Chiroptical Properties of Lactones. Part I. Rotatory Strengths of Electronic Transitions in Substituted and Unsubstituted 1,4-Dioxan-2,5-diones (Dilactones)

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The chiroptical properties of dissymmetric conformational isomers and asymmetrically substituted derivatives of 1,4-dioxan-2,5-dione (I) are examined with a theoretical model in which the electronic wave functions are obtained from semi-empirical all-valence-shell molecular orbital calculations. The INDO molecular orbital model is used to perform SCFMO calculations on the ground states of four conformational isomers of (I), seven conformational isomers of the (*S*)-3-methyl derivative of (I), and five conformational isomers of the (*S*,*S*)-3,6-dimethyl derivative of (I). Excited state wave functions are constructed in the virtual orbital-configuration interaction approximation. The rotatory strengths, dipole strengths, oscillator strengths, and transition energies are calculated for the two lowest-lying singlet–singlet transitions ($n \longrightarrow \pi^*$) in each of the 16 structures. Additionally, ground state dipole moments, net atomic charges, and the first four ionization potentials (calculated according to Koopmans' theorem) are computed for each structure. The signs and magnitudes of the $n\pi^*$ rotatory strengths are found to be extremely sensitive to the conformation of the 1,4-dioxan ring as well as to methyl substitution at the α-carbon sites of the ring. Both ring dissymmetry and vicinal effects due to asymmetric ring substitution make substantial contributions to the optical activity of the $n \longrightarrow \pi^*$ transition in the monocyclic dilactone systems examined here.

RELATIONSHIPS between chiroptical observables and the stereochemical and electronic structural features of dissymmetric lactone and carboxylic acid derivatives have attracted considerable attention over the past ten years.[1-3] In this regard special attention has been given to developing 'sector rules' whereby the sign of the circular dichroism (c.d.) associated with the lowest energy spin-allowed electronic transition in these systems can be related to the spatial configuration of atoms or groups lying outside the chromophores. Theoretical interpretations of sector rules and other spectra–structure relationships commonly used in chiroptical spectroscopy are generally based on models in which (1) the spectroscopic (electronic) states of interest are localized on an identifiable chromophore and the nodal patterns of these states are well-defined; (2) interactions between the chromophore and extrachromophoric groups (perturbers) are electrostatic in nature; and (3) the signs and magnitudes of the electronic rotatory strengths induced in the chromophoric transitions by the extrachromophoric groups reflect the spatial configuration and the chemical nature of these groups. Use of such models (often referred to as 'independent systems' models) requires that the electronic structure and spectroscopic states of the interacting subsystems within the molecule be well characterized and that the dominant interaction mechanisms be identified and understood. These models suffer from a lack of good, or accurate, input data (*i.e.*, detailed electronic structure information on the ground and excited states of the interacting molecular fragments) and the difficulties inherent to calculations of intramolecular interaction energies. The independent systems models enjoy the great advantage, however, of providing a particularly clear conceptual representation of the spectroscopic processes and stereochemical features responsible for the observed optical activity. Furthermore, if a few calibration calculations are available for appropriate model systems, then these methods can be used to make qualitative predictions about a large number of similar systems with only minimal (and usually non-numerical) effort.

An alternative to the independent systems models for calculating molecular chiroptical properties is a *direct* calculational model in which electronic wave functions are calculated for the entire molecule and these molecular (rather than fragment or subsystem) wave functions are then used to calculate, directly, the rotatory strength parameters. This type of model is especially appropriate for molecules having 'extended' chromophoric units, cyclic systems in which ring strain may influence spectroscopic properties, and molecules not easily partitioned into weakly coupled fragments (weakly coupled with respect to their spectroscopic states). In most of the direct calculations of electronic rotatory strengths reported to date, semi-empirical MO models have been used to calculate the ground state molecular wave functions and excited states have been constructed from

