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Chiroptical Properties of Cyclic α-Diketones*

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The chiroptical properties of dissymmetric cyclopentanedione, 3-methylcyclopentane-1,2-dione, and glyoxal structures are examined on a theoretical model in which the electronic wave functions are obtained from semiempirical all-valence-shell molecular orbital calculations. Excited state wave functions are constructed in the virtual orbital-configuration interaction approximation. The rotatory strengths, dipole strengths, oscillator strengths, and dissymmetry factors of the lower energy singlet-singlet transitions in eleven cyclopentanedione and ten glyoxal structures are calculated and reported. The signs and relative magnitudes of the rotatory strengths associated with the two lowest energy singlet transitions are found to be extraordinarily sensitive to ring substituents and ring conformational parameters as well as to inherent chirality within the α-dicarbonyl moiety of the cyclopentanedione structures. Vicinal effects play a significant role in determining the signs and magnitudes of the electronic rotatory strengths. For a given configurational isomer of an inherently dissymmetric α-dicarbonyl group (i.e., ***P*** or ***M***), the signs of the electronic rotatory strength of the lowest energy transition in glyoxal and in cyclopentanedione are opposite. This result suggests that cisoid glyoxal structures may not be useful models for the chiroptical properties of cyclic α-diketone systems with cisoid dicarbonyl moieties.

Key words: Chiroptical properties – Cyclic α-diketones

1. Introduction

Relationships between the electronic structural details, the stereochemical features, and the chiroptical observables of dissymmetric α-diketone systems have been examined in a number of theoretical and experimental studies over the past five years. The primary focus of the theoretical studies has been on the contribution of inherent chirality within the α-dicarbonyl moiety to the rotatory strengths of the lower energy singlet-singlet transitions. Hug and Wagnière [1] chose a skewed glyoxal molecule as a model for calculating the optical rotatory properties of α-diketone systems as a function of the OCC′/CC′O dihedral twist angle (henceforth referred to as angle ϕ). In their very thorough study of this model system, they calculated the ground state electronic wave functions of the glyoxal molecule on a valence-shell-only molecular orbital model and constructed excited electronic states in the virtual orbital approximation. Both the extended Hückel model [2] and the CNDO model [3] were used in the molecular orbital calculations, and the spectroscopic calculations based on CNDO wave functions

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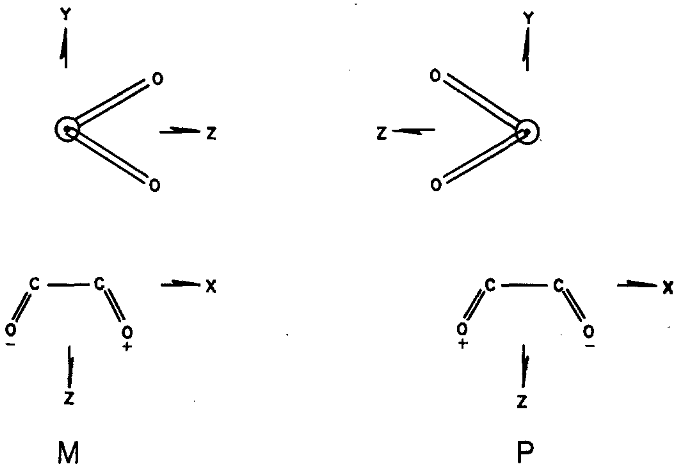
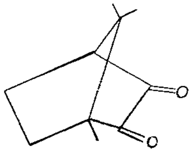


Fig. 1. Configurational isomers of the cisoid α-dicarbonyl group. ϕ is the dihedral twist angle. The XZ-plane bisects the angle ϕ

were carried out both with and without configuration interaction calculations of the excited states. Furthermore, Hug and Wagnière examined the sensitivity of the computed rotatory strengths to the inclusion or neglect of two-center (or "interatomic") terms in their calculations of electric and magnetic transition dipoles.

Although the results calculated by Hug and Wagnière displayed a disconcerting sensitivity to the parameters of the computational models used, the qualitative and semi-quantitative features of the calculations did allow certain conclusions to be drawn concerning the nature of the low lying spectroscopic states and the relationship between ϕ (α-dicarbonyl twist angle) and the electronic rotatory strengths. The most prominent conclusions were: (1) α-diketones have only two singlet-singlet transitions between 500 nm and 250 nm, both of which are essentially $n \rightarrow \pi^*$ in character; (2) the lowest lying singlet state in cisoid structures of ***P*** chirality (see Fig. 1) is of B symmetry with a positive rotatory strength, and the second lowest lying singlet state in these structures is of A symmetry with a negative rotatory strength; (3) the lowest lying singlet state in transoid structures of ***P*** chirality is of A symmetry with a negative rotatory strength, and the second lowest lying singlet state in these structures is of B symmetry with a positive rotatory strength. Furthermore, the relative magnitudes of the rotatory strengths of the first two transitions and the energy separations between them were found to be quite sensitive to $|\phi|$. Based on these conclusions and findings drawn from the skewed glyoxal model, Hug and Wagnière assigned "most likely" conformations to a number of cyclic α-diketone molecules [1b]. A challenge to several of these assignments was subsequently posed by Burgstahler and Naik [4]. They suggested that for a number of α-diketones considered by Hug and Wagnière the major contribution to the observed chiroptical properties of the lowest energy transition is attributable to vicinal effects from substituent groups beyond the α-dicarbonyl chromophore, rather than to inherent chirality of the dicarbonyl group. Furthermore, they asserted that the conformations predicted by Hug and Wagnière for several systems are improbable on steric grounds, assuming the validity and reliability of Dreiding models for determining intramolecular steric effects. The major point made by Burgstahler and Naik is that the decisive factor in determining the sign and magnitude of the lowest energy circular dichroism band of α-diketone systems may *not* always be inherent chirality of the α-dicarbonyl moiety. Substituent groups adjacent to the dicarbonyl group may exert a direct (vicinal) influence on the optical rotatory properties as well as an indirect influence (as, for example, by biasing the screw sense of the dicarbonyl group through steric interactions).

