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CONFORMATIONAL DEPENDENCE OF THE ^1L_b AND $n \rightarrow \pi^*$ ROTATORY STRENGTHS IN α-SUBSTITUTED PHENYLACETIC ACIDS

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Abstract—The chiroptical properties of a series of chiral phenylacetic acid derivatives are examined on a theoretical model in which electronic rotatory strengths are calculated *directly* from molecular wave functions derived from semiempirical molecular orbital calculations. The CNDO/S SCF-MO model is used to calculate ground state wave functions and excited states are constructed in the virtual orbital-configuration interaction approximation. Of special interest are the rotatory strengths associated with the ^1L_b transition of the phenyl chromophore and the $n \rightarrow \pi^*$ transition of the carboxyl chromophore. Calculations are carried out on a large number of conformational isomers of the compounds: α-methyl phenylacetic acid (and its methyl ester), α-methylmandelic acid (and its methyl ester), and mandelic acid (and its methyl ester). The dependence of rotatory strength (^1L_b and $n \rightarrow \pi^*$) on conformational variables is examined and discussed, and comparisons between available experimental data and the calculated results are made. Coupling between the phenyl and carboxyl chromophoric moieties is considered and possible spectra-structure relationships are examined.

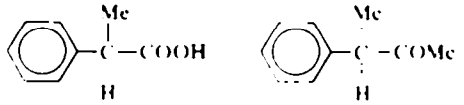
The electronic transitions associated with the phenyl chromophore of benzene derivatives exhibit optical activity when substituent groups on the benzene ring contain chiral centers or are dissymmetrically disposed about the benzene ring. The signs and relative magnitudes of the Cotton effects (CE's) associated with these transitions are presumed to be determined by the conformational and configurational relationships which the substituent groups bear with respect to the benzene moiety. Several "sector" or "regional" rules have been proposed for relating the signs and relative magnitudes of the CE's associated with transitions of the phenyl chromophore to specific conformational features or spatial distributions of substituent groups or atoms.[1,2] Complications arise in the interpretation of the chiroptical properties of dissymmetric benzene derivatives when substituents on the benzene ring contain chromophoric groups which may be strongly coupled to (although not necessarily conjugated to) the phenyl chromophore. Coupling between the phenyl and nonphenyl chromophoric transitions and/or overlap between these two sets of transitions present severe difficulties in developing reliable and accurate spectra-structure relationships. The α-substituted phenylacetic acids and esters represent one class of systems in which these difficulties are encountered.[3-5]

In the 200–300 nm spectral region, the carboxylate chromophore is expected to exhibit at least one transition ($n \rightarrow \pi^*$) and the phenyl moiety is expected to exhibit at least two transitions (the ^1L_b and ^1L_a $\pi \rightarrow \pi^*$ excitations). It is uncertain whether these three transitions will be strongly or weakly coupled in molecules of the α-substituted phenylacetic acid class and whether additional transitions will appear at $\lambda > 200$ nm due to charge-transfer excitations or to perturbations from higher energy free-chromophore (phenyl or carboxylate) states.

In the present study we examine the chiroptical properties of a series of chiral phenylacetic acid derivatives by calculating electronic rotatory strengths directly from molecular wave functions derived from semiempirical molecular orbital calculations. Ground state wave functions for the chiral systems are calculated using the CNDO/S semiempirical molecular orbital model[6] and excited states are constructed in the virtual orbital-configuration interaction (CI) approximation. It has been well documented that the CNDO/S-CI molecular orbital model is reliable for calculating the transition energies and oscillator strengths associated with the intravalence-shell electronic transitions in benzene and benzene derivatives, and we have recently employed this model in calculating the chiroptical properties of a series of dissymmetric benzene derivatives which contain various saturated substituent groups (nonchromophoric in the near UV region).[2]

Previous calculations of molecular chiroptical properties based on CNDO/2-CI,[7] INDO-CI[8] and CNDO/S-CI[9] molecular orbital models demonstrate that *direct* calculations of electronic rotatory strengths from wave functions computed with these models provide useful alternative representations to the independent systems approaches.[10,11] The reliability and accuracy of independent systems calculations of molecular optical activity are limited by one's ability to model the electronic states of the interacting subsystems and to represent the interaction mechanisms operating between subsystems. On the other hand, the reliability and accuracy of *direct* calculational models are limited by the approximations one must use in calculating total molecular wave functions (especially those of excited states). Given the uncertainty regarding the extent to which the carboxylate and phenyl moieties of phenylacetic acid derivatives may interact or couple, a *direct* calculational model is perhaps to be preferred over an independent systems perturbation approach for these systems.