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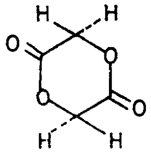
[1] See, for example, (*a*) H. Wolf, *Tetrahedron Letters*, 1965, 1075; (*b*) A. F. Beecham, *ibid.*, 1968, 2355; (*c*) H. Meguro, K. Tuzimura, and N. Takahashi, *ibid.*, p. 6305; (*d*) D. Urry, *Ann. Rev. Phys. Chem.*, 1968, **19**, 477; (*e*) F. I. Carroll, A. Sobti, and R. Meck, *Tetrahedron Letters*, 1971, 405; (*f*) A. F. Beecham, *ibid.*, 1968, 3591; (*g*) 1969, 4897; (*h*) O. Korver, *Tetrahedron*, 1970, **26**, 2391; (*i*) J. P. Jennings, W. Klyne, and P. M. Scopes, *J. Chem. Soc.*, 1965, 7211, 7229; (*j*) H. Wolf, *Tetrahedron Letters*, 1966, 5151; (*k*) M. Keller and G. Snatzke, *Tetrahedron*, 1973, **29**, 4013; (*l*) M. Legrand and R. Bucourt, *Bull. Soc. chim. France*, 1967, 2241; G. Snatzke, H. Ripperger, C. Horstmann, and K. Schreiber, *Tetrahedron*, 1966, **22**, 3103.

[2] C. Roniolo, V. Perciaccante, J. Falcetta, R. Rupp, and M. Goodman, *J. Org. Chem.*, 1970, **35**, 6.

[3] (*a*) P. Crabbe, 'An Introduction to the Chiroptical Methods in Chemistry,' Section II-11, Syntex Corp., Mexico City, 1971; (*b*) 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry,' ed. G. Snatzke, Heyden, London, 1967.

singly excited configurations involving use of virtual orbitals.[4,5]

In the present study we examine the chiroptical properties of a series of dissymmetric monocyclic dilactone structures which are either derivatives of or conformational isomers of 1,4-dioxan-2,5-dione (I). The ring system in (I) is expected to be flexible so that conformational isomerism is possible. The 3-methyl derivative of (I) possesses one asymmetric centre and can be prepared in an optically active form. The 3,6-dimethyl derivative possesses two asymmetric centres and may also be prepared in an optically active form.



(I)

We calculate the electronic states and chiroptical properties of the dilactone structures using an MO model in which the ground state is represented as an antisymmetrized product of SCF orbitals constructed in the INDO approximation, and excited-state wave functions are constructed from linear combinations of determinantal wave functions formed by the replacement of one occupied molecular orbital in the ground-state determinant with a virtual orbital. The object of this study is to provide a theoretical basis for relating the chiroptical observables of dissymmetric cyclic dilactones to electronic structural and stereochemical features in these systems. Of special interest is the relative influence of ring conformation *versus* asymmetric ring substitution (*via* ' vicinal ' effects) on the rotatory strengths of the lowest energy electronic transitions. The rotatory strengths of these transitions are quite commonly adopted as diagnostic indicators of stereochemical or conformational structure in lactones.

STRUCTURES

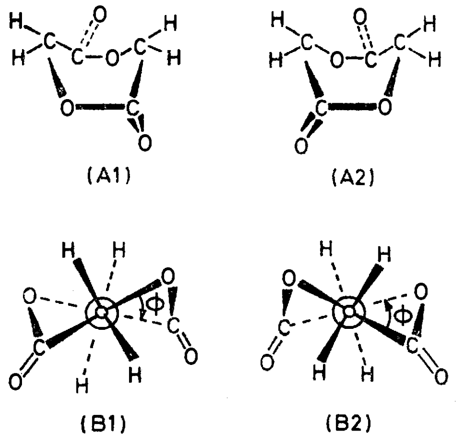
Sixteen structures were examined in the present study. Four are conformational isomers of (I), seven are conformational isomers of the 3-methyl derivative of (I), and five are conformational isomers of the 3,6-dimethyl derivative of (I). Four different conformational isomers of the 1,4-dioxan ring are represented among these structures. These ring conformational isomers are (a) planar; (b) regular boat; (c) skewed (or twist) boat with 4° twist angle; and, (d) skewed (or twist) boat with 8° twist angle. The sixteen structures are listed and labelled in Table 1. The nonplanar ring structures are depicted in the Figure and atomic positional co-ordinates for the ring atoms (plus the carbonyl oxygen atoms) of three of the ring structures are listed in Table 2. The methyl substituents were placed on the ring assuming a C–C bond distance of 1.54 and C–H 1.08 Å.