Charney and Tsai [5] carried out an extraordinarily thorough spectroscopic study of the cisoid α-diketone, camphorquinone. They measured the unpolarized absorption and emission spectra of this compound in solution at room temperature, in solution (solid glass) at liquid nitrogen temperature, and in pure solid form at liquid helium temperature. Additionally, they reported the infrared and Raman spectra of several isotopically substituted derivatives of camphorquinone, and measured the CD spectrum of the isomer, (*I*′), down to 180 nm.



(I′), d-camphorquinone

In discussing their results, Charney and Tsai adopted a qualitative molecular orbital model for describing the electronic states of the α-dicarbonyl chromophore, and assumed that the observed chiroptical properties could be attributed entirely to inherent chirality within this group. They postulated that the two lowest energy $n \to \pi^*$ transitions are nearly degenerate (with an energy separation of $\sim 1500\ \mathrm{cm}^{-1}$), and that the CD band observed in the 480 nm region originates with a ^1G (ground state)$\to {}^1A(n\pi^*)$ transition, while the absorption band in this region arises from a $^1G \to {}^1B(n\pi^*)$ transition. They further predicted that the strong CD associated with the $^1G \to {}^1A(n\pi^*)$ transition should be negative in sign for a dicarbonyl group of ***P*** chirality and that the weak CD associated with the $^1G \to {}^1B(n\pi^*)$ transition should be positive for the same structure. The $^1B(n\pi^*)$ state was postulated to lie below the ^1A state in energy (by $\sim 1500\ \mathrm{cm}^{-1}$). The 480 nm CD band in *d*-camphorquinone is negative in sign, so the dicarbonyl group was assumed to be twisted with ***P*** chirality. The positive CD band observed at ~ 290 nm in *d*-camphorquinone was assigned to another $n \to \pi^*$ transition of B symmetry.

If the absorption and CD band assignments proposed by Charney and Tsai for the 480 nm region are correct, then the fluorescence of (*I*′) can be assigned to the $^1G \leftarrow {}^1B(n\pi^*)$ transition. Furthermore, if the α-dicarbonyl moiety remains twisted in the $^1B(n\pi^*)$ excited state with ***P*** chirality, then the circularly polarized fluorescence spectrum of (*I*′) should exhibit a weak, positive band in the 480–560 nm spectral region according to the Charney and Tsai model. Luk and Richardson [7] measured the circularly polarized fluorescence of (I') in ethanol and in cyclohexane and found a *negative* band in the 480–560 nm region which, in shape, is a near mirror-image of the 480 nm CD band. The dissymmetry factors for the fluorescence spectra were, however, about an order of magnitude smaller than those for the CD/absorption spectra. That is, g(abs.)$\cong$10 g (lum) across the absorption and fluorescence bands, respectively, where

$$g(\mathrm{abs}) = (\varepsilon_L - \varepsilon_R)/(1/2)\,(\varepsilon_L + \varepsilon_R) = \Delta\varepsilon/\varepsilon$$

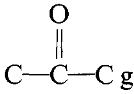
$$g(\mathrm{lum}) = (I_L - I_R)/(1/2)\,(I_L + I_R) = \Delta I/I\,.$$

ε_L and ε_R are the extinction coefficients for left- and right-circularly polarized light in the absorption experiments, and I_L and I_R are the intensities of the left- and right-circularly polarized components of the emitted light in the fluorescence experiments.

The circularly polarized fluorescence results lead to the following tentative conclusions regarding the nature and identity of the lower singlet excited states of (I'): (1) the fluorescent state and the excited singlet state responsible for CD and absorption in the 480 nm region are identical; (2) molecular dimensions and stereochemical variables other than the dicarbonyl twist angle ϕ are similar in the fluorescent and ground states (as indicated by the near mirror-image relationships observed in the circularly polarized fluorescence/CD and total luminescence/absorption spectra); (3) the chirality of the dicarbonyl moiety in the fluorescent state is the same as in the ground state; and, (4) the dihedral twist angle ϕ is smaller in the fluorescent state than in the ground state (as evidenced by the reduced dissymmetry factor in emission). These conclusions must remain tentative, of course, since the possible dominance of vicinal effects over inherent dicarbonyl chirality was ignored and there exists the possibility that the inherent chirality of the dicarbonyl moiety could change upon excitation (that is, the twist angle could have a different sign in the ground and excited states). In any case, it seems unlikely that the Charney and Tsai model for the lower excited states of camphorquinone can be supported by the results from these circularly polarized fluorescence experiments. Additionally, the small energy separation between the two dicarbonyl "non-bonding" or "n" molecular orbitals as proposed by Charney and Tsai would appear to be at variance with recent theoretical calculations [1, 7, 10, 11] and photoelectron spectral data [9, 10] on α-dicarbonyl systems.