In the present study we report calculations on various conformational isomers of the following compounds.



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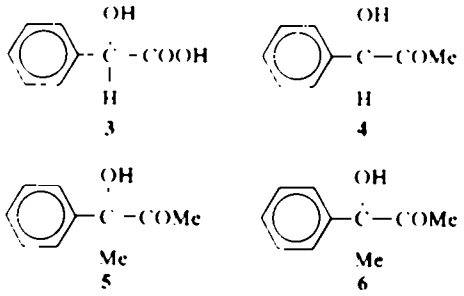


The CD spectra of **1** (hydratropic acid), **3** (mandelic acid), **5** (atrolactic acid), and the corresponding esters have been reported by Barth *et al.*,[3] and Korver[4,5] has reported the CD spectra of a wide variety of mandelic acid derivatives. Although tentative band (CD) assignments and spectra-structure relationships have been offered for these systems studied in solution, there remains considerable uncertainty regarding the interpretation of their CD spectra.

METHODS OF CALCULATION

The semiempirical CNDO/S-SCF-MO model was used to calculate ground state electronic wave functions for each of the structures examined in this study. Excited states were constructed in the virtual orbital-configuration interaction (CI) approximation with 35 singly-excited configurations included in each CI calculation. Electric dipole transition integrals were calculated in the dipole velocity formalism, and all one-, two- and three-center terms were included in calculating both the electric dipole and the magnetic dipole transition moments. Rotatory strengths, dipole strengths, oscillator strengths, and dissymmetry factors were calculated for singlet–singlet transitions only.

Rotatory strengths are expressed in terms of "reduced rotatory strengths" where, for the electronic transition $i \rightarrow j$, $[R_{ij}]$ = reduced rotatory strength

$$= (100/\beta\mathscr{D}) \operatorname{Im} \langle \psi_i | \hat{\underline{\mu}} | \psi_j \rangle \cdot \langle \psi_j | \hat{\underline{m}} | \psi_i \rangle. \quad (1)$$

In Eqn (1), β is the Bohr magneton, $\mathscr{D}$ is the Debye unit $\hat{\underline{\mu}}$ is the electric dipole operator, and $\hat{\underline{m}}$ is the magnetic dipole operator. Dipole strengths,

$$D_i = |\langle \psi_i | \hat{\underline{\mu}} | \psi_j \rangle|^2 \quad (2)$$

are expressed in Debye^2 ($\mathscr{D}^2$) units, and dissymmetry factors are defined by:

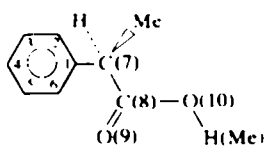
$$g_{ij} = 4R_{ij}/D_{ij} \quad (3)$$

where,

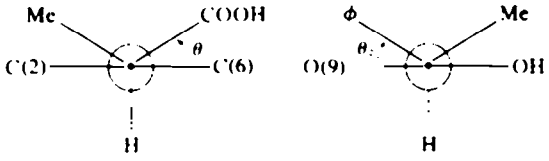
$$R_{ij} = (\beta\mathscr{D}/100)[R_{ij}]. \quad (4)$$

STRUCTURES

(a) *Hydratropic acid* (**1**) *and its methyl ester* (**2**)

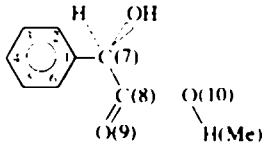


Conformational isomers of **1** and **2** were generated by varying two torsion angles, θ_1 and θ_2, involving rotations about the C(1)–C(7) and C(7)–C(8) bonds, respectively. All other geometrical parameters (bond angles and distances) were held constant as θ_1 and θ_2 were varied. The CO bond and the O–H(Me) bond were maintained in a *cis* arrangement for all isomers. The angles θ_1 and θ_2 are defined in the following projection drawings:



When $\theta_1 = 0°$ the C(1)–C(6) and C(7)–C(8) bonds are *cis*, and when $\theta_2 = 0°$ the C(8)–O(9) and C(1)–C(7) bonds are *cis*. The angle θ_1 was varied from 0° to 360° in 15° increments, and θ_2 was varied over 360° in 90° increments.

