.

Applying the localized analysis of eqs. (16, 18) to the calculated rotatory strengths, we see in Table II that no clear candidate emerges for the dominant intensity mechanism in either valence excitation. Interestingly, the intrinsic contribution for the $N \rightarrow V_1$ excitation obeys the Diene Rule, but the net R is dominated by the $\mu - m$ and $\mu - \mu$ terms which violate it. Table II also shows the analysis of R for the two valence excitations in terms of groups of contributing bonds, according to eq. (18), and reveals that the largest single contribution to R (total) comes from π ($C_3=C_4$), albeit with its sign opposite to that of R (total). Nearly the entire intrinsic contribution in $N \rightarrow V_1$ comes from the four-carbon chain comprising the π-system. Adding the other sigma bonds appropriate for a »butadiene« moiety does not change the intrinsic term, but accounts for the full amount of the $\mu - m$ mechanistic contribution, whereas the $\mu - \mu$ terms for the fragments up to and including »butadiene« are opposite in sign to the total $\mu - \mu$ term for the molecule. The remainder, nearly all of $\mu - \mu$ type, is contributed by bonds throughout the molecule.

For the short-wavelength valence band ($N \rightarrow V_2$), the main contribution to R also comes from the *trans*-substituted $C_3=C_4$ bond, even though the normalization favors the π ($C_1=C_2$) bond by over 2 : 1. In this case the rest of the diene moiety also contributes to a negative R value, so that the total intensity is very large and negative. Once again, the intrinsic terms sum to a small, positive R value, while both the $\mu - m$ and $\mu - \mu$ terms are large and negative. The extrachromophoric part of the molecule contributes very little, either to the excitation normalization or to the intensities, in marked contrast to the nature of the $N \rightarrow V_1$ band.

Our calculations thus not only reproduce the overall features of the experimental spectrum but also confirm the estimates made by Sandström *et al.* of the importance of different parts of the molecule for the total rotatory intensities. The major role played by the *trans*-substituted $C_3=C_4$ bond invites comparison between the spectroscopic properties of CTCO and those of trans-cyclooctene (TCO),[14] since the view of CTCO in Figure 1 indeed shows a striking structural similarity to TCO as shown in Figure 2 of ref. [14]. Also the overall rotatory intensity of the $N \rightarrow V_1$ band in CTCO correlates well with that of the $\pi \rightarrow \pi^*$ band in TCO, and in terms of the normalization of the transition, *eq.* (9), both bands are dominated by the *trans*-substituted C=C bond. However, the mechanisms for generating the intensities differ somewhat, since although the $\mu - m$ and $\mu - \mu$ terms in the two molecules are similar in sign and magnitude, the non-trivial intrinsic terms are of opposite sign. Moreover, as noted above, the π ($C_3=C_4$) orbital itself contributes a large *positive* R value, which must be offset by the rest of the molecule, unlike the behavior of the ethylenic fragment in TCO. The $N \rightarrow V_2$ band of CTCO is of course of $\pi \rightarrow \pi^*$ character, in contrast to the $\sigma \rightarrow \pi^*$ band in TCO, although the former does have some sigma character with respect to the $C_3=C_4$ bond.

The spectroscopic properties of CTCO are thus intermediate between those of a »normal« cisoid diene and those of a twisted mono-olefin. On the one hand, the twist of the $C_3{=}C_4$ bond introduces a major perturbation into the diene system, while on the other hand, the $C_1{=}C_2$ chromophore exerts a significant electronic, if not geometric, effect on the twisted double bond.