There can be little question that the quantitative and semi-quantitative theoretical work of Hug and Wagnière [1] has been enormously useful in providing a framework within which the chiroptical properties of α-diketones can be considered. Their predictions concerning structure-spectra relationships have provided a valuable stimulus to further experimental and theoretical work in this area. The qualitative model set forth by Charney and Tsai also has appeal owing to its simplicity, its straightforward use of symmetry-based selection rules, and its apparent success in explaining many (but not all) of the spectroscopic properties of the camphorquinone system.

The study we report here grew out of our experimental work on the circularly polarized luminescence of camphorquinone and it was designed to extend the theoretical model and calculations of Hug and Wagnière on the chiroptical properties of α-diketones. Several aspects of the Hug and Wagnière model were of concern to us. Our first concern was whether the glyoxal molecule provides an adequate physical model for representing the electronic properties of the α-dicarbonyl chromophore in cyclic α-diketones, many of which have highly strained ring systems. Our second concern was the question of whether inherent dicarbonyl chirality or dissymmetric vicinal effects play the decisive role in determining the chiroptical observables in typical cyclic diketones with cisoid dicarbonyl groups. In our study, we performed calculations on eleven dissymmetric cyclopentanedione or substituted cyclopentanedione structures in an attempt to clarify these points.

We also performed calculations on the rotatory strengths of the lowest energy transition for a number of glyoxal molecules in which the carbonyl groups were pyramidally distorted and ϕ was varied. The geometries of the emitting states in dicarbonyl systems are not known, but it is possible that the two  $\mathrm{C{-}\overset{O}{\overset{\|}{C}}{-}C}$ groups in these states are individually nonplanar. A possible nonplanar structure is the pyramidal structure assumed by formaldehyde [11] in the $n\pi^*$ excited state and by *trans*-β-hydrindanone [12] in the $n\pi^*$ excited state. In circularly polarized fluorescence experiments, the sign and intensity of the observed spectrum depends upon the geometry of the emitting state, rather than the geometry of the ground state.

The theoretical model we adopt for calculating the molecular electronic states rests on the INDO semiempirical molecular orbital method [3]. Excited states are constructed in the virtual orbital-configuration interaction approximation and all two-center terms are included in calculating the electric and magnetic transition dipoles. The transition integrals are not calculated directly from the molecular orbitals obtained from the INDO-MO calculation. The INDO molecular orbitals are first "renormalized" or "deorthogonalized" to include two-center overlaps [13], and these renormalized functions are then used in calculating the electric and magnetic dipole transition integrals. Our computational model differs in just two ways from the one employed by Hug and Wagnière [1b]. We use the INDO-MO model rather than the CNDO-MO model, and we renormalize or deorthogonalize the wave functions obtained from INDO-MO calculations before computing transition integrals. Hug and Wagnière used the CNDO-MO wave functions in their calculations without renormalization.

2. Methods of Calculation

The methods of calculation employed in the present study are similar to those reported previously [13–16]. The SCF-MO calculations on molecular ground states are carried out in the INDO approximation using "standard" parameters [4]. The eigenvector matrix, $\tilde{C}_\lambda$, obtained from the INDO calculation is subjected to the transformation,

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

in which $\tilde{S}_\chi$ is the overlap matrix over Slater orbitals, χ. The INDO molecular orbitals, φ, are then expressed as

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

where the functions λ comprise the orthogonal INDO basis set. In this procedure the basis set $\{\lambda\}$ is conceived to be derived from the usual Slater one $\{\chi\}$ by means of the Löwdin transformation [17],

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

This "renormalization" or "deorthogonalization" of the molecular orbitals obtained from the INDO calculation overcomes the conflict between inclusion of two-center integrals in the calculation of magnetic dipole and electric dipole transition moments and the neglect of two-center overlap integrals in the INDO approximation.

Excited states are constructed in the virtual orbital-configuration interaction (CI) approximation, and 20 singly-excited configurational wave functions were employed in the CI calculations carried out in the study reported here. The optical properties calculated and reported are: (a) reduced rotatory strength,

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

where β is the Bohr magneton, D is the Debye unit, $\hat{\boldsymbol{\mu}}$ is the electric dipole operator, and $\hat{\boldsymbol{m}}$ is the magnetic dipole operator; (b) dipole strength,

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

(c) oscillator strength,

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

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

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

The electric dipole transition integrals are calculated in the dipole velocity formalism. Ground state electric dipole moments are calculated according to the procedure outlined by Pople and coworkers [3].

3. Structures

Eleven cyclopentanedione .structures were examined in this study. Five of these Structures, (I)–(V), are conformationel isomers of the unsubstituted cyclopentanedione molecule and six are conformational isomers of 3-methylcyclopentane-1,2-dione. Structures (I)–(V) are optically active by virtue of inherent dissymmetry within the dicarbonyl and carbocyclic ring moieties of unsubstituted cyclopentanedione. Structures (VI)–(IX) are isomers of 3-methylcyclopentane-1,2-dione in which the dicarbonyl group and the ring are dissymmetric. In Structures (X) and (XI) of 3-methylcyclopentane-1,2-dione, the dicarbonyl group and the ring atoms are in a conformation having C_s symmetry. The optical activity of these structures arises solely from the presence of an asymmetric carbon atom in the ring.

