Chiroptical Properties of Lactones. Part III.[1] Electronic Rotatory Strengths of the $n \rightarrow \pi^*$ Transition in αβ-Unsaturated γ-Lactone Systems

By **Harry Kreigh** and **Frederick S. Richardson,*** Department of Chemistry, University of Virginia, Charlottesville, VA 22901, U.S.A.

The chiroptical properties associated with the $n \rightarrow \pi^*$ transition of dissymmetric αβ-unsaturated γ-lactone systems 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 INDO-MO model for the electronic structure of the molecular systems and excited states are constructed in the virtual orbital–configuration interaction approximation. The lowest-energy singlet–singlet transition is calculated to be of the $n \rightarrow \pi^*$ type for each of the αβ-unsaturated γ-lactone structures examined. The *n* orbital in this transition is found to be somewhat localized on the carbonyl oxygen atom of the O=C–O moiety, whereas the π^* orbital is delocalized over the C=C and O–C–O fragments. Oscillator strengths, rotatory strengths, and dissymmetry factors are calculated for the $n \rightarrow \pi^*$ transition in a number of *exo*-ene and *endo*-ene αβ-unsaturated γ-lactone systems. The signs and magnitudes of the calculated rotatory strengths are related to specific structural features in these systems.

RECENTLY we have reported calculations on the electronic rotatory strengths associated with $n \rightarrow \pi^*$ transitions in a number of saturated lactone and dilactone systems.[1] These calculations were based on a semi-empirical molecular orbital model in which ground-state wave functions are obtained using the INDO method of Pople and his co-workers [2] and excited-state wave functions are constructed in the virtual orbital-configuration interaction approximation. The results obtained for the saturated γ- and δ-lactone systems led to spectra–structure relationships which were in substantial agreement with those previously deduced from purely empirical and semi-empirical correlations. Furthermore, the calculated results for both the lactone and dilactone systems indicated the relative contributions made to the $n \rightarrow \pi^*$ rotatory strengths by asymmetric substitution (vicinal effects) and by chiral distortions within lactone (or dilactone) ring structures.

Here we report calculations on the $n \rightarrow \pi^*$ rotatory strength for a series of αβ-unsaturated γ-lactone structures. The chiroptical properties of dissymmetric αβ-unsaturated lactones have been studied experimentally by a number of workers,[3-8] but detailed calculations on these systems have not yet been reported. Spectra–structure relationships which have been proposed for this class of molecules have generally been based either on purely empirical correlations or on sector (or regional) rules which represent extensions or modifications of the

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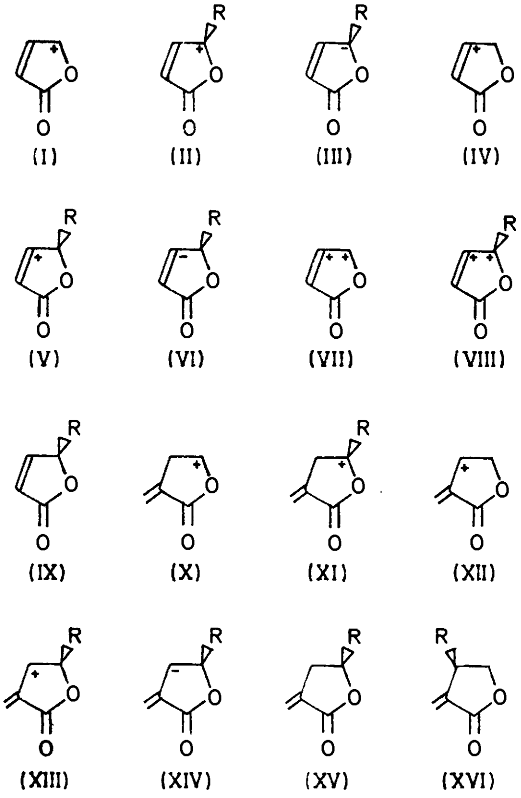
famous ' octant rule ' applied so successfully to dissymmetric ketone systems.[9,10] These sector rules have their theoretical basis in the static coupling (or ' one-electron ') and dynamical coupling variants of the independent systems model of molecular optical activity.[11] Direct calculation of electronic rotatory strengths from wave functions generated by semi-empirical molecular orbital methods offers an alternative to the independent systems model and is the procedure adopted in the present study. This approach has been used in a number of studies on molecular optical activity over the past ten years.[12,13]

Methods of Calculation.—The methods of calculation employed in the present study were identical to those used in the previously reported calculations on saturated lactone and dilactone systems.[1] SCF-MO calculations were carried out in the INDO approximation using ' standard ' parameters.[2] The MOs obtained from these calculations were renormalized to include overlap,[13a] and all electric and magnetic dipole transition integrals were calculated in a Slater orbital basis set. Excited states were constructed in the virtual orbital–configuration interaction approximation. Electric-dipole transition integrals were calculated using the dipole velocity formalism and all one-, two-, and three-centre terms were included in calculating both the electric and the magnetic-dipole transition matrix elements. Ground-state dipole moments were calculated according to the procedure outlined by Pople and his co-workers.[2]

Structures.—Sixteen different αβ-unsaturated γ-lactone structures were examined in the present study. In nine of these structures the olefinic double-bond is endocyclic and in the other seven structures the olefinic double-bond is exocyclic (α-methylene-γ-lactone structures). The sixteen different structures are depicted below.