Unsaturated Ketones

A particularly interesting example of the sensitivity of circular dichroism to structural perturbations is found in the compound (1*S*,4*S*)-bicyclo[2.2.1]-hept-5-en-2-one (»HEO«, Figure 2), especially as compared with the corresponding saturated ketone.[45,46] The latter compound absorbs weakly near 290 nm and, in the enantiomer (Figure 2, *mutatis mutandis*), gives a weak *positive* CD band ($\Delta\varepsilon \approx +0.25$ at 305 nm), whereas the enone HEO shows a strongly *negative* band ($\Delta\varepsilon = -18.8$, $R \approx -51.1 \times 10^{-40}$ cgs) with no concomitant wavelength shift.[45] The simple Octant Rule picture cannot account for these differences, and an extended Octant Rule was therefore proposed.[46] An early semiempirical calculation[47] indicated that a μ—m exciton (coupled chromophore) model can account correctly for the sign and magnitude of the 300 nm CD band in β,γ-enone systems, and indicated that overlap and charge transfer effects were of minor importance. Recently Schippers and Dekkers[48] have proposed a chirality rule based upon the cosine of the angle ξ between the C=C bond and the C=O bond. The latter authors also assume a coupled chromophore model, with electric and magnetic dipole transition moments contributed exclusively by the olefinic $\pi\rightarrow\pi^*$ excitation and the carbonyl $n\rightarrow\pi^*$ excitation, respectively, but they avoid specific assumptions about the nature of the coupling. Experimental support for this chirality rule has been recently provided.[49]

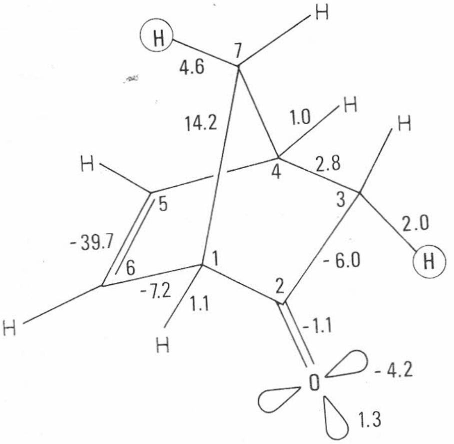

Figure 2. Numbering scheme and leading effective bond contributions. $R_{\alpha,\mathrm{eff}}^{q}$, eq. (18), to the $n\rightarrow\pi$ rotatory strength of bicyclo[2.2.1]hept-5-en-2-one (HEO). Bond contributions not marked sum to less than 1×10^{-40} cgs. The two hydrogens marked explicitly are referenced in the discussion.

We have performed *ab initio* RPA calculations on HEO and have analyzed the results in terms of the decompositions in Section III. The basis set consisted of 112 atomic orbital basis functions: $[3s2p]$ plus a single set of diffuse s and p functions (C: $\alpha_s = 0.023$, $\alpha_p = 0.021$; O: $\alpha_s = 0.032$, $\alpha_p = 0.028$) on each heavy atom and STO-5G on H,[43] which yielded a Hartree-Fock ground state energy of — 344.440470 hartrees. This basis generated 1743 singly-excited configurations out of the valence occupied orbitals.

The computed and experimental intensities and the leading decompositions are shown in Table III and in Figure 2. The calculation yields a transition energy of 4.51 eV, compared to an experimental band maximum at 4.1 eV.[45] The overall agreements between calculated and experimental results are thus quite satisfactory, and the deviations are typical of RPA calculations in atomic basis sets of this size.

For the oscillator strength Table III shows that the local contribution from the olefinic chromophore is quite large, but bond-bond couplings to the rest of the molecule almost counterbalance this contribution. This hypochromic effect of the extrachromophoric part of the molecule was also observed in our work on mono-olefins[14] and dienes.[17,33] The calculations also show that neither the C=C electric dipole bond transition moment, eq. (12, 13), nor the total electric dipole transition moment for this excitation lie along the C=C bond direction. In the velocity (∇) form the bond and total moments form angles of respectively 42° and 50° with the C=C bond; in the length form (r) the total moment forms an angle of 36° with the C=C direction. This difference between the length and velocity predictions of the polarization properties of weak transitions is common for calculations in basis sets of the present size.