TABLE 1

Summary of 1,4-dioxan-2,5-dione structures studied [a, b]

(I)	Unsubstituted, planar conformation
(II)	3-Methyl substituted, planar conformation
(III)	3,6-Dimethyl substituted, planar conformation
(IV)	Unsubstituted, regular boat conformation (A1)
(V)	3-Methyl substituted, regular boat conformation (A1), methyl group axial
(VI)	3-Methyl substituted, regular boat conformation (A2), methyl group equatorial
(VII)	3,6-Dimethyl substituted, regular boat conformation (A1), methyl groups axial
(VIII)	3,6-Dimethyl substituted, regular boat conformation (A2), methyl groups equatorial
(IX)	Unsubstituted, skewed boat conformation [(B1), $\phi = 4^\circ$]
(X)	3-Methyl substituted, skewed boat conformation [(B1), $\phi = 4^\circ$]
(XI)	3-Methyl substituted, skewed boat conformation [(B2), $\phi = 4^\circ$]
(XII)	Unsubstituted, skewed boat conformation [(B1), $\phi = 8^\circ$]
(XIII)	3-Methyl substituted, skewed boat conformation [(B1), $\phi = 8^\circ$]
(XIV)	3-Methyl substituted, skewed boat conformation [(B2), $\phi = 8^\circ$]
(XV)	3,6-Dimethyl substituted, skewed boat conformation [(B1), $\phi = 4^\circ$]
(XVI)	3,6-Dimethyl substituted, skewed boat conformation [(B2), $\phi = 4^\circ$]

[a] The nonplanar ring structures (A1), (A2), B(1), and (B2) are depicted and ϕ defined in the Figure. [b] The configuration at each asymmetric site in the substituted structures is S.


(A1) (A2)
(B1) (B2)

Conformational isomers of 1,4-dioxan-2,5-dione. (A1) and (A2) are enantiometric forms of a regular boat structure. (B1) and (B2) are enantiomeric forms of a skewed (or twist) boat structure

The sixteen structures listed in Table 1 obviously do not completely span the conformational space accessible to 1,4-dioxan-2,5-dione and its 3-methyl and 3,6-dimethyl derivatives. The calculations involved in our theoretical model are lengthy so that a detailed map of the optical properties over the conformational space available to the

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[4] See, for example (*a*) V. Pao and D. P. Santry, *J. Amer. Chem. Soc.*, 1966, **88**, 4157; (*b*) M. Yaris, A. Moscowitz, and S. Berry, *J. Chem. Phys.*, 1968, **49**, 3150; (*c*) R. R. Gould and R. Hoffman, *J. Amer. Chem. Soc.*, 1970, **92**, 1813; (*d*) C. C. Levin and R. Hoffmann, *ibid.*, 1972, **94**, 3446; (*e*) J. M. Howell, *J. Chem. Phys.*, 1970, **53**, 4152; (*f*) S. Hagishita and K. Kuriyama, *Bull. Chem. Soc. Japan*, 1971, **44**, 617; (*g*) W. Hug and G. Wagniere, *Theor. Chim. Acta*, 1970, **18**, 57; (*h*) A. Imamura, T. Hirano, C. Nagata, and T. Tsurata, *Bull. Chem. Soc. Japan*, 1972, **45**, 396.