Structures (I), (IV), (VII), (X), and (XII) are optically active by virtue of chiral distortions within the five-membered ring system. Structures (IX), (XV), and (XVI) gain optical activity through asymmetric substitution at ring carbon atoms. Optical activity in structures (II), (III), (V), (VI), (VIII), (XI), (XIII), and (XIV) arises from both asymmetric substitution and chiral ring distortions. Structure parameters (bond distances and bond angles) were adapted from those reported for various compounds containing the αβ-unsaturated γ-lactone moiety.[14] The C=O carbonyl bond distance was maintained at 1.208 Å in all structures, the C–O bond distance was set at 1.365 Å, and the C=C bond distance was maintained at 1.320 Å in the *endo*-structures and at 1.330 Å in the *exo*-structures. Displacement of C(γ) from the O=C–C plane in structures (I), (II), (III), (X), and (XI) was set at 0.40 Å. Displacement of C(β) from the O=C–O plane in structures (IV), (V), (VI), (XII), (XIII), and (XIV) was set equal to 0.37 Å. In structures (VII) and (VIII), the C(γ) and C(β) displacements were set equal to 0.39 and 0.37 Å, respectively.



R = Me

+ or − indicates displacement of ring atom above or below the plane defined by the O=C–O group.

In each of the eleven asymmetrically substituted structures the absolute configuration at the asymmetric

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[11] See, for example: E. G. Höhn and O. E. Weigang, jun., *J. Chem. Phys.*, 1968, **48**, 1127.

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[14] See, for example: (*a*) R. D. Gilaridi and I. Karle, *Acta Cryst.*, 1970, **B26**, 207; (*b*) I. Karle and J. Karle, *Acta Cryst.*, 1969, **B25**, 434; (*c*) F. Mo and B. K. Silvertsen, *Acta Cryst.*, 1971, **B27**, 115; (*d*) D. F. Koenig, C. C. Chu, B. Krebs, and R. Walter, *Acta Cryst.*, 1969, **B25**, 2111.

ring carbon atom is *R* (in the Cahn–Ingold–Prelog convention).

Calculations were performed on rotameric isomers generated by rotation about C-CH_3 bonds. However, the results from these calculations showed that the properties of interest in this study are not sensitive to this structural variable and we do not report separate results for these various rotameric isomers.

RESULTS

The lowest-energy singlet excited state of each structure examined in this study is best characterized according to our calculations as an $n\pi^*$ state. The '*n*' orbital is principally localized on the carbonyl oxygen atom and the π^* orbital in this state (or configuration) is somewhat delocalized over the entire C=C–C=O moiety, with slightly larger amplitudes on the olefinic carbon atoms. This π^* orbital has nodal planes bisecting the C=C double-bond and the C=O double-bond (it is antibonding ***within*** each of these two groups but bonding ***between*** the two groups). The lowest-energy $n\rightarrow\pi^*$ transition has significant intergroup charge-transfer character with net charge density being transferred from the carbonyl group to the olefin group.

In both the *exo*-ene and *endo*-ene structures the highest-occupied molecular orbital was calculated to be essentially a carbonyl oxygen '*n*'-type orbital. The second highest-occupied molecular orbital was calculated to be a π-type orbital which is bonding ***within*** both the olefin group and the carbonyl group (with slightly larger amplitudes on the carbonyl group atoms), and which is antibonding ***between*** the olefin and carbonyl groups (that is, it has a nodal plane bisecting the carbon–carbon bond between the two groups). This π-type orbital also includes significant contributions from the noncarbonyl ring oxygen atom.

The optical properties computed for the lowest-energy singlet–singlet transition ($n\rightarrow\pi^*$) in each structure are listed in the Table.