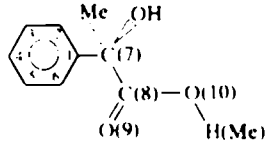
(b) *Mandelic acid* (**3**) *and its methyl ester* (**4**).



Conformational isomers of **3** and **4** were generated by varying the same two torsion angles as were defined above for compounds **1** and **2**. Again, all other geometrical parameters were held constant as θ_1 and θ_2 were varied. The CO bond and the O–H(Me) bond were maintained in a *cis* arrangement for all isomers, and the O–H bond of the α-OH substituent was directed to eclipse the C(7)–C(8) bond.

The angle θ_1 was varied from 0° to 360° in 15° increments, and θ_2 was varied over 360° in 90° increments.

(c) *Atrolactic acid* (**5**) *and its methyl ester* (**6**)



Conformational isomers of compounds **5** and **6** were generated in the same way as was described above for compounds **3** and **4**. However, due to the relatively larger sizes of **5** and **6**, calculations were carried out on fewer conformational isomers of these compounds.

RESULTS AND DISCUSSION

(a) *Conformational preferences*

The CNDO/S molecular orbital model was not designed (or parameterized) to provide necessarily reliable or accurate results regarding molecular conformational energies. Furthermore, since only two conformational or structural variables (θ_1 and θ_2) were included in the calculations reported here, our results cannot be used to draw definitive conclusions or to make definitive statements regarding conformational preferences. It is likely that the chiroptical properties of interest will be most sensitive to the variables θ_1 and θ_2, but it is *not* certain

that these will be the most important variables in determining energy minimization. However, it is reasonable to assume that our CNDO/S-MO results may be useful in identifying the *least* favored and the *most* favored conformations (defined with respect to θ_1 and θ_2) and that *qualitative* use of relative conformational energies is valid.

For all the compounds studied we found that conformations with $\theta_2 = 0°$ (the CO bond pointing back towards the aromatic ring) were energetically unfavorable when $15° > \theta_1 > -15°$ and $195° > \theta_1 > 165°$. This presumably may be interpreted in terms of strong repulsions between the carbonyl pi and lone-pair electrons and the pi electrons of the phenyl moiety. Near $\theta_1 = 0°$ and 180°, the $\theta_2 = 0°$ conformations were found to be stabilized through weak homoconjugation between the pi systems of the phenyl and carboxyl moieties. The $\theta_2 = 180°$ isomers (in which the carbonyl bond points away from the aromatic ring) were found to be more stable than the analogous $\theta_2 = \theta°$ isomers (for given values of θ_1), and variations in energy with θ_1 were found to be less dramatic.

For compounds **1** and **2**, conformational energies for the $\theta_2 = +90°$ and $\theta_2 = -90°$ isomers were nearly identical (for a given value of θ_1). However, for compounds **3–4** the $\theta_2 = -90°$ isomers were much preferred (lower in energy) over the $\theta_2 = +90°$ isomers for a given value of θ_1. This latter result can be explained in terms of a favorable intramolecular H-bonding arrangement between the α-OH group and the CO oxygen atom in the $\theta_2 = -90°$ isomers. This type of arrangement would be of lesser importance in compounds **1** and **2** which do not possess a α-OH group.