[5] (*a*) F. S. Richardson, D. D. Shillady, and J. E. Bloor, *J. Phys. Chem.*, 1971, **75**, 2466; (*b*) F. S. Richardson, R. Strickland, and D. D. Shillady, *J. Phys. Chem.*, 1973, **77**, 248; (*c*) J. Webb, R. Strickland, and F. S. Richardson, *Tetrahedron*, 1973, **29**, 2499; (*d*) J. Webb, R. Strickland, and F. S. Richardson, *J. Amer. Chem. Soc.*, 1973, **95**, 4775; (*e*) F. S. Richardson and W. Pitts, *Biopolymers*, 1974, **13**, 703.

model dilactone systems was not possible. Instead, structures (I)—(XVI) were chosen to represent the more important and prominent stereochemical features of these systems.

TABLE 2

Atomic co-ordinates for 1,4-dioxan-2,5-dione ring atoms[a] in regular boat (A1), skewed boat (B1), and planar conformations (Å)

		O	C_α	C'	O(carbonyl)
(A1)	X	−0.683	−1.373	−0.672	−1.336
	Y	−1.218	0	1.246	2.221
	Z	0	0.513	0	−0.382
[(B1) $\phi = 4°$]	X	−0.687	−1.431	−0.676	−1.349
	Y	−1.326	0	1.262	2.245
	Z	0.131	0	−0.139	−0.383
(Planar)	X	−0.685	−1.471	−0.675	−1.348
	Y	−1.301	0	1.272	2.260
	Z	0	0	0	0

[a] Each ring structure has C_2 symmetry about the z-axis so that the co-ordinates of only half of the atoms need be specified.

Structure (I) is nondissymmetric and optically inactive (C_{2h} symmetry). Structures (IV), (IX), and (XII) possess C_2 symmetry and are optically active by virtue of dissymmetry within the 1,4-dioxan ring system. Structure (II) has a planar ring but is optically active since it possesses one asymmetric carbon atom. Structure (III) has C_2 symmetry and is optically active by virtue of its possessing two asymmetric centres (of like configurational symmetry). Structures (V), (VI), (X), (XI), (XIII), and (XIV) are devoid of symmetry and have dissymmetric ring systems as well as a single asymmetric carbon atom each. Structures (VII), (VIII), (XV), and (XVI) each possess C_2 symmetry and can gain their optical activity from both dissymmetric ring systems as well as from asymmetric carbon atoms.

Structures (A1) and (A2) (Figure) are enantiomers as are (B1) and (B2) (for a given angle ϕ). The 1,4-dioxan ring has exact C_2 symmetry in each of the sixteen structures (I)—(XVI).

METHODS

SCFMO calculations were carried out on structures (I)—(XVI) in the INDO approximation using the 'standard' parameters of Pople and Beveridge.[6] The molecular orbitals obtained from the INDOMO calculations were renormalized ('deorthoganolized') by subjecting the eigenvector matrix, $\tilde{C}_\lambda$, obtained from the INDOMO output to the transformation (1) where χ denotes Slater orbitals, λ de-

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

notes INDO basis functions, and $\tilde{S}_\chi$ is the overlap matrix over Slater orbitals. The renormalized molecular orbitals, $\tilde{\varphi}$, are then expressed as linear combinations (2) of Slater orbitals. In this procedure the basis set $\tilde{\lambda}_\chi$ is considered to

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

be derived from the usual Slater one $\tilde{\chi}$ by means of the Löwdin transformation (3).

$$\tilde{\lambda} = \tilde{\chi}\tilde{S}^{-1/2}. \tag{3}$$

Excited state wave functions were constructed in the virtual orbital-configuration interaction (CI) approximation, and 25 singly excited configurational wave functions were employed in the CI calculations reported here. The optical properties calculated and reported are (a) reduced rotatory strength [equation (4) where β is the Bohr magneton, D is

$$[R_{ij}] = (100/\beta D)Im[\langle\psi_i|\hat{\boldsymbol{\mu}}|\psi_j\rangle\cdot\langle\psi_j|\hat{\boldsymbol{m}}|\psi_i\rangle] \tag{4}$$

