Chiroptical Properties of Lactones. Part II.[1] Electronic Rotatory Strengths of the $n \longrightarrow \pi^*$ Transition in Saturated γ- and δ-Lactones

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The chiroptical properties associated with the $n \longrightarrow \pi^*$ transition of dissymmetric saturated γ- and δ-lactones are calculated and relationships between the chiroptical observables and the stereochemical and electronic structural features of these systems are examined. The calculations are based on the INDOMO model for the electronic structure of the molecular systems and excited states are constructed in the virtual orbital-configuration interaction approximation. The highest and second highest occupied orbitals calculated for each of the 17 structures studied are, respectively, the in-plane n and out-of-plane π° nonbonding orbitals localized on the O=C–O group. The lowest lying singlet state is $n\pi^*$ and the calculated transition wavelengths for transitions to this state lie in the range 197—230 nm. The $n \longrightarrow \pi^*$ rotatory strengths and dissymmetry factors calculated for the various structures are in general agreement with experiment. Furthermore, spectra–structure relationships deduced from the calculated results tend to support the empirical and semi-empirical relationships presently applied to chiral γ- and δ-lactones.

THE use of o.r.d. and c.d. to probe the stereochemical features of saturated γ- and δ-lactones has been studied intensively in recent years. Of special interest have been the studies conducted by Klyne and his co-workers,[2] Beecham,[3] Snatzke and his co-workers,[4] Wolf,[5] Legrand and Bucourt,[6] and Korver.[7] In these studies special efforts were made to relate the sign and relative magnitudes of the Cotton effect (CE) associated with the lowest lying singlet–singlet electronic transition ($n \longrightarrow \pi^*$) to specific stereochemical features in a number of saturated γ- and δ-lactones (or molecules containing γ- or δ-lactone groups). Sector rules similar to the octant rule for ketones [8] and the quadrant rule for lactams [9,10] were proposed and/or tested, and the origins of the observed CEs were examined with the objective of differentiating between contributions from inherent chirality within the lactone ring systems and contributions arising from ' vicinal ' effects due to asymmetric substitution on the lactone ring.

The empirical and semi-empirical spectra–structure relationships [2-7] have been enormously useful for providing systematic interpretations of the chiroptical observables associated with the $n \longrightarrow \pi^*$ transition in dissymmetric γ- and δ-lactones. The proposed sector rules are based, however, on a somewhat qualitative and heuristic representation of the electronic structure and spectroscopic states of the O=C–O chromophore in these systems. This is made necessary by the lack of highly accurate theoretical calculations on the O=C–O group and the absence of any definitive characterizations of the spectroscopic states of the O=C–O chromophore. The theoretical underpinnings of the ' lactone sector rules ' and the validity of the assumptions (about the O=C–O electronic structure) on which they are based can only be tested after such information becomes available.

An alternative method for examining spectra–structure relationships in the lactone systems is to perform semi-empirical MO calculations on complete structures and to calculate the chiroptical properties of these structures from the wave functions obtained in the MO calculations. The approximate nature of such calculations do not permit using the results to ' test ' empirical or semi-empirical rules, but this method *does* in many cases provide an alternative theoretical basis (albeit, approximate in nature) on which to interpret the observed optical properties in terms of various stereochemical and electronic structural variables. Semi-empirical MO models have been used recently to

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study the chiroptical properties of a number of dissymmetric molecular systems.[11,12]

In the study reported here we performed SCFMO calculations in the INDO[13] approximation on a series of γ- and δ-lactones. Excited states of these systems were constructed in the virtual orbital-configuration interaction (CI) approximation using MOs calculated from the INDOMO model. Transition energies, electric and magnetic dipole transition integrals, dipole strengths, rotatory strengths, and dissymmetry factors were then calculated for the lowest-lying singlet–singlet transition in each lactone.

It must be emphasized from the outset that calculations based on semi-empirical MO models such as that adopted in this study cannot be used reliably to test, refute, or support empirical or semi-empirical sector rules or spectra–structure relationships. They do, however, provide a useful alternative representation of such relationships. They are especially useful for studying dissymmetric systems in which the chromophore is included in a strained ring system. In such systems, the electronic structure of the chromophore generally is strongly coupled to the non-chromophoric atoms of the ring and perturbation treatments based on the independent systems model[14] for molecular optical activity are inappropriate.