TABLE III

Computed intensities and leading decompositions for the n→π* *transition in bicyclo[2.2.1]hept-5-en-2-one (HEO)*

	$R/10^{40}$ cgs			f
	total	μ—m	μ—μ	
∇[a]	—30	—25	—6	.002
r[a]	—32			.003
$r\nabla$[a]				.002
expt.[b]	—51			.006
n/n[c/d]	5.2	2.1	1.0	.000
n/1—6	—11.6	—9.6	—1.9	
n/1—7	23.6	19.4	4.1	
n/5—6	—70.7	—58.8	—11.9	
n/3—4	5.4	4.3	1.1	
n/3-H	5.9	4.6	1.3	
n/7-H	8.4	7.0	1.4	
n/others	8.4	7.3	1.1	
5—6/5—6	—1.5	—1.5	.0	.007
5—6/others[e]	—76.4	—60.7	—15.7	—.006

[a] ∇, r, and $r\nabla$ indicate velocity, length and mixed forms of the intensity expressions, see eqs. (2—1a′) and ref. [1]. [b] From ref. [45] converted to present enantiomer. [c] Bond-bond couplings $R_{\alpha\beta}^{q}$ and $f_{\alpha\beta}^{q}$, eqs. (16, 17). [d] n stands for the non-bonding oxygen orbital plus bonds 1—2 and 2—3, and these contributions are summed accordingly. See Figure 2 for atomic numbering. [e] Includes the 5—6/n=n/5—6 coupling.

The decompositions in Table III show, as expected, that the rotatory strength of this excitation is strongly dominated by the μ—m mechanism. The total intrinsic contribution is only about 1×10^{-40} cgs, and intrinsic contributions are therefore omitted in the Table. The μ—μ contributions, which however are of some importance, in all cases follow the μ—m contributions in sign and general magnitude. These trends agree with our observations for saturated ketones.[31] The difference lies in the enhancement apparent in the coupling labelled n/5—6 between the extended nonbonding orbital system and the olefinic double bond, where the contributions to this coupling from orbitals 1—2 and 2—3 account for half its total magnitude.[50] We note also that the olefinic chromophore couples almost exclusively to the non-bonding system, whereas the non-bonding system couples to a number of bonds. The latter terms follow the octant rule in sign and expected magnitude and contain a number of large contributions which reduce the overall R value notably. This asymmetry in the extrachromophoric rotatory strength couplings for the olefinic group and the non-bonding system is evident in the gross bond terms displayed in Figure 2, making the C=C bond the apparent main contributor to the rotatory strength. Figure 2 also illustrates the octant rule behavior of the extrachromophoric contributions, in particular the zigzag effect[18] making the 1—7—H bond contributions large.

To establish the connection to earlier approaches, we emphasize that although the above analysis confirms the leading role played by the μ—m contribution containing a C=O magnetic bond transition moment and a C=C electric bond transition moment, it does not address the question of the nature of the coupling between the two chromophores. This follows because the definition of the bond moments, eqs. (12—15) leads to a loss of distinction between local and charge transfer character of the excitations, as discussed in Section III. Some features of the nature of the excitation can be studied, however, by performing an analysis in which we localize one virtual orbital per bonding occupied orbital, as in our discussion of CTCO above. Reassuringly, this analysis confirms that it is primarily an $n \rightarrow \pi^*$ transition since 75% of the normalization calculated according to eq. (9) is contributed by excitations out of the extended non-bonding system into the local C=O π^* orbital. More importantly, it shows that although the total normalization contribution arising from excitations out of the C=C π orbital is 5.6%,[50] only 0.6% comes from the local C=C $\pi \rightarrow \pi^*$ excitation whereas 3.4% comes from a charge transfer excitation from the C=C π orbital into the C=O π^* orbital. Hence the assumption inherent in many models and qualitative treatments that the local C=C $\pi = \pi^*$ excitation is essentially the sole contributor to the total electric dipole transition moment is not supported by the present analysis, and it appears that this charge transfer excitation plays an important role in twisting the transition moment away from the C=C direction, as noted above. Charge transfer from the non-bonding system into the C=C π^* orbital amounts to only 1.2% and is hence not significant. The fact that excitations out of extrachromophoric bonds provide the remaining *ca.* 20% of the normalization accounts for the significant contributions from those bonds shown in Figure 2.