the Debye unit, $\hat{\boldsymbol{\mu}}$ is the electric dipole operator, and $\hat{\boldsymbol{m}}$ is the magnetic dipole operator]; (b) dipole strength [equation

$$D_{ij} = |\langle\psi_i|\hat{\boldsymbol{\mu}}|\psi_j\rangle|^2 \tag{5}$$

(5)]; (c) oscillator strength [equation (6) where m = electron

$$f_{ij} = (4\pi m\nu_{ij}/3he^2)D_{ij} \tag{6}$$

mass and $\nu_{ij} = (E_j - E_i)/h$; and, (d) dissymmetry factor

$$g_{ij} = 4R_{ij}/D_{ij} \tag{7}$$

[equation (7)]. The electric dipole transition integrals

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.)	IP_3 (a.u.)	IP_4 (a.u.)
(I)	0	−5.2616	0.4450	0.5048	0.5100	0.5412
(II)	0.34	−6.3125	0.4369	0.4973	0.5024	0.5343
(III)	0.35	−7.4632	0.4296	0.4899	0.4962	0.5264
(IV)	3.26	−5.4609	0.4565	0.4913	0.5298	0.5364
(V)	3.50	−6.4879	0.4475	0.4835	0.5226	0.5319
(VI)	3.20	−6.4859	0.4493	0.4869	0.5243	0.5285
(VII)	3.73	−7.7060	0.4389	0.4759	0.5177	0.5263
(VIII)	3.16	−7.7235	0.4428	0.4830	0.5196	0.5202
(IX)	0.08	−5.2997	0.4575	0.5034	0.5257	0.5451
(X)	1.28	−6.0882	0.4374	0.4844	0.5116	0.5244
(XI)	1.37	−6.1319	0.4441	0.4962	0.5066	0.5145
(XII)	0.12	−5.1864	0.4666	0.5134	0.5337	0.5511
(XIII)	1.31	−5.9860	0.4574	0.4944	0.5128	0.5284
(XIV)	1.46	−6.0987	0.4641	0.5002	0.5184	0.5195
(XV)	1.19	−7.0608	0.4233	0.4617	0.4992	0.5172
(XVI)	0.95	−7.1011	0.4306	0.4917	0.4960	0.5011

TABLE 4

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

Structure	ΔE(eV)	f	D(Debye)	$[R]$	$\|g\|$
(I)	5.92	0.0131	0.583	0	0
	5.94	0	0	0	0
(II)	5.94	0.0062	0.277	−1.86	0.0025
	6.32	0.0186	0.777	−7.74	0.0037
(III)	6.13	0.0316	1.298	4.24	0.0012
	6.13	0.0194	0.794	−19.02	0.0089
(IV)	5.97	0.0085	0.376	−12.43	0.0123
	6.03	0.0293	1.280	106.06	0.0308
(V)	5.67	0.0124	0.579	23.72	0.0152
	6.78	0.0237	0.923	44.59	0.0179
(VI)	5.81	0.0097	0.442	−13.82	0.0116
	6.31	0.0262	1.096	−40.62	0.0138
(VII)	6.01	0.0190	0.809	30.14	0.0149
	6.51	0.0269	1.041	63.16	0.0243
(VIII)	5.89	0.0234	1.045	−45.28	0.0160
	5.91	0.0077	0.344	22.73	0.0245
(IX)	5.75	0.0020	0.089	17.50	0.0723
	5.89	0.0065	0.289	−13.52	0.0174
(X)	5.92	0.0035	0.154	13.68	0.0330
	6.14	0.0097	0.415	3.46	0.0031
(XI)	5.70	0.0039	0.183	−4.68	0.0095
	6.07	0.0116	0.493	−10.49	0.0079
(XII)	5.80	0.0026	0.101	29.42	0.1165
	5.96	0.0085	0.387	−19.41	0.0201
(XIII)	5.87	0.0056	0.202	20.07	0.0397
	6.18	0.0115	0.468	6.62	0.0057
(XIV)	5.76	0.0060	0.197	−9.41	0.0191
	6.14	0.0137	0.522	−14.60	0.0112
(XV)	5.71	0.0105	0.450	22.02	0.0185
	6.15	0.0198	0.810	36.68	0.0204
(XVI)	6.08	0.0061	0.244	0.53	0.0008
	6.14	0.0178	0.708	−4.53	0.0024