TABLE

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

Structure	ΔE/eV	f[a]	$[R]$[b]	$\lvert g\rvert$[c]
(I)	6.05	0.010 8	−13.25	0.011 6
(II)	6.07	0.009 7	−17.24	0.016 7
(III)	6.06	0.008 9	11.31	0.011 9
(IV)	6.26	0.004 4	−9.31	0.020 6
(V)	6.16	0.005 1	−14.62	0.026 9
(VI)	6.23	0.005 7	5.91	0.009 7
(VII)	6.44	0.004 6	−11.97	0.025 5
(VIII)	6.39	0.005 2	−14.12	0.025 4
(IX)	6.09	0.005 4	−2.40	0.004 2
(X)	6.03	0.002 2	−2.16	0.009 2
(XI)	6.01	0.002 8	−3.02	0.010 1
(XII)	6.08	0.003 4	−4.14	0.011 5
(XIII)	6.14	0.004 1	−4.43	0.010 2
(XIV)	6.10	0.003 9	3.64	0.008 8
(XV)	5.96	0.001 9	−1.01	0.005 0
(XVI)	5.83	0.002 6	−2.06	0.007 4

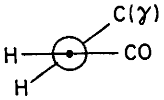
[a] Oscillator strength. [b] Reduced rotatory strength, $[R_{ij}] = (100/\beta D)\mathrm{Im}\langle\psi_i|\hat{u}|\psi_j\rangle.\langle\psi_j\hat{m}||\psi_i\rangle$, where β = Bohr magneton, D = Debye unit, $\hat{u}$ = electric dipole operator, and $\hat{m}$ = magnetic dipole operator. [c] Dissymmetry factor, $g = 4R_{ij}/D_{ij}$ where D_{ij} is the dipole strength of the transition $i\rightarrow j$.

DISCUSSION

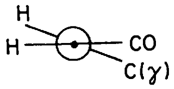
It is clear from the data presented in the Table that chiral distortions within the γ-lactone ring system produce substantially larger $n\rightarrow\pi^*$ rotatory strengths than does asymmetric substitution at ring carbon atoms. That is, ring conformational effects predominate over substituent vicinal effects. The sign of the vicinal contribution to $n\rightarrow\pi^*$ rotatory strength is the same in all the *endo*-ene structures in which C(γ) is asymmetrically substituted. Furthermore, examination of the data listed in the Table reveals that vicinal and ring conformational contributions to the $n\rightarrow\pi^*$ rotatory strengths are nearly additive. The signs of vicinal contributions to the $n\rightarrow\pi^*$ rotatory strength are also identical for all the *exo*-ene structures studied here. However, asymmetric substitution at the ring carbon atom adjacent to the α-methylene group in the *exo*-ene structures produces a larger vicinal effect than does asymmetric substitution at the ring carbon atom bound to the oxygen atom of the lactone ring [compare the data for structures (XV) and (XVI)].

In structures (I), (II), and (III), the olefinic double-bond is twisted so that the C=C moiety is no longer planar. However, in these structures the five atoms of the C=C–C(=O)–O group share a common plane. In structures (IV), (V), and (VI), the olefinic double bond is also twisted and, in addition, the C=C–C(carbonyl) group is non-coplanar with the O=C–O group. In structures (VII) and (VIII), there is only a very slight twist in the olefinic double-bond, but the C=C–C(carbonyl) and O=C–O groups are again non-coplanar. It is evident from the data given in the Table that the $n\rightarrow\pi^*$ rotatory strength is quite sensitive to the magnitude and sense (chirality) of twist about both the olefinic double-bond and about the carbon–carbon bond connecting the C=C and O=C–O groups in the *endo*-ene structures.

Chiral distortions within the olefin group are depicted and characterized in diagrams (a) and (b). In structures (I) and (II) the olefin group has intrinsic ***M*** chirality (left-handed helical twist) with a dihedral angle of ~16° [see diagram (a)]. In structure (III) the olefin group has intrinsic ***P*** chirality (right-handed helical twist) with a dihedral angle of *ca.* 16° [see diagram (a)]. In structures (VII) and (VIII) the olefinic group has intrinsic ***M*** chirality with a very small dihedral angle (*ca.* 1°).



(a) ***M*** Helix
(left-handed screw sense)

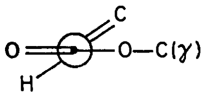


(b) ***P*** Helix
(right-handed screw sense)

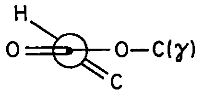
In structures (IV) and (V) the intrinsic chirality of the olefin group is ***P*** (dihedral angle *ca.* 15°), whereas in structure (VI) the twisted olefin group has ***M*** chirality with a dihedral angle of *ca.* 15°.

Chiral distortions about the C(α)–C(carbonyl) bond are depicted and characterized in diagrams (c) and (d). In structures (IV), (V), (VII), and (VIII) the intrinsic chirality associated with twisting about the C(α)–C(carbonyl) bond is ***M*** (dihedral angle *ca.* 18°). In structure (VI) this intrinsic chirality is ***P*** (dihedral angle *ca.* 18°).