For **1** and **2**, the most stable conformational isomers are calculated to be the following: (1) (θ_1, θ_2) = (0°, 0°), (0°, 180°), (180°, 0°) and (180°, 180°); and, (2) (θ_1, θ_2) = (variable, ±90°). For **3–6**, the most stable conformational isomers are calculated to be the following: (1) (θ_1, θ_2) = (0°, 0°), (0°, 180°), (180°, 0°), and (180°, 180°); and, (2) (θ_1, θ_2) = (variable, −90°). These lists of "preferred" conformational isomers are rather large and are not of great use in detailing the expected conformational mixes of the various compounds under equilibrium conditions. They merely exclude the least favorable isomers. Energy differences calculated between the socalled "preferred" isomers listed above are of the order of 0.001–0.100 eV. These differences are probably too small to be meaningful given the nature of our calculational model. Only the chiroptical properties calculated for the "preferred" conformational isomers will be discussed in subsequent sections.

(b) *^1L_a Transition*

For all the structures examined in the present study the lowest-energy singlet–singlet $\pi \rightarrow \pi^*$ transition of the phenyl chromophore is calculated to be in the 255–265 nm region of the spectrum. Using Platt's notation,[12] we shall refer to this transition as ^1L_a. In agreement with experiment, this transition is calculated to have weak oscillator strengths and weak rotatory strengths. However, whereas the oscillator strength of this transition is relatively insensitive to variations in the structural variables θ_1 and θ_2, both the sign and the magnitude of the calculated rotatory strength are quite sensitive to changes in θ_1 and θ_2.

The reduced rotatory strengths of the ^1L_a transition are plotted in Fig. 1 for the (θ_1, θ_2) = (variable, ±90°) conformational isomers of **1** and the (θ_1, θ_2) = (variable, −90°) conformational isomers of **3** and **5**. The ^1L_a rotatory strengths calculated for the methyl ester derivatives of **1**, **3**, and **5**, exhibit conformational dependencies which are qualitatively similar to those found for the parent acid systems. Reduced rotatory strengths calculated for the ^1L_a transition are listed in Table 1 for additional conformational isomers of **1**, **3**, **5**. Again the ^1L_a rotatory strengths calculated for the methyl ester derivatives of these compounds are qualitatively similar to those calculated for the parent acid compounds.

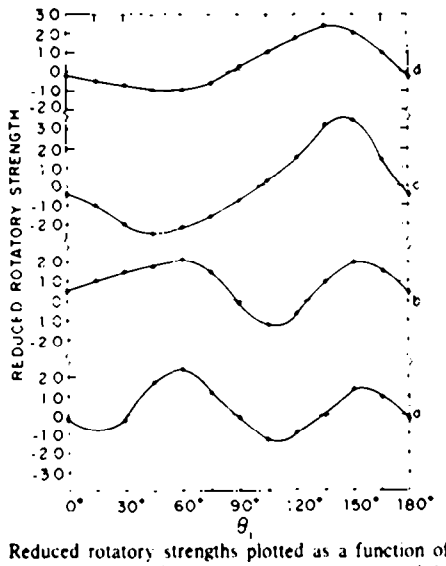


Fig. 1. Reduced rotatory strengths plotted as a function of the torsion angle θ_1 for the ^1L_a transition in: (a) 1(θ_2 = +90°); (b) 1(θ_2 = −90°); (c) 3(θ_2 = −90°); and, (d) 5(θ_2 = −90°).

Experimentally, the ^1L_a transition in **1** and **2** exhibits a positive Cotton effect for the S enantiomers.[1] However, the experimentally determined Cotton effect associated with the ^1L_a transition in **3–6** is negative for the S enantiomers.[2–5] All of our calculations were carried out on the R enantiomeric forms of **1–6**. The data displayed in Fig. 1 for **3** and **5** are in agreement with experiment if we assume that the conformational isomers (θ_1, θ_2) = (105°–170°, ±90°) predominate in solution. The ^1L_a rotatory strengths calculated for the isomers listed in Table 1 are also compatible with experimental observation for **3** and **5**. Korver *et al.*[5] have reported that the (θ_1, θ_2) = (−135°, ±90°) conformational isomer is found in the solid state for R-mandelic acid (**3**).