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[6] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

TABLE 5

Components of the electric and magnetic transition dipoles calculated for the two lowest energy transitions ($n \longrightarrow \pi$

Structure	Electric [a]			Magnetic [b]		
	x	y	z	x	y	z
(I)	0	0	−0.0645	0	0	0
	0	0	0	0.5915	−0.9737	0
(II)	−0.0005	0.0023	0.0451	0.4198	−0.6658	0.0037
	0.0489	0.0227	0.0598	−0.3432	0.6966	−0.1015
(III)	−0.0906	−0.0548	0	0.524	−0.939	0
	0	0	−0.0824	0	0	0.215
(IV)	0	0	−0.0529	0	0	0.2072
	0.0589	−0.0792	0	0.5118	−0.7879	0
(V)	0.0301	−0.0257	0.0482	0.3619	−0.5992	−0.1424
	0.0111	−0.0866	−0.0352	0.3164	−0.5304	0.1633
(VI)	−0.0233	0.0170	0.0478	−0.3398	0.5785	−0.1288
	0.0148	0.0916	−0.0230	−0.4030	0.5400	0.2776
(VII)	−0.0425	0.0358	0	−0.2518	0.5140	0
	−0.0261	0.0873	0	−0.3471	0.6048	0
(VIII)	0.0608	0.0624	0	−0.237	0.827	0
	0	0	−0.0502	0	0	−0.387
(IX)	−0.0063	−0.0233	0	0.5452	−0.7796	0
	0	0	−0.0450	0	0	0.2720
(X)	0.0198	−0.0051	−0.0267	0.4383	−0.7141	0.0222
	0.0131	0.0404	−0.0383	−0.2442	0.3440	0.1996
(XI)	0.0101	0.0101	−0.0322	−0.4231	0.4632	0.1898
	0.0029	0.0017	−0.0628	0.3354	−0.6109	0.1485
(XII)	−0.0072	−0.0462	0	0.5264	−0.8640	0
	0	0	−0.0861	0	0	0.2928
(XIII)	0.0202	−0.0009	−0.0387	0.5171	−0.8144	0.0281
	0.0101	0.0506	−0.0298	−0.2661	0.3616	0.2006
(XIV)	0.0206	0.0111	−0.0422	−0.47211	0.6633	0.1891
	0.0031	0.0019	−0.0831	0.3752	−0.6507	0.1272
(XV)	−0.0289	0.0282	0	−0.4021	0.2838	0
	−0.0068	0.0349	0	−0.5759	0.8653	0
(XVI)	−0.0404	−0.0243	0	−0.5506	0.8936	0
	0	0	0.0806	0	0	−0.0538

[a] Dipole velocity integrals, $\langle\psi_0|\partial/\partial_q|\psi_n\rangle$, expressed in atomic units. $q = x, y$, or z. [b] $(e/2mc)\ \langle\psi_0|\hat{L}_q|\psi_n\rangle$ in Bohr magneton units. $\hat{L}_q = \hat{L}_x, \hat{L}_y$, or $\hat{L}_z$.

TABLE 6

Net charges computed for atoms or groups of atoms (in a.u.)