An atomic numbering system and the basic conformations adopted by the ring in Structures (I)–(XI) are displayed in Fig. 2. With reference to Figs. 1 and 2,

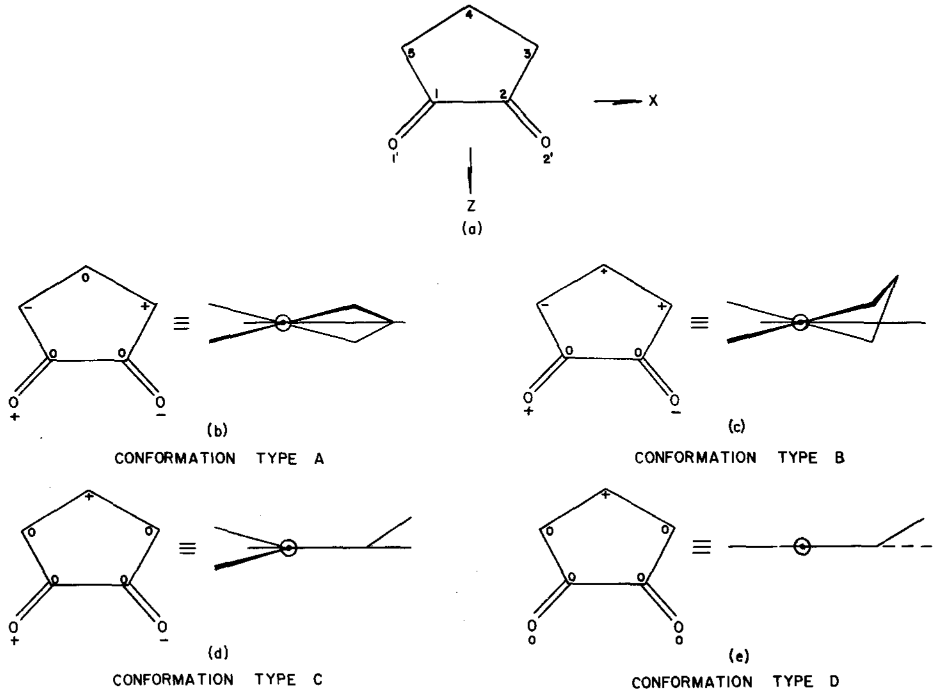


Fig. 2a–e. Basic cyclopentanedione structures. a Coordinate system and atomic numbering system. b Conformation type A. c Conformation type B. d Conformation type C. e Conformation type D

the eleven cyclopentanedione structures examined in this study may be described as follows:

Cyclopentanedione

Structure (I): conformation type A, $\phi = 5°$.
Structure (II): conformation type A, $\phi = 15°$.
Structure (III): conformation type B, $\phi = 5°$.
Structure (IV): conformation type B, $\phi = 10°$.
Structure (V): conformation type C, $\phi = 10°$.

3-*Methylcyclopentane*-1,2-*dione*

Structure (VI): conformation type A, $\phi = 15°$, methyl substituent axial.
Structure (VII): conformation type A, $\phi = 15°$, methyl substituent equatorial.
Structure (VIII): conformation type B, $\phi = 10°$, methyl substituent equatorial.
Structure (IX): conformation type B, $\phi = 10°$, methyl substituent axial.
Structure (X): conformation type D, $\phi = 0°$, methyl substituent equatorial.
Structure (XI): conformation type D, $\phi = 0°$, methyl substituent axial.

Certain bond angles and bond distances were held fixed for all eleven Structures, (I)–(XI). These are: $C(1)\text{–}O(1') = C(2)\text{–}O(2') = 1.22$ Å, $C(1)\text{–}C(2) = 1.53$ Å, $C(1)\text{–}C(5) = C(2)\text{–}C(3) = 1.53$ Å, $\sphericalangle O(1')\ C(1)\ C(2) = \sphericalangle C(1)\ C(2)\ O(2') = 123°$, $\sphericalangle C(5)\ C(1)\ C(2) = \sphericalangle C(1)\ C(2)\ C(3) = 110°$, all C–H bond distances = 1.1 Å, $C(3)\text{–}CH_3 = 1.54$ Å, and all $\sphericalangle HCH$ bond angles = 109°. The remaining bond