Denoting intrinsic olefin chirality by ***P*′** (or ***M*′**) and chirality about the C(α)–C(carbonyl)bond by ***P*″** (or ***M*″**), we have then for the *endo*-ene structures: (I) (***M*′**, 0), (II) (***M*′**, 0), (III) (***P*′**, 0), (IV) (***P*′**, ***M*″**), (V) (***P*′**, ***M*″**), (VI) (***M*′**, ***P*″**), (VII) (***M*′**,***M*″**), and (VIII) (***M*′**, ***M*″**), where 0 denotes no chirality (achirality). A comparison of the calculated $n\rightarrow\pi^*$ rotatory strengths for structures (I) and (IV) (both unsubstituted) suggests that ***M*′** chirality makes a large negative contribution and ***M*″** chirality makes an even larger negative contribution. If we make the rather tenuous assumption that contributions from these two sources of chirality are strictly additive, then R(I) + R(IV) should yield the net contribution of ***M*″** chirality in structure (IV). Doing this (with due reservations), we obtain a value of −22.56 for the ***M*″** contribution. In structure (VII), the ***M*′** contribution to the rotatory should be very small since the associated dihedral angle is extremely small (*ca.* 1°). In this case, then, the ***M*″** contribution should dominate and again it is found to be negative (but somewhat less than −22.56).

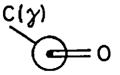


(c) ***M*** Helix
(left-handed screw sense)

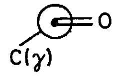


(d) ***P*** Helix
(right-handed screw sense)

Another possibly important source of chirality in structures (I), (II), (III), (VII), and (VIII) arises from non-planarity within the O=C–O–C(γ) fragment [see diagrams (e) and (f)]. In structures (I), (II), (VII), and (VIII) this fragment has ***M*** chirality (dihedral angle *ca.* 17°), whereas in structure (III) this fragment has ***P*** chirality (dihedral angle *ca.* 17°). This source of chirality, of course, does not exist for structures (IV), (V), and (VI).

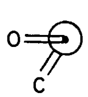


(e) ***M*** Helix

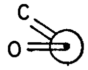


(f) ***P*** Helix

In the *exo*-ene structure (X), the methylene and O=C–O groups are coplanar and the principal source of chirality resides in the non-planarity of the O=C–O–C(γ) fragment. This type of chirality is depicted in diagrams (g) and (h). In structure (X) [and in structure (XI)] the chirality of this fragment is ***M*** (dihedral angle *ca.* 17°) and the calculated $n\rightarrow\pi^*$ rotatory strength is small and negative (−2.16). In the *exo*-ene structure (XII), the methylene and O=C–O groups are no longer planar. The dihedral angle defined by C=C–C/C–C=O is *ca.* 15° and the chirality about the C(α)–C(carbonyl) bond is ***M***. The reduced rotatory strength calculated for the $n \longrightarrow \pi^*$ transition of this structure (XII) is −4.14.



(g) ***M*** Helix



(h) ***P*** Helix

The approximations inherent in the theoretical model adopted for this study preclude our drawing quantitative conclusions regarding the computed results and specific spectra–structure relationships. We may, however, make the following qualitative statements: (1) asymmetric substitution at the C(γ) ring atom in the *endo*-ene αβ-unsaturated γ-lactone systems produces a negatively signed vicinal contribution to the $n\rightarrow\pi^*$ rotatory strength when the absolute configuration at C(γ) is *R*; (2) asymmetric substitution at either of the two saturated carbon ring atoms in the α-methylene-γ-lactone system produces a negatively signed vicinal contribution to $n\rightarrow\pi^*$ rotatory strength when the absolute configuration at the substituted site is *R*; (3) chiral distortions within the γ-lactone ring system produce significantly greater $n\rightarrow\pi^*$ optical activity than do substituent-induced vicinal effects; (4) vicinal and non-vicinal effects are nearly additive; (5) inherent chirality of an ***M*** screw sense within the olefin moiety of the *endo*-structures [see diagram (a)] produces a negative $n\rightarrow\pi^*$ rotatory strength contribution; (6) ***M*** chirality associated with dissymmetrically disposed C=C and O=C–O moieties [see diagram (c)] leads to a negative $n\rightarrow\pi^*$ rotatory strength contribution in both the *exo*(*cisoid*)- and *endo*(*transoid*)-ene structures; (7) ***M*** chirality within the C(γ)–O–C=O moiety of the *exo*-ene structures [see diagram (g)] examined in this study leads to a negative $n\rightarrow\pi^*$ rotatory strength.

Although the magnitudes of the $n\rightarrow\pi^*$ rotatory strengths calculated in this study are in good approximate agreement with available experimental data, the calculated transition energies are *ca.* 20% too high [experimentally, ΔE ($n\rightarrow\pi^*$) ≅ 4.80—5.10 eV].

This work was supported in part by a grant from the donors of the Petroleum Research Fund administered by the American Chemical Society and by the Camille and Henry Dreyfus Foundation (through a Teacher–Scholar Award to F. R.)

[6/128 *Received, 20th January,* 1976]