Atom or group	Unsubstituted				Disubstituted				
	(I)	(IV)	(IX)	(XII)	(III)	(VII)	(VIII)	(XV)	(XVI)
O	−0.29	−0.27	−0.29	−0.29	−0.30	−0.29	−0.29	−0.30	−0.32
C_α	0.11	0.13	0.10	0.11	0.13	0.13	0.14	0.19	0.20
C′	0.47	0.45	0.45	0.45	0.47	0.45	0.44	0.43	0.44
O (carbonyl)	−0.34	−0.33	−0.33	−0.33	−0.35	−0.34	−0.34	−0.33	−0.34
CH_3 [a]					0.04	0.04	0.05	0.03	0.03

[a] Methyl group attached to ring at C_α.

were calculated from the dipole velocity formalism and equation (8) where E_i and E_j were taken as computed state energies. All transition integrals were calculated including both one- and two-centre terms.

$$\langle\psi_i|\hat{\mu}|\psi_j\rangle = (eh^2/m)\langle\psi_i|\hat{\nabla}|\psi_j\rangle/(E_j - E_i) \qquad (8)$$

RESULTS

The ground state dipole moments, binding energies, and first four ionization potentials (vertical ionization potentials calculated according to Koopman's theorem [7]) computed for structures (I)—(XVI) are listed in Table 3. The first two singlet excited states of each structure are calculated to be predominantly of the $n\pi^*$ type localized on the O=C–O group of the dilactone systems. The optical properties calculated for transitions to these states are given in Table 4. In Table 5 are displayed the Cartesian components of the electric and magnetic transition dipole integrals associated with the two lowest energy singlet–singlet transitions.

The highest occupied molecular orbital calculated for each structure can be described best as an antisymmetric

TABLE 7

Sums of computed dipole strengths and rotatory strengths for the $n \longrightarrow \pi^*$ transitions

Structure	D(Debye)	$[R]$
(I)	0.583	0
(II)	1.054	−9.60
(III)	2.092	−14.78
(IV)	1.656	93.63
(V)	1.502	68.31
(VI)	1.538	−54.44
(VII)	1.850	93.30
(VIII)	1.389	−22.55
(IX)	0.378	3.98
(X)	0.569	17.14
(XI)	0.676	−15.17
(XII)	0.488	10.01
(XIII)	0.670	26.69
(XIV)	0.719	−24.01
(XV)	1.260	58.70
(XVI)	0.952	−4.00

[7] T. Koopmans, *Physics*, 1934, **1**, 104.

combination of carbonyl oxygen n orbitals. In the planar structures the second highest energy SCF orbital was calculated to be a symmetric combination of carbonyl oxygen n orbitals. For the nonplanar ring structures, the second highest energy SCF orbital was calculated to be a mixture of n carbonyl and π° O=C–O orbitals, where π° denotes a π-type orbital with maximum amplitude on the oxygen atoms of the O=C–O groups and nodes at the carbonyl carbons of the dilactone systems.

The net charges calculated for atoms or groups of atoms in the unsubstituted [(I), (IV), (IX), (XII)] and disubstituted [(III), (VII), (VIII), (XV), (XVI)] structures are listed in Table 6. Note that each of these structures has at least C_2 symmetry (about the z axis) so that only half the atoms (or methyl groups) of each structure are listed in Table 6.

Sums of the dipole strengths and rotatory strengths computed for the two lowest energy singlet–singlet transitions ($n \longrightarrow \pi^*$) in each structure are presented in Table 7.

DISCUSSION

According to the results listed in Table 4 the lowest lying $n \longrightarrow \pi^*$ transition of the dilactone structures (I)—(XVI) should occur in the 205—220 nm region. This result is in accord with the experimental finding that the isotropic absorption spectrum of (*S*,*S*)-3,6-dimethyl-1,4-dioxan-2,5-dione shows a maximum at *ca.* 207 nm (ε 228.8) in methanol.[8] The c.d. spectrum of (*S*,*S*)-3,6-dimethyl-1,4-dioxan-2,5-dione exhibits a negative maximum ([θ] *ca.* −19 000 deg. cm^2 dmol^{-1}) at 221 nm in trimethyl phosphate solution and a negative maximum ([θ] *ca.* −20 000) at *ca.* 216 nm in hexafluoropropan-2-ol solution.[2] Our calculations indicate that the *two* lowest lying singlet–singlet transitions (both $n \longrightarrow \pi^*$) of the dilactone chromophore will lie in the region, 195—220 nm.