METHODS

The methods of calculation employed in the present study are similar to those reported previously.[12f] SCFMO Calculations were carried out in the INDO approximation using 'standard' parameters.[13] The MOs obtained from these calculations were renormalized to include overlap by performing transformation (1) where $\tilde{C}_\lambda$ is the eigenvector

$$\tilde{C}_\chi = \tilde{S}_\chi^{-1/2}\tilde{C}_\lambda \tag{1}$$

matrix obtained from an INDOMO calculation, $\tilde{S}_\chi$ is an overlap matrix whose basis functions are the Slater orbital set $\tilde{\chi}$, and $\tilde{\lambda}$ represents the orthogonal INDO atomic basis set. The molecular orbitals may be expressed as (2).

$$\tilde{\varphi} = \tilde{C}_\lambda\tilde{\lambda} = \tilde{C}_\chi\tilde{\chi} \tag{2}$$

Having found $\tilde{C}_\chi$ from transformation (1) we expressed our wave functions in terms of the $\tilde{\chi}$ basis set before calculating electric and magnetic dipole transition integrals.

Excited states were constructed in the virtual orbital-configuration interaction approximation. Electric dipole transition integrals were calculated using the dipole velocity formalism and all two-centre terms were included in the calculations of both the electric and magnetic dipole transition moments. Ground-state electric dipole moments were calculated according to the procedure outlined by Pople and his co-workers.[13]

The optical properties calculated and reported are (a) dipole strength, $D_{ij} = |\langle\psi_i|\hat{\mu}|\psi_j\rangle|^2$; (b) oscillator strength, $f_{ij} = (4\nu m\pi_{ij}/3he^2)D_{ij}$, where $\nu_{ij} = (E_i - E_j)/h$; (c) reduced rotatory strength, $[R_{ij}] = (100/\beta D)Im\langle\psi_i|\hat{\mu}|\psi_j\rangle\,.\,\langle\psi_j|\hat{m}|\psi_i\rangle$, where β is the Bohr magneton, D is the Debye unit, $\hat{\mu}$ is the electric dipole operator, and $\hat{m}$ is the magnetic dipole operator; and (d) dissymmetry factor, $g_{ij} = 4R_{ij}/D_{ij}$.

STRUCTURES

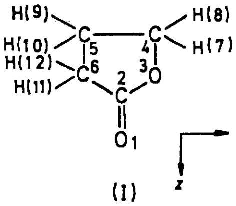
(a) *γ-Lactones*.—Calculations were performed in 15 γ-lactone structures given in Table 1. The ring conformation and geometry of these structures are identical, so that the 15 structures differ only with respect to ring substitution and the nature and geometrical parameters of the substituent groups. The basic ring structure is reflected by the geometry of γ-butyrolactone (I). The α- and δ-carbon atoms along with the O=C–O group of (I) all lie in one plane (the *xz*-plane of our co-ordinate system), and the β-carbon atom lies above this plane (in the positive *y* direction). The atomic positional co-ordinates for (I) (Table 2) were derived from reported crystal structure data on γ-lactone systems.[15]

TABLE 1

Summary of structures studied

Structure	
(I)	γ-Butyrolactone
(IIa, b)	(*S*)-α-OH-γ-butyrolactone[a]
(IIIa, b)	(*R*)-α-OH-γ-butyrolactone[a]
(IVa, b)	(*S*)-β-OH-γ-butyrolactone[a]
(Va, b)	(*R*)-β-OH-γ-butyrolactone[a]
(VI)	(*S*)-α-OH-(*R*)-β-OH-γ-butyrolactone
(VII)	(*S*)-α-OH-(*S*)-β-OH-γ-butyrolactone
(VIII)	(*R*)-α-OH-(*R*)-β-OH-γ-butyrolactone
(IX)	(*R*)-α-OH-(*S*)-β-OH-γ-butyrolactone
(X)	(*R*)-α-NH_2-γ-butyrolactone (D-homsoerine γ-lactone)
(XI)	(*S*)-α-NH_2-γ-butyrolactone (L-homoserine γ-lactone)
(XIIa)	δ-Valerolactone (half-chair conformation)
(XIIb)	δ-Valerolactone (skewed-boat conformation)

[a] Structures (IIa and b) *etc.* differ only in respect of rotation about the C(α)–OH bond. *S* and *R* isomers are *not* related enantiomerically.



(I)

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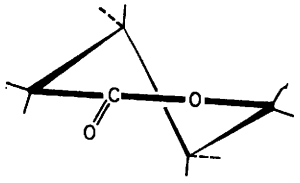
(b) *δ-Lactones.*—Only two δ-lactone structures were examined in this study. These are the skewed-boat (XIIb) and half-chair (XIIa) conformers of unsubstituted δ-valerolactone. These conformers are depicted in the Figure. In (XIIa and b), the C(α) (O=) COC(δ) group lies in the *xz*-plane while C(β) and C(γ) lie either above or below this plane.