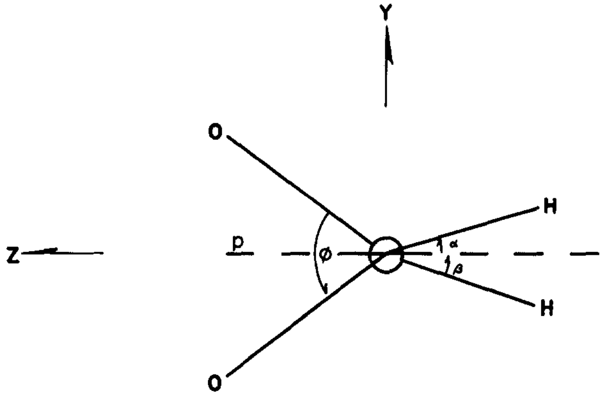


Fig. 3. Glyoxal distortion parameters. Both α and β are measured from the XZ-plane (which bisects the angle ϕ)

angles and bond distances were adjusted to achieve the conformations shown in Fig. 2. For all structures the angles $\sphericalangle C(1)\,C(5)\,C(4)$, $\sphericalangle C(5)\,C(4)\,C(3)$, and $\sphericalangle C(4)\,C(3)\,C(2)$ are within the range 96°–109°, and the C–C bond distances in this segment of the ring are between 1.50 and 1.55 Å. The ring atom, C(4) is 0.48 Å out of the plane of the remaining four ring atoms in conformational types C and D (see Fig. 2). Note that conformational type B (Fig. 2) is obtained from conformational type D by rotating O(1′) C(1) C(5) and O(2′) C(2) C(3) in opposite senses about an axis defined by C(1)–C(2). Conformational type A has exact C_2 symmetry, conformational type D has C_s symmetry, and conformational types B and C are devoid of any symmetry.

The optical activity of chiral systems is extraordinarily sensitive to conformational and stereochemical features. The primary purpose of the study reported here was to examine the dependence of electronic rotatory strengths upon the more prominent stereochemical features of dissymmetric molecules containing the cyclopentanedione moiety. The calculations involved in our theoretical model are lengthy so that a detailed map of optical properties over the conformational space of the model cyclopentanedione systems was not possible. Instead, Structures (I)–(XI) were chosen to represent the more important and prominent stereochemical features of these systems.

In our calculations on glyoxal conformational isomers, we held the following structure parameters fixed:[1] C–C = 1.52 Å, C=O = 1.30 Å, C–H = 1.10 Å, $\sphericalangle$CCO = 121.1°, and $\sphericalangle$CCH = 112.2°. We performed calculations on ten different glyoxal structures. The structural variables, ϕ, α, and β, used to generate these ten isomers are defined in Fig. 3. In *cis*-planar glyoxal, $\phi=\alpha=\beta=0$, and all four atoms lie in the plane, p. In the ground electronic state of glyoxal, it is presumed that cisoid structures are defined by $90° > |\phi| > 0°$, $\alpha=\beta$, and $\alpha+\beta=\phi$.

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[1] Note that we choose a C=O bond distance, 1.30 Å, which is somewhat larger than the experimentally determined C=O bond distance in the ground electronic state of glyoxal (1.207 Å) (Ref. [18]). For these calculations we are interested in the geometry of glyoxal in the lowest $^1n\pi^*$ excited state. It is to be expected that the C=O bond lengths in this excited state will be longer than those characteristic of the ground state since the π^* orbital is strongly antibonding with respect to the carbon and oxygen atoms.

That is, each $H\overset{\overset{O}{\|}}{C}C$ moiety maintains its planarity, but the two planes defined by these two moieties are skewed with respect to one another by an angle ϕ. In the thermally equilibrated electronic excited states of glyoxal (as opposed to the excited states reached by Franck-Condon transitions from the ground state), it is possible that each $H\overset{\overset{O}{\|}}{C}C$ group is *nonplanar*. In this case, $\alpha+\beta$ need not equal ϕ, and α and β are not necessarily equal. We considered the following glyoxal structures:

	(*G*1)	(*G*2)	(*G*3)	(*G*4)	(*G*5)	(*G*6)	(*G*7)	(*G*8)	(*G*9)	(*G*10)
ϕ	5°	10°	10°	−10°	10°	−10°	0	0	10°	10°
α	0	0	2.5°	2.5°	10°	10°	2.5°	10°	10°	2.5°
β	0	0	2.5°	2.5°	10°	10°	2.5°	10°	−10°	− 2.5°
$\alpha+\beta$	0	0	5°	5°	20°	20°	5°	20°	0°	0°

A positive value of ϕ is associated with a OCCO ***P*** helix, and a negative ϕ indicates a OCCO ***M*** helix. Likewise, a positive value of $(\alpha+\beta)$ denotes a HCCH ***P*** helix. Note that in structures (*G*1), (*G*2), (*G*9), and (*G*10) the inherent chirality of the system resides in the configuration of OCCO. In isomers (*G*3)–(*G*8) the overall chirality of the system is influenced by the configurations of both the OCCO and the HCCH groupings. In structures (*G*4) and (*G*6), these two groups have opposite chiralities.

4. Results

Cyclopentanediones. The ground state dipole moments, binding energies, and first three ionization potentials (vertical ionization potentials calculated according

Table 1. Calculated dipole moments[a], binding energies[b], and vertical ionization potentials[c]

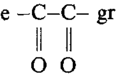
Structure	Dipole Moment	Binding Energy	IP_1	IP_2	IP_3
(I)	4.23	-5.9464	0.4186	0.4951	0.5060
(II)	4.23	-5.9462	0.4179	0.4959	0.5043
(III)	4.30	-5.9286	0.4256	0.4841	0.5060
(IV)	4.31	-5.9287	0.4271	0.4873	0.5075
(V)	4.31	-5.9284	0.4273	0.4871	0.5068
(VI)	4.17	-7.0697	0.4101	0.4817	0.4984
(VII)	4.32	-6.8043	0.3984	0.4210	0.4799
(VIII)	4.37	-6.7581	0.4158	0.4307	0.4864
(IX)	4.25	-6.0002	0.4178	0.4681	0.4904
(X)	4.48	-6.7510	0.4246	0.4524	0.4876
(XI)	4.37	-6.0068	0.4269	0.4652	0.4914

[a] In Debye units. [b] In atomic units. [c] In atomic units.