Table 1. Reduced rotatory strengths calculated for the ^1L_a transition in selected low-energy conformational isomers of compounds **1**, **3** and **5**

Compound	θ_1	θ_2	[R]
1	0	0	0.36
	0	180	0.11
	180	0	0.36
	180	180	−0.11
3	0	0	0.06
	0	180	0.31
	180	0	0.06
	180	180	0.31
5	0	0	0.12
	0	180	0.38
	180	0	0.12
	180	180	0.38

Agreement between experimental results and the theoretically calculated results for **1** and **2** is achieved only for the following conformational isomers considered in Fig. 1 and in Table 1: (θ_1, θ_2) = (0–30°, 90°), (90–135°, 90°), (90–125°, −90°), and (0°, 180°).

Korver *et al.*[1] have used an extended Hückel molecular orbital model to calculate the ^1L_a rotatory strength of **R**-mandelic acid (**3**) as a function of the torsion angle θ_1. Their results appear to differ significantly from those obtained by us (as plotted in Fig. 1), although a direct comparison is not possible since they did not state what value of θ_2 they assumed.

(c) *L_a Transition*

The phenyl localized ^1L_a transition is calculated to lie in the 205–215 nm region for each of the structures examined in this study. The oscillator strengths calculated for this transition are about an order of magnitude greater than those calculated for the ^1L_b transition, but are still relatively small. The rotatory strengths calculated for the ^1L_b and ^1L_a transitions are of the same order of magnitude.

The reduced rotatory strengths of the ^1L_a transition are plotted in Fig. 2 for the (θ_1, θ_2) = (variable, ±90°) conformational isomers of **1** and the (θ_1, θ_2) = (variable, −90°) conformational isomers of **3** and **5**. The ^1L_a rotatory strengths calculated for the methyl esters of **1**, **3**, and **5** exhibit conformational dependencies which are qualitatively similar to those found for the parent acid compounds. Additional reduced rotatory strengths calculated for the ^1L_a transition in various low-energy conformational isomers of **1**, **3**, and **5** are listed in Table 2.

Except for conformers in which θ_1 and θ_2 are near 0° (or 180°) (Table 2), the reduced rotatory strengths calculated for the ^1L_a transition are somewhat smaller than those calculated for the ^1L_b transition. This is especially true for θ_1 values where the ^1L_b rotatory strengths are relatively large (and when $\theta_2 = \pm 90°$). The Cotton effects of the ^1L_a transition in **1**–**6** have not been experimentally identified and characterized, so comparisons between theory and experiment are not possible in this case.

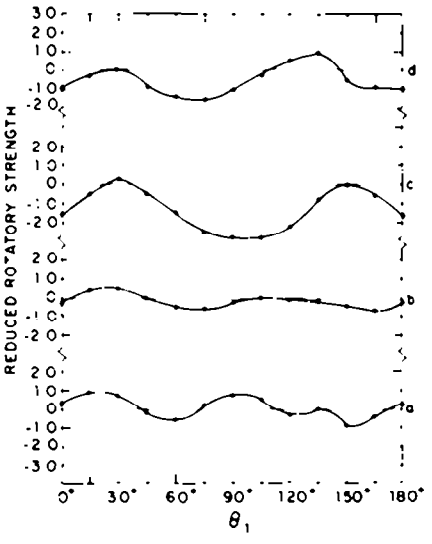


Fig. 2. Reduced rotatory strengths plotted as a function of the torsion angle θ_1 for the ^1L_a transition in: 1(θ_2 = −90°); (b) 1(θ_2 = 90°); (c) 3(θ_2 = −90°); and, (d) 5(θ_2 = 90°).