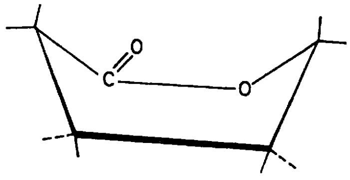
TABLE 2

Atomic positional co-ordinates for structure (I) (in A)

Atom	*x*	*y*	*z*
O(1)	0	0	1.22
C(2)	0	0	0
O(3)	1.112	0	−0.812
C(4)	0.612	0	−2.170
C(5)	−0.820	0.512	−2.121
C(6)	−1.311	0	−0.780
H(7)	0.551	−0.921	−2.560
H(8)	1.140	0.591	−2.782
H(9)	−1.510	0.239	−2.800
H(10)	−0.881	1.540	−2.012
H(11)	−1.612	−0.941	−0.921
H(12)	−2.011	0.501	−0.272



(a) Half-chair



(b) Boat

Conformation isomers of δ-valerolactone

RESULTS

The ground state dipole moments, binding energies, and first two ionization potentials (vertical ionization potentials calculated according to Koopmans' theorem) computed for structures (I)—(XII) are presented in Table 3. The optical properties calculated for the lowest energy singlet–singlet transition of each structure are listed in Table 4. In Table 5 are displayed the Cartesian components of the electric and magnetic transition dipole integrals calculated for the lowest lying singlet–singlet transition on structures (I) and (XIIa and b).

The lowest energy singlet state of each structure examined here is best characterized as an $n\pi^*$ state localized on the O=C–O group. The highest occupied orbital in each structure is calculated to be predominantly localized on the carbonyl oxygen atom ($2p_x$), and the next highest occupied orbital is a π°-type ($2p_y$) with a large amplitude on both oxygen atoms of the O=C–O group. The lowest unoccupied orbital calculated for each structure is of the π-type with significant amplitude on all three atoms of the O=C–O group.

TABLE 3

Calculated dipole moments, binding energies, and vertical ionization potentials

Structure	Dipole moment (D)	Binding energy (a.u.)	IP_1(a.u.)	IP_2(a.u.)
(I)	4.40	−4.9626	0.4564	0.5011
(IIa)	4.21	−5.2091	0.4089	0.4942
(IIb)	4.34	−5.2148	0.4170	0.4980
(IIIa)	4.12	−5.2141	0.4126	0.4994
(IIIb)	4.35	−5.2156	0.4133	0.5007
(IVa)	4.38	−5.2098	0.4299	0.4736
(IVb)	4.47	−5.2199	0.4392	0.4897
(Va)	3.28	−5.2049	0.4509	0.4806
(Vb)	3.40	−5.2201	0.4519	0.4828
(VI)	4.39	−5.4726	0.4028	0.4720
(VII)	4.82	−5.4794	0.3932	0.4685
(VIII)	4.28	−5.4687	0.3920	0.4692
(IX)	4.79	−5.4819	0.3932	0.4723
(X)	5.58	−5.4936	0.3736	0.4959
(XI)	5.46	−5.3242	0.3949	0.4501
(XIIa)	4.29	−6.0602	0.4437	0.5010
(XIIb)	4.51	−6.0806	0.4348	0.4866

TABLE 4

Calculated optical properties for lowest energy singlet–singlet transition ($n \longrightarrow \pi^*$)

Structure	ΔE(eV)	λ(nm)	*f*	*D*(Debye)	[R]	|g|
(I)	5.83	213	0.0124	0.562	7.25	0.0048
(IIa)	5.42	229	0.0190	0.924	13.87	0.0055
(IIb)	5.37	231	0.0184	0.919	15.36	0.0062
(IIIa)	5.63	220	0.0180	0.836	−13.26	0.0061
(IIIb)	5.60	221	0.0176	0.830	−14.89	0.0067
(IVa)	5.92	209	0.0148	0.592	16.82	0.0104
(IVb)	5.91	210	0.0132	0.588	19.70	0.0124
(Va)	5.83	213	0.0100	0.453	−1.23	0.0010
(Vb)	5.81	213	0.0121	0.471	−2.03	0.0018
(VI)	5.42	228	0.0174	0.901	12.60	0.0051
(VII)	5.42	228	0.0219	1.065	28.51	0.0099
(VIII)	5.59	222	0.0181	0.860	−15.10	0.0069
(IX)	5.59	221	0.0156	0.733	−10.25	0.0052
(X)	5.66	219	0.0243	1.136	−18.66	0.0061
(XI)	5.39	229	0.0197	0.962	14.83	0.0057
(XIIa)	6.00	207	0.0155	0.683	6.55	0.0036
(XIIb)	6.31	197	0.0213	0.891	2.12	0.0009