The Schippers and Dekkers chirality rule[48] is based on the expression

$$R/\sqrt{D} = |m| \cos\theta \qquad (20)$$

relating the rotatory strength R and the dipole strength D to the magnitude of the magnetic dipole transition moment and the angle θ between the electric and magnetic transition moments. By assuming that the two moments are directed along the C=C and C=O bonds, respectively, θ is identified with the angle ξ between the bond directions, and by further assuming a value of 1.10×10^{-20} cgs for $|m|$, eq. (20) provides a direct link between the experimental observables R and D and the structural parameter ξ. From the experimental data for HEO, eq. (20) yields a value of -48° for θ in the enantiomer shown in Figure 2, compared with a structure angle ξ of -55° obtained from a Dreiding model.[48] Inserting our computed intensities and magnitude of $\mathbf{m}$ in eq. (20) we obtain θ values of -45° and -42° from the dipole length and dipole velocity results, respectively, and we note that our optimized geometry provides a value of -52° for ξ. Hence in terms of overall results, the present approach agrees with the model proposed by Schippers and Dekkers, whereas the results of our more detailed analysis, in particular concerning the direction of the electric dipole transition moment and the involvement of the extrachromophoric parts, do not support the assumptions behind that model.

V. CONCLUDING REMARKS

The mechanistic and structural analyses expressed in eqs. (16, 17) presuppose an all-electron calculation of the transition energies and total intensities. It is important for the formulation that this computational scheme allows the total transition moments to be expressed as linear combinations of simple occupied into virtual orbital excitations (single particle-hole terms) as given by eqs. (4—6), and that the occupied orbitals can be localized. The Random Phase Approximation employed here is not the only candidate for such a scheme, but it has a number of attractive formal features,[1,25,37] including the built-in invariance with respect to the transformation to localized orbitals,[37] and we have found that it is an effective and economical procedure which can provide quite satisfactory results for a variety of molecules.

Relative to the model approaches it should be noted that, although the present analysis helps clarify the relative importance of the various mechanisms, and hence can assist in construction and improvements of such approaches, an important difference remains. In exciton-type calculations,[1,3,11] the transition energies and the ordinary and rotatory intensities are all determined by the local energies and transition moments, either by simple expressions like eqs. (V. 24, 25) of ref. [1] or by more elaborate multipolar expansions.[3] Because of the *a posteriori* nature of our analysis no such direct coupling between energetics and intensities is implied in the present approach. A study of the possibility of extracting transferable local energies and transition moments, and of the relationship between such derived local properties and the computed overall transition properties, remains to be done.

In application of the above analysis to the extended chromophore systems of the present paper, we find that all three mechanistic types occur, however the intrinsic contribution is large only for the long-wavelength excitation in the twisted diene, but its sign is opposite to that of the total rotatory strength. The μ—m and μ—μ mechanisms are both important in all the excitations considered here, and they consistently agree in sign with each other and with the overall R value. This trend for the dynamic couplings follows our previous observations,[14] as does the lack or correlation of the sign of the intrinsic contribution to that of the entire rotatory strength.