Table 2. Reduced rotatory strengths calculated for the L_a transition in selected low-energy conformational isomers of compounds **1**, **3** and **5**

Compound	θ_1	θ_2	[R]
1	0	0	−0.31
	0	180	−1.37
	180	0	−0.31
	180	180	−1.37
3	0	0	−1.97
	0	180	−1.08
	180	0	−1.97
	180	180	−1.80
5	0	0	−0.86
	0	180	−0.37
	180	0	−0.86
	180	180	0.37

(d) *Carboxyl $n \rightarrow \pi^*$ transition*

In our calculations on each of the structures examined in the present study an easily identifiable transition appears which may be assigned as an $n \rightarrow \pi^*$ excitation localized on the carboxyl moiety. In each case this transition has a relatively weak oscillator strength but a quite large rotatory strength. This transition involves excitation of an electron out of an "n" orbital on the carbonyl oxygen atom and into the carbonyl π^* orbital. The magnetic dipole transition integrals calculated for this transition are large (0.6–0.8 Bohr magneton) and the electric dipole transition integrals are calculated to be small. The transition energies calculated for this transition are quite sensitive to the number of singly-excited configurations included in our CI calculations. For CI basis sets <15, the transition energies fall in the 220–240 nm region. However, when the CI basis set size is increased from ~15 to 35 the transition wavelengths are pushed down into the 260–275 nm region (generally just below the calculated ^1L_b transition wavelengths). The qualitative and semi-quantitative aspects of the calculated oscillator strengths and rotatory strengths are unaffected by an increase in CI basis size beyond 15. Previous calculations carried out in this laboratory on various carboxylic acid derivatives suggest that the CNDO/S-MO-CI model tends to predict $n \rightarrow \pi^*$ transition energies which are too low by 10–30%. Previous interpretations[3] of the CD spectra exhibited by **1**–**6** have assigned the very strong Cotton effects observed in the 220–230 nm region to the carboxyl $n \rightarrow \pi^*$ transition. We agree with this assignment and attribute the lower transition energies calculated here for the $n \rightarrow \pi^*$ transition (for CI basis set sizes >15) to a failure in the CNDO/S-MO-CI model to accurately calculate the $n \rightarrow \pi^*$ transition energies.

The reduced rotatory strengths calculated for the carboxyl $n \rightarrow \pi^*$ transition are plotted in Fig. 3 for the (θ_1, θ_2) = (variable, ±90°) conformational isomers of **1** and the (θ_1, θ_2) = (variable, −90°) conformational isomers of **3** and **5**. Additional $n \rightarrow \pi^*$ rotatory strengths are listed in Table 3 for selected low-energy conformational isomers of **1**, **3**, and **5**. Again, the methyl ester derivatives of **1**, **3**, and **5** were found to exhibit $n \rightarrow \pi^*$ chiroptical properties similar to those calculated for the parent acids.

Experimentally the Cotton effect observed in the 220–230 nm region for **1**–**6** is found to be positive for the S enantiomers. All six compounds exhibit identically signed Cotton effects. These (presumably) $n \rightarrow \pi^*$ Cotton effects

exhibit ellipticities which are generally about two orders of magnitude stronger than those observed for the ^1L_a transition. Our calculated $n \rightarrow \pi^*$ rotatory strengths are about an order of magnitude greater than the ^1L_a rotatory strengths for corresponding conformational isomers, and a negative $n \rightarrow \pi^*$ Cotton effect is predicted for most of the conformational isomers of the R enantiomeric form in **1–6** (Fig. 3 and Table 3).

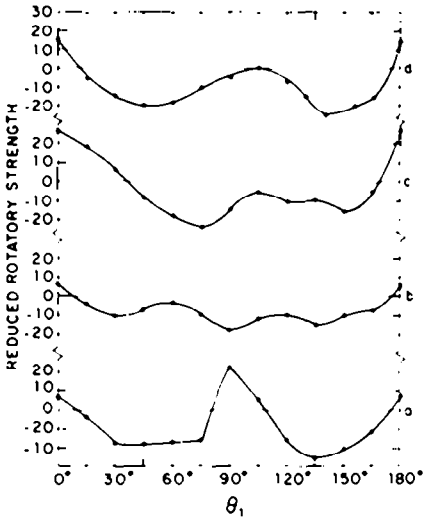


Fig. 3. Reduced rotatory strengths plotted as a function of the torsion angle θ_1 for the $n \rightarrow \pi^*$ transition in: (a) $1(\theta_2 = +90°)$; (b) $1(\theta_2 = -90°)$; (c) $3(\theta_2 = -90°)$; and, (d) $5(\theta_2 = -90°)$.