TABLE 5

Components of the electric and magnetic dipole transition integrals for the lowest energy transition ($n \longrightarrow \pi^*$) for structures (I) and (XIIa and b)

	Electric [a]			Magnetic [b]		
Structure	*x*	*y*	*z*	*x*	*y*	*z*
(I)	0.015	−0.061	0.010	−0.039	0.025	0.801
(XIIa)	−0.001	0.071	−0.010	0.077	−0.031	−0.784
(XIIb)	−0.028	0.081	−0.002	−0.158	−0.009	0.778

[a] Dipole velocity integrals, $\langle\psi_0|\partial/\partial_q|\psi_n\rangle$, expressed in atomic units. $q = x, y,$ or z. [b] $(e/2mc)\langle\psi_0|L_q|\psi_n\rangle$ in Bohr magneton units. $L_q = L_x, L_y,$ or L_z.

DISCUSSION

The lowest energy singlet excited state calculated for each of the 17 saturated lactone structures considered in this study is clearly of the $n\pi^*$ type where the *n* and π^* orbitals are localized on the O=C–O. Only in the α-substituted structures are there significant admixtures of substituent orbitals into the *n* molecular orbital. When the α-substituent (OH or NH_2) is equatorial to the ring and when the substituent ' lone-pair ' orbital(s) is directed towards the carbonyl oxygen atom, this admixture of substituent orbital character can be as high as 15—20%. According to the INDOMOCI model adopted in this study, the lowest energy singlet–singlet transition is accurately described as $n \longrightarrow \pi^*$. This agrees with the designation or assignment commonly used in previous empirical and semi-empirical studies of optical activity in saturated lactones.[2-7]

Our calculations place the n orbital as the highest occupied orbital in each structure studied and the essentially 'non-bonding' π° orbital as the second highest occupied orbital. The π° orbital has maximum amplitude on the two oxygen atoms of O=C–O group and has a node in the plane of the C(α)(O=)COC(γ) group. This calculated result is in agreement with the findings obtained from photoelectron spectral studies of carboxylic acids and esters of carboxylic acids.[16] Sweigart and Turner [16] reported vertical ionization potentials in the range 10.4—11.7 eV for the n orbital and in the range 10.8—12.5 eV for the π° orbital (referred to as π_2). Our calculated ionization potentials (vertical) for the n orbital fall in the range 10.3—12.0 eV and our calculated values for the π° orbital are in the range 12.2—13.6 eV (see Table 3). So far as we are aware, experimental values for the ionization potentials of lactone compounds have not been reported.

Absorption and c.d. band maxima associated with the $n \longrightarrow \pi^*$ transition in saturated γ- and δ-lactone compounds of the type studied here generally occur in the 205—230 nm region of the spectrum. The positions of the maxima are somewhat dependent upon solvent and upon the exact nature of the environment nearby to the O=C–O chromophore. The calculated $n \longrightarrow \pi^*$ transition wavelengths displayed in Table 4 fall within the range 207—231 nm, with the exception of structure (XIIb) (half-chain conformer of δ-valerolactone) in which the $n \longrightarrow \pi^*$ transition wavelength is calculated to be 197 nm.

The results presented in Table 5 demonstrate that the $n \longrightarrow \pi^*$ transition can be characterized as strongly magnetic dipole allowed with polarization direction nearly coincident with the z-axis (along the C=O bond). In this regard, the $n \longrightarrow \pi^*$ transition in saturated γ- and δ-lactones is similar to the analogous transitions in lactones [9,12b] and saturated ketones.[12a,14]

The rotatory strength results tabulated in Table 4 indicate that chirality within the ring system of the γ-lactone structures can make substantial contributions to the $n \longrightarrow \pi^*$ rotatory strength. Substituent contributions to the $n \longrightarrow \pi^*$ rotatory strengths of structures (II)—(XI) may be separated out by subtracting the calculated value for structure (I) (unsubstituted) from the values calculated for (II)—(XI). These substituent contributions are given in Table 6.