The sensitivity of the $n \longrightarrow \pi^*$ rotatory strengths and dipole strengths to both ring conformation and ring substitution is readily apparent from the results presented in Tables 4 and 7. Structures (II) and (III) derive their chirality entirely from asymmetric substitution on the dilactone ring. Structures (IV), (IX), and (XII) do not include any asymmetric atomic centres, but are chiral by virtue of dissymmetric distortions within the dilactone ring. Using the calculated rotatory strengths for structures (I), (IV), (IX), and (XII) as measures of the contributions of ring chirality to $n \longrightarrow \pi^*$ optical activity, we can separate out substituent or 'vicinal' contributions to the $n\pi^*$ rotatory strengths of structures (II), (III), (V)—(VIII), (X), (XI), and (XIII)—(XVI). These 'vicinal' contributions are given in Table 8.

Structures (III), (VII), (VIII), (XV), and (XVI) are conformational isomers of (*S*,*S*)-3,6-dimethyl-1,4-dioxan-2,5-dione. Based on our calculations of rotatory strengths the single negative c.d. band observed[2] for this compound at $\lambda > 200$ nm can be accounted for only if the planar conformation (III), the regular boat conformation (A2), (VIII), and/or the skewed boat conformation (B2), (XVI) are dominant in solution. These structures [(III), (VIII), and (XVI)] yield a net negative $n\pi^*$ rotatory strength in the 200—220 nm region, whereas our calculations predict positive $n\pi^*$ rotatory strengths for structures (VII) and (XV). Structure (VIII) is predicted to be the most stable of the five 3,6-dimethyl substituted structures studied (see computed binding energies in Table 3).

TABLE 8

'Vicinal' contributions

	Transition ($n \longrightarrow \pi^*$)		
	1	2	1 + 2
3-Methyl substituted			
(II) (Planar)	−1.86	−7.74	−9.60
(V) [Regular boat (A1)]	36.15	−61.47	−25.32
(VI) [Regular boat (A2)]	−26.65	54.40	28.15
(X) [Skewed boat (B1), ϕ 4°]	−3.82	16.98	13.16
(XI) [Skewed boat (B2), ϕ 4°]	−22.18	3.03	−19.15
(XIII) [Skewed boat (B1), ϕ 8°]	−9.35	26.04	16.69
(XIV) [Skewed boat (B2), ϕ 8°]	20.01	−34.01	−14.00
3,6-Dimethyl substituted			
(III) (Planar)	4.24	−19.02	−14.78
(VII) [Regular boat (A1)]	42.57	−42.90	−0.33
(VIII) [Regular boat (A2)]	−57.71	128.79	71.08
(XV) [Skewed boat (B1), ϕ 4°]	4.52	50.20	54.72
(XVI) [Skewed boat (B2), ϕ 4°]	18.03	−18.05	−0.02

The only other monocyclic dilactone compound whose c.d. spectrum has been reported is (*R*,*R*)-3,6-diphenyl-1,4-dioxan-2,5-dione. The c.d. spectrum of this compound in hexafluoropropan-2-ol solution is nearly a mirror-image (equal in intensity, opposite in sign) of that of the 3,6-dimethyl substituted compound in the 200—240 nm region. The 3,6-diphenyl compound exhibits additional c.d. in the region of the L_b transitions of the phenyl groups (240—275 nm).

The calculations performed in this study reveal the sensitivity of the electronic structure and spectroscopic properties of 1,4-dioxan-2,5-dione (I) to both ring substitution and ring conformation. The rotatory strengths of the $n \longrightarrow \pi^*$ electronic transitions are especially sensitive to ring conformation and asymmetric ring substitution. Our results indicate that the signs and magnitudes of the $n\pi^*$ rotatory strengths reflect both 'vicinal effects' due to asymmetric ring substitution and inherent dissymmetry originating with chiral distortions of the dioxan ring. It is clear that spectra–structure relationship for the cyclic dilactone systems studied here must take into account both ring conformational dissymmetry and configurational dissymmetry at substituent sites.

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