Table 2. Calculated optical properties for the two lowest energy singlet-singlet transitions in Structures (I)–(XI)

Structure	λ(nm)	f	[R]	$\lvert g \rvert$	Symmetry[a]
(I)	422	0.0113	- 8.92	0.0033	B
	245	0.0090	- 7.14	0.0091	A
(II)	412	0.0099	-24.77	0.0107	B
	244	0.0060	-19.24	0.0215	A
(III)	441	0.0072	- 6.41	0.0042	B
	262	0.0041	3.95	0.0098	A
(IV)	449	0.0068	- 9.62	0.0058	B
	270	0.0033	3.08	0.0096	A
(V)	448	0.0076	-27.22	0.0140	B
	268	0.0052	47.92	0.0616	A
(VI)	400	0.0064	-22.26	0.0154	B
	231	0.0119	-13.36	0.0085	A
(VII)	410	0.0023	- 9.08	0.0170	B
	240	0.0086	-46.91	0.0399	A
(VIII)	398	0.0038	6.16	0.0097	B
	218	0.0068	-30.70	0.0407	A
(IX)	407	0.0018	3.47	0.0084	B
	227	0.0037	- 6.28	0.0148	A
(X)	412	0.0028	5.64	0.0086	B
	224	0.0047	-26.79	0.0448	A
(XI)	431	0.0026	- 3.31	0.0066	B
	242	0.0040	7.29	0.0214	A

[a] In this column the approximate symmetries of the excited states are designated either A or B according to whether the states are symmetric (A) or antisymmetric (B) with respect to 180° rotation about the C_2 axis of the $-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$ group in each structure. Of course, these designations are exact only for Structures (I) and (II) since these are the only structures with exact C_2 symmetry.



to Koopmans' theorem [20]) computed for Structures (I)–(XI) are listed in Table 1. The first two singlet excited states of each structure are calculated to be predominantly of the $n\pi^*$ type localized almost entirely on the dicarbonyl group. The calculated properties for transitions to these states are displayed in Table 2. The next set of four singlet excited states are less readily identified with carbonyl or dicarbonyl progenitor states and, in fact, several of these states are somewhat delocalized about the carbocyclic ring and onto the ring substituent atoms. The oscillator strengths and rotatory strengths calculated for these transitions are given in Table 3.

Glyoxal. The lowest energy transition calculated for each glyoxal structure, (G1)–(G10), is of the $n \rightarrow \pi^*$ type and is localized on the dicarbonyl group. The transition energies, dipole strengths, rotatory strengths, and dissymmetry factors calculated for this transition in structures (G1)–(G10) are displayed in Table 4.

Table 3. Oscillator strengths and rotatory strengths calculated for transitions Nos. 3–6 in Structures (I)–(XI)

Structure	No. 3 f	No. 3 $[R]$	No. 4 f	No. 4 $[R]$	No. 5 f	No. 5 $[R]$	No. 6 f	No. 6 $[R]$
(I)	0.0001	- 6.65	0.0060	6.64	0.0002	1.10	0.0191	- 1.05
(II)	0.0014	-19.91	0.0031	17.40	0.0016	3.49	0.0184	- 4.00
(III)	0.0016	- 5.43	0.0068	3.24	0.0033	1.12	0.0280	- 0.14
(IV)	0.0012	- 8.43	0.0075	5.35	0.0027	- 0.94	0.0241	- 0.26
(V)	0.0021	-24.08	0.0081	10.21	0.0041	- 0.93	0.0254	9.08
(VI)	0.0021	- 4.42	0.0063	17.83	0.0074	0.72	0.0161	6.10
(VII)	0.0175	-15.11	0.0004	5.88	0.0038	- 6.81	0.0029	0.86
(VIII)	0.0026	- 2.30	0.2392	24.55	0.0040	- 8.33	0.1051	21.30
(IX)	0.0831	-77.93	0.0199	15.48	0.0944	34.63	0.1515	9.86
(X)	0.0028	- 2.79	0.2020	26.34	0.0035	- 4.98	0.0936	41.87
(XI)	0.0311	-44.13	0.0384	9.84	0.0963	14.97	0.0563	-34.80

Table 4. Calculated optical properties for the lowest energy singlet-singlet transition in glyoxal structures (*G*1)–(*G*10)

Structure	λ(nm)	D(debye^2)	$[R]$	$\lvert g \rvert$	ϕ	α	β
(G1)	488	0.012	1.85	0.0610	5°	0°	0°
(G2)	479	0.018	3.30	0.0695	10	0	0
(G3)	591	0.074	-13.59	0.0682	10	2.5	2.5
(G4)	596	0.114	-18.52	0.0602	-10	2.5	2.5
(G4)	566	1.365	-47.17	0.0128	10	10	10
(G6)	620	1.531	-64.84	0.0157	-10	10	10
(G7)	610	0.097	-17.10	0.0650	0	2.5	2.5
(G8)	566	1.263	-53.57	0.0157	0	10	10
(G9)	505	0.504	0.06	0	10	10	- 10
(G10)	530	0.385	0.93	0.0009	10	-2.5	-2.5