TABLE 6

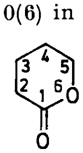
Substituent contributions

Structure	Substituent contribution to $[R(n\pi^*)]$	
(IIa)	6.62	α(*S*)-OH, equatorial
(IIb)	8.11	α(*S*)-OH, equatorial
(IIIa)	−20.51	α(*R*)-OH, axial
(IIIb)	−22.14	α(*R*)-OH, axial
(IVa)	9.57	β(*S*)-OH, equatorial
(IVb)	12.45	β(*S*)-OH, equatorial
(Va)	−8.48	β(*R*)-OH, axial
(Vb)	−9.28	β(*R*)-OH, axial
(VI)	5.35	α(*S*)-OH-β(*R*)-OH
(VII)	21.26	α(*S*)-OH-β(*S*)-OH
(VIII)	−22.35	α(*R*)-OH-β(*R*)-OH
(IX)	−17.50	α(*R*)-OH-β(*S*)-OH
(X)	−25.91	α(*R*)-NH_2, axial
(XI)	7.58	α(*S*)-NH_2, equatorial

The signs of the substituent contributions to $[R(n \longrightarrow \pi^*)]$ in the monosubstituted structures (II)—(V), (X), and (XI) correlate directly with the absolute configuration (*R* or *S*) at the respective substituent sites. The sign of $[R(n \longrightarrow \pi^*)]$ for the disubstituted structures (VI)—(IX) is entirely dominated or determined by the absolute configuration at the α-substituent site. That is, it is predicted that the sign of the $n \longrightarrow \pi^*$ CE will reflect the absolute configuration at C(α) in the α-β-disubstituted γ-lactone structures examined here. This calculated result supports a similar suggestion, based on empirical findings, previously set forth by Beecham.[3] Beecham [3] also suggested that a γ-lactone ring of the same geometry (and chirality) as that of structure (I) (Table 2) should make a positive contribution to the $n \longrightarrow \pi^*$ CE. This, too, is supported by our calculated results.

Urry [17] reported the c.d. of L-homoserine γ-lactone in 95% dioxan and in water (pH 3.6—7.6). In water at pH 7.6, the $n \longrightarrow \pi^*$ rotatory strength was determined to be 7.6×10^{-40} ($[R] = 8.3$) and the c.d. band was centred at *ca.* 220 nm. An 8 nm red shift was observed when water was replaced by 95% dioxan. The dissymmetry factor (g) associated with the $n \longrightarrow \pi^*$ transition was reported to be 0.005. The results shown in Table 4 for L-homoserine γ-lactone [structure (XI) with the amino-group equatorial] are in remarkable agreement with these experimental data. Urry noted that the sign of the $n \longrightarrow \pi^*$ CE in the corresponding lactam compound, L-3-amino-2-pyrrolidone, was opposite that found for L-homoserine γ-lactone. This experimental observation is also in agreement with calculations [12b] based on the INDOMOCI model employed in the present study.

The δ-lactone systems were too large to be investigated extensively in this study. Instead, we examined only the unsubstituted δ-valerolactone and considered just two chiral conformational isomers of this compound. The conformers on which we performed calculations are the ones purported to determine the sign of the $n \longrightarrow \pi^*$ rotatory strength of δ-lactone systems. The $n \longrightarrow \pi^*$ rotatory strength for both the half-chair conformer (XIIa) and the skewed-boat conformer (XIIb) was calculated to be >0. This calculated result is in agreement with the conclusions arrived at by Korver [7] and by Beecham [3] based on analyses of experimental c.d. data on δ-lactone systems. Furthermore, according to the rules proposed by Legrand and Bucourt,[6] ring chirality in both (XIIa and b) should produce a positive $n \longrightarrow \pi^*$ CE. The dihedral angle between C(3)C(2)C(1) and C(2)C(1)0(6) in system (A) is negative in both (XIIa and b). Wolf [5] has shown that the c.d. maximum of a δ-lactone in a half-chair conformation usually lies at longer wavelengths than that of an analogous δ-lactone in a boat conformation. This experimental observation also appears to be reflected in the calculated transition wavelengths for the $n \longrightarrow \pi^*$ transition in structures (XIIa and b).



(A)

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In general, the calculations performed in this study give results which support the empirical and semiempirical spectra–structure relationships presently applied to chiral γ- and δ-lactone systems. The model employed in making these calculations is not suitable for examining the theoretical basis of the various sector rules proposed for lactone compounds. To do this one would require very accurate wave functions for the O=C–O group, a detailed description of the nodal patterns of these wave functions, and a model for intramolecular interactions between the –O=C–O– group and the remaining atoms in the lactone structures.

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