Table 3. Reduced rotatory strengths calculated for the $n \rightarrow \pi^*$ transition in selected low-energy conformational isomers of compounds 1, 3 and 5

Compound	θ_1	θ_2	[R]
1	0	0	1.14
	0	180	-5.69
	180	0	1.14
	180	180	-5.69
3	0	0	0.98
	0	180	-3.65
	180	0	0.98
	180	180	3.65
5	0	0	1.32
	0	180	-2.85
	180	0	1.32
	180	180	2.85

(e) *Other transitions*

In most of the structural isomers of the six compounds examined in this study the $n \rightarrow \pi^*$ carboxyl transition and the ^1L_a and ^1L_b phenyl transitions lie lowest in energy. However, in certain conformational isomers in which the CO bond is pointed back towards the phenyl ring ($\theta_2 = 0°$) one or more low-energy ($\lambda > 220$) charge-transfer transitions appear. These transitions generally involve both $n(CO) \rightarrow \pi^*(Ph)$ and $\pi(CO) \rightarrow \pi^*(Ph)$ excitations, and in some cases $\pi(Ph) \rightarrow \pi^*(CO)$ excitations are included. The excited states in these transitions are generally comprised of complicated mixtures of various configurational states in our CNDO/S-MO-CI model and are difficult to characterize precisely in simple terms. The rotatory strengths calculated for these strongly coupled phenyl/carboxyl transitions are much weaker than those calculated for the $n \rightarrow \pi^*$ carboxyl transition, but are of the same order of magnitude as those calculated for the ^1L_a phenyl transition. Their oscillator strengths are calculated to be only slightly stronger than those of the $n \rightarrow \pi^*$, ^1L_a, and ^1L_b transitions. There appears to be little evidence for the presence of these transitions in the CD and absorption spectra of **1–6** in solution media, although **5** and **6** do show a CD band in the 240 nm region (between the presumably ^1L_a and $n \rightarrow \pi^*$ bands)[1] which may possibly be due to an interchromophoric (phenyl/carboxyl) charge-transfer transition. It is more likely, however, that the 240 nm CD band observed in **5** and **6** arises from a highly perturbed $n \rightarrow \pi^*$ carboxyl transition (in one of the conformational isomers present in solution), and the strongly temperature-dependent intensity of this band[1] would seem to support this latter interpretation.

The low-energy charge-transfer transitions do not appear in the calculations with $\theta_2 = \pm 90°$ or $\theta_2 = 180$ (CO group pointing away from the phenyl group). In these conformations strong homoconjugation between the phenyl and carboxyl moieties is not possible.

Our study included calculations on higher energy transitions in **1–6**, but these will not be discussed here. The excited states involved in these transitions were found to be complicated mixtures of phenyl $\pi\pi^*$, carbonyl $\pi\pi^*$, and phenyl/carboxyl interchromphoric charge transfer configurational states. Detailed consideration of our calculated results for these higher energy transitions is not justified given the approximations of the theoretical model employed. Most serious in this latter regard are: (a) consideration of "valence-shell-only" orbitals in the CNDO/S-MO basis set; (b) inclusion only of singly-excited configurations in the CI calculations; (c) inadequate treatment of $\sigma - \pi$ interactions; and, (d) neglect of vibronic interactions.

CONCLUSIONS

The results obtained in this study suggest that the chiroptical spectra for **1–6** at $\lambda > 205$ nm may be interpreted in terms of Cotton effects associated with the ^1L_a and ^1L_b phenyl localized transitions and a carboxyl localized $n \rightarrow \pi^*$ transition. The $n \rightarrow \pi^*$ Cotton effect is predicted to be much more intense than the ^1L_a and ^1L_b Cotton effects, in apparent agreement with experiment. The most consistent agreement with experimental data is achieved when it is assumed that the preferred value of θ_2 is $\pm 90°$ for the α-OH substituted structures (**3–6**) and $\pm 90°$ for structures **1** and **2**. For **3–6**, a θ_1 torsion angle of 110–170° yields results most consistent with experimental observation. For **1** and **2**, a θ_1 torsion angle near 120° yields results in closest agreement with experiment.

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