5. Discussion

Cyclopentanediones. The ionization potentials given in Table 1 were calculated by taking the negatives of the energies computed for the three highest occupied molecular orbitals (Koopmans' theorem). The highest energy molecular orbital (MO) computed for each of the cisoid Structures, (I)–(XI), can be described best as a *symmetric* combination of carbonyl oxygen "*n*" orbitals. That is, this MO is localized on the dicarbonyl moiety of each structure, has its largest amplitude in or

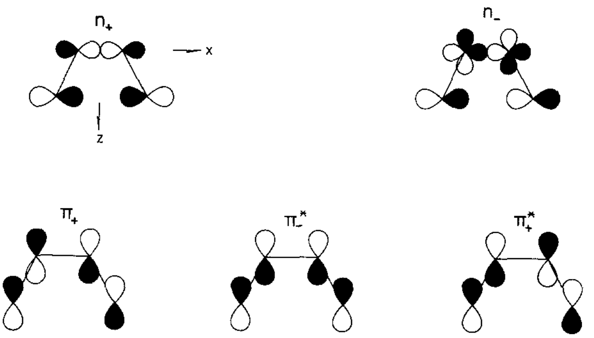


Fig. 4. Schematics of the highest occupied and lowest unoccupied molecular orbitals localized on the α-dicarbonyl group of cyclopentanedione Structures, (I)–(XI)

near the XZ-plane (see Fig. 4), and is symmetric in sign [but not necessarily in magnitude, except for Structures (I) and (II)] with respect to 180° rotation about the Z-axis (the C_2 symmetry axis of the OCCO moiety). Furthermore, this MO (designated n_+) has predominantly oxygen $2p_x$ character, with additional oxygen $2s$, $2p_z$ and carbon (carbonyl) $2s$, $2p_x$ character mixed in. The n_+ MO has a node between the carbon and oxygen atoms of each carbonyl group.

The second highest energy SCF orbital calculated for Structures (I)–(XI) can be characterized approximately as a *symmetric* combination of carbonyl group π-bonding orbitals. This MO is comprised primarily of oxygen $2p_y$ and carbon $2p_y$ atomic orbital contributions and is symmetric in sign with respect to 180° rotation about the Z-axis. It has a node between the two carbon atoms of the dicarbonyl group, but is nodeless between the carbon and oxygen atoms of each carbonyl group. We designate this MO as π_+. This MO is not generally as localized on the dicarbonyl group as is the n_+ orbital. For example, in the structures having ring conformations of Types B, C, and D (see Fig. 2), the $2p_z$ and $2p_y$ orbitals on ring carbon 4 contribute significantly to π_+. Additionally, in those structures with *axial* substituents at the 3 position of the ring, the substituent atoms contribute to the π_+ MO.

The third highest energy occupied orbital calculated for Structures (I)–(XI) is essentially an *antisymmetric* combination of carbonyl group orbitals comprised mostly of oxygen $2p_x$, $2p_z$, and carbon $2p_z$ atomic orbitals. We label this MO, n_-. The atomic orbital composition of n_- is somewhat sensitive to ring conformation and substitution. Equatorial substituents at the 3 position of the ring have an especially pronounced effect on this MO.

It must be recognized that the concept of orbital ordering and its direct relation to successive ionization potentials is an artifact of the Hartree-Fock approximation. However, this concept is a useful one especially in the interpretation of photoelectron spectra. The photoelectron spectra of a number of α-dicarbonyl compounds have been measured and the following values have been reported for the ionization energies of electrons in the n_+ and n_- molecular orbitals [20, 21]:

Molecule	$IP(n_+)$	$IP(n_-)$	Δ
Glyoxal	10.59 eV	12.19 eV	1.60 eV
Biacetyl	9.55	11.63	2.08
Camphorquinone	8.80	10.40	1.60
3,3-dimethylindanedione	8.7	10.8	2.1
Benzil	9.1	11.1	2.0

Among these compounds, only camphorquinone and 3,3-dimethylindanedione possess rigidly cisoid dicarbonyl groups. The calculated ionization potentials displayed in Table 1 have the following ranges of values for $IP_1(n_+)$ and $IP_3(n_-)$: $IP_1(n_+)$, 10.8–11.6 eV; $IP_3(n_-)$, 13.0–13.8 eV. The range of values calculated for $\Delta = IP_3(n_-) - IP_1(n_+)$ is 1.6–2.2 eV. Although our calculated values of $IP(n_+)$ and $IP(n_-)$ appear to be too high by ~20–30%, the calculated n_+, n_- splitting energies are in approximate agreement with experiment. Additionally, the ordering of highest occupied orbitals, n_+, π_+, n_-, as calculated here for the cyclopentanedione Structures (I)–(XI), is identical to the ordering of the highest occupied orbitals in glyoxal as calculated by *ab initio* methods [8].