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REFERENCES AND NOTES

1. For a survey of the literature and basic relations, see Aa. E. Hansen and T. D. Bouman, *Adv. Chem. Phys.* **44** (1980) 545.
2. A. Moscowitz, *Tetrahedron* **13** (1961) 48. A. Moscowitz, *Adv. Chem. Phys.* **4** (1962) 67.
3. J. A. Schellman, *Acc. Chem. Res.* **1** (1968) 144.
4. J. G. Kirkwood, *J. Chem. Phys.* **5** (1937) 479; **7** (1939) 139.
5. E. U. Condon, *Rev. Mod. Phys.* **9** (1937) 432; E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.* **5** (1937) 753; W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Revs.* **26** (1940) 339.
6. Y. H. Pao and D. P. Santry, *J. Amer. Chem. Soc.* **88** (1966) 4157.
7. In atomic units the »length« form of the electronic electric dipole moment operator is given as $\mu = \sum_i \mathbf{r}_i$, where $\mathbf{r}_i$ is the position vector of electron i. We assume real wave functions, and in order to employ purely real transition moments we express the magnetic dipole moment operator as $\mathbf{m} = (1/2c) \sum_i \mathbf{r}_i \times \nabla_i$, where ∇_i is the gradient (velocity) operator for the i'th electron. In eqs. (2, 3) we suppress the summations in the operators, whereas the right hand sides of eqs. (4—6) contain one-electron moments.
8. A. D. Buckingham and P. J. Stiles, *Acc. Chem. Res.* **7** (1974) 258.
9. J. Applequist, *Acc. Chem. Res.* **10** (1977) 79.
10. K. R. Sundberg, *J. Chem. Phys.* **68** (1978) 5271.
11. I. Tinoco, *Adv. Chem. Phys.* **4** (1962) 113.
12. V. Fock, *Z. Phys.* **89** (1934) 744.
13. C. Møller and M. S. Plesset, *Phys. Rev.* **46** (1933) 618.
14. Aa. E. Hansen and T. D. Bouman, *J. Amer. Chem. Soc.* **107** (1985) 4828.
15. D. A. Lightner, T. D. Bouman, W. M. D. Wijekoon, and Aa. E. Hansen, *J. Amer. Chem. Soc.* **108** (1986) 4484.
16. Aa. E. Hansen and T. D. Bouman, in: J. S. Avery, J. P. Dahl, and Aa. E. Hansen (Eds.), *Understanding Molecular Properties,* Dordrecht, Reidel Publishing Co, 1987, p. 343.
17. Aa. E. Hansen and T. D. Bouman, in: M. Kajtár (Ed.), *Proceedings of the Second International Conference on Circular Dichroism,* Budapest, 1987, p. 1; T. D. Bouman and Aa. E. Hansen, *Ibid.*, p. 21.
18. T. D. Bouman and D. A. Lightner, *J. Amer. Chem. Soc.* **98** (1976) 3145.
19. T. D. Bouman and Aa. E. Hansen, *J. Chem. Phys.* **66** (1977) 3460.
20. G. Bendazzoli, P. Biscarini, P. Palmieri, and G. Gottarelli, *J. Chem. Soc. Faraday Trans. 2* **77** (1981) 503.
21. G. A. Segal, K. Wolf, and J. J. Diamond, *J. Amer. Chem. Soc.* **106** (1984) 3175.
22. A. Rauk, *J. Amer. Chem. Soc.* **106** (1984) 6517.
23. C. F. Chabalowski, G. M. Maggiora, and R. E. Christoffersen, *J. Amer. Chem. Soc.* **107** (1985) 1632.
24. P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry,* New York, Academic Press, 1981.

25. J. Oddershede, P. Jørgensen, and D. L. Yeager, *Comput. Phys. Repts.* **2** (1984) 33.
26. J. Oddershede, *Adv. Chem. Phys.* **69** (1987) 201.
27. Aa. E. Hansen and T. D. Bouman, *Mol. Phys.* **37** (1979) 1713.
28. T. D. Bouman, Aa. E. Hansen, B. Voigt, and S. Rettrup, *Int. J. Quantum Chem.* **23** (1983) 595.
29. D. A. Lightner, T. D. Bouman, W. M. D. Wijekoon, and Aa. E. Hansen, *J. Amer. Chem. Soc.* **106** (1984) 934.
30. S. Bohan and T. D. Bouman, *J. Amer. Chem. Soc.* **108** (1986) 3261.
31. D. A. Lightner, T. D. Bouman, B. V. Crist, S. L. Rodgers, M. A. Knobeloch, and A. M. Jones, *J. Amer. Chem. Soc.* **109** (1987) 6248.
32. T. D. Bouman and Aa. E. Hansen, *Chem. Phys. Lett.* **117** (1985) 461.
33. D. A. Lightner, T. D. Bouman, J. K. Gawroński, K. Gawrońska, J. L. Chappuis, B. V. Crist, and Aa. E. Hansen, *J. Amer. Chem. Soc.* **103** (1981) 5314.
34. G. L. Bendazzoli, P. Palmieri, S. Evangelisti, and F. Ortolani, *Il Nuovo Cimento* **60B** (1980) 106. P. Palmieri, G. Poggi, and J. Vrbanicich, *J. Comput. Chem.* **4** (1983) 260.
35. J. P. Flament and H. G. Gervais, *Int. J. Quantum Chem.* **16** (1979) 1347.
36. J. Olsen, H. J. Aa. Jensen, and P. Jørgensen, *J. Comput. Phys.* **74** (1988) 265.
37. T. D. Bouman, B. Voigt, and Aa. E. Hansen, *J. Amer. Chem. Soc.* **101** (1979) 550.
38. J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32** (1960) 300.
39. A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.* **83** (1961) 4661.
40. A. W. Burgstahler and R. C. Barkhurst, *J. Amer. Chem. Soc.* **92** (1970) 7601.
41. R. Isaksson, J. Roschester, J. Sandström, and L.-G. Wistrand, *J. Amer. Chem. Soc.* **107** (1985) 4074.
42. T. D. Bouman and Aa. E. Hansen, RPAC 8.2, Program 556, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN (1988).
43. T. H. Dunning and P. J. Hay, in: H. F. Schaefer (Ed.), *Methods of Electronic Structure Theory*, New York, Plenum Press, 1977, p. 1.
44. P. N. Van Kampen, F. A. A. M. de Leeuw, G. F. Smits, and C. Altona, QCPE 437, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, 1982; J. A. Pople, *et al.* QCPE 406, 1981.
45. D. A. Lightner and W. A. Beavers, *J. Amer. Chem. Soc.* **93** (1971) 2677.
46. A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.* **84** (1962) 1945.
47. A. Moscowitz, Aa. E. Hansen, L. S. Forster, and K. Rosenheck, *Biopolymers Symp.* **1** (1964) 75.
48. P. H. Schippers and H. P. J. M. Dekkers, *J. Amer. Chem. Soc.* **105** (1983) 79.
49. A. Lettieri, P.-A. Carrupt, and P. Vogel, *Chimia* **42** (1988) 27.
50. The importance of the 1—2 and 2—3 bonds for the definition of the $n \rightarrow \pi^*$ chromophore is also apparent in the fact that excitations out of these bonds account for 25% of the normalization according to eq. (10). Excitations out of the oxygen non-bonding orbital and out of the C=C π orbital account for 65% and 5%, respectively.

SAŽETAK

Ab initio **računi i mehanistička analiza optičke aktivnosti organskih molekula s produženim kromoforima**

Thomas D. Bouman i Aage E. Hansen

Dan je pregled molekulsko-orbitalnih računa energija elektronskih prijelaza, te snage oscilatora i rotacijske snage, prema »random phase« aproksimaciji (RPA), i pokazano je kako ova tri mehanizma koja su sadržana u Kirkwoodovoj teoriji optičke rotcijske snage, i druge pojave vezane uz elektronsku pobudu mogu biti izvedene iz takvih računa. Metoda je primijenjena na kiroptička svojstva *cis-trans-*

-(1,3)-ciklooktadiena i bisiklo[2,2,1]hept-5-en-2-ona, koji posjeduju produženi kromoforni sustav. Rezultati za dien podupiru Sandströmovo pripisivanje *P*-heliciteta (—)-enantiomeru, uprkos suprotnom predviđanju jednostavnoga dienskog pravila te znatnih strukturnih i spektralnih sličnosti s (—)-*trans*-ciklooktenom.

Računi za enon potvrđuju modelnu pretpostavku da prevladava μ-m mehanizam za rotacijsku snagu, dok se analiza doprinosa veza i pravca prijelaznog momenta znatno razlikuje od pretpostavki na osnovi kiralitetnog pravila Schippersa i Dekkersa, i drugih modela.