The lowest energy singlet-singlet transition in each of the Structures, (I)–(XI), is calculated to be a nearly pure $n_+ \rightarrow \pi^*_-$ excitation localized on the dicarbonyl group. The π^*_- MO is antisymmetric in sign with respect to 180° rotation about the z-axis, and is a combination of two carbonyl π^* group orbitals. This first transition is electric-dipole allowed with y-polarization in the local C_{2v} or C_2 point group symmetry of the dicarbonyl moiety. However, in agreement with experimental observation, the oscillator strength of this transition is calculated to be rather weak. The magnetic dipole moment associated with the $n_+ \rightarrow \pi^*_-$ transition is computed to be predominantly x-polarized and >0.500 Bohr magneton for each of the eleven cyclopentanedione structures studied here. This transition can be characterized, then, as moderately strong in magnetic dipole radiation and weak in electric dipole radiation.

The second lowest energy singlet-singlet transition cannot be characterized as simply as was the first. Configuration interaction calculations on the Structures (I)–(XI) yield a second singlet state which has a strong $n_-\pi^*_-$ contribution and a weaker $n_+\pi^*_+$ contribution for each structure. However, depending upon ring conformation and ring substituents, other singly-excited configurations may contribute significantly to this state for certain structures. Given the dominant $n_-\pi^*_-$ character of this state, the second singlet-singlet transition is electric-dipole forbidden in local C_{2v} point group symmetry, but is magnetic dipole allowed with Z-polarization. The oscillator strengths computed for this transition are generally smaller than those computed for the first singlet transition. This result is in general agreement with experimental observation. For example, ε(max) ~ 40 in the region of the first singlet transition in camphorquinone, whereas ε(max) ~ 20 in the region of the second singlet transition.

The magnetic-dipole character of the second singlet-singlet transition is computed to be moderately strong (>0.600 Bohr magneton) and mostly Z-polarized. The dissymmetry factors calculated for this transition are larger than those calculated for the first singlet-singlet transition in all structures.

The rotatory strengths displayed in Table 2 demonstrate the sensitivity of chiroptical properties to changes in molecular stereochemistry. Structures (I) and (II) have similar ring conformations but they differ in the magnitude of the dicarbonyl twist angle ϕ. Structures (III) and (IV) also have similar ring conformations but different twist angles. The ring conformations of (I) and (II), however, are significantly different than those of (III) and (IV), and this is reflected in the sign patterns of the rotatory strengths calculated for the first two transitions in each of these four structures. These results suggest that while the sign of the rotatory strength of the first transition is sensitive to the screw sense of the dicarbonyl twist distortion, it is not sensitive to the type of conformation assumed by the ring. However, the sign of the rotatory strength associated with the second transition *is* sensitive to the type of conformation assumed by the ring.

The inherent chirality of the twisted dicarbonyl group in each of the unsubstituted cyclopentanedione Structures, (I)–(V), is ***P*** (that is, the screw sense is that of a right-handed helix). The sign of the rotatory strength for the lowest energy singlet-singlet transition in each of these structures is negative. Furthermore, the symmetry of this transition is B (referred to the local C_2 symmetry group of the OCCO moiety). This latter result is in agreement with the calculations performed by Hug and Wagnière [2] on cisoid glyoxal structures. However, the former result, $R < 0$ for the first transition of a cisoid dicarbonyl structure of ***P*** configuration, is in disagreement with the calculations of Hug and Wagnière and with our own calculations in which glyoxal was used as a model structure. This suggests that glyoxal is not a suitable model for studying the chiroptical properties of α-dicarbonyl systems.

Substituents on the cyclopentanedione ring can influence the optical activity of the α-dicarbonyl transitions in three ways. First, they can stablize or destablize certain ring conformations which in turn direct the preferred geometry of the dicarbonyl group. Second, they can interact directly ("through-space") with the chromophoric electrons on the dicarbonyl group, thus influencing the electronic charge distributions on this group. Third, they can influence the electronic states principally localized on the dicarbonyl group by indirect, "through-bond" interactive mechanisms. The second mechanism leads to the so-called vicinal effect in the traditional theories of molecular optical activity. The consequences of the third mechanism can also be classified as a kind of vicinal effect.

The vicinal effects of the ring substituents in Structures (VI) and (VIII) of the present study may be assessed by comparing the computed rotatory strengths for these structures with those computed for Structure (II). The conformations of the ring and dicarbonyl group are identical for these three structures. That is, each has a ring conformation of type A (see Fig. 2) and a twisted dicarbonyl group of configuration ***P***, $\phi = 15°$. The only differences between these structures lie in substitution at the 3 position of the ring: (II) is unsubstituted, (VI) is 3-methyl (axial) substituted, and (VII) is 3-methyl (equatorial) substituted. From the results displayed in Table 2 it is seen that the ring substituents in these structures alter the magnitudes but not the signs of the electronic rotatory strengths of the two lowest singlet-singlet transitions.

Similar comparisons can be made between the calculated properties of Structures (IV), (VIII), and (IX). These structures possess identical ring conformations (Type B) and dicarbonyl geometries (***P***, $\phi = 10°$), but differ with respect to ring substitution. In these cases, vicinal effects due to 3-methyl ring substitution apparently dominate the rotatory strengths and determine both their signs and magnitudes. Structure (IV) is unsubstituted, (VIII) is 3-methyl (equatorial) substituted, and (IX) is 3-methyl (axial) substituted.

The rotatory strengths calculated for Structures (X) and (XI) are due entirely to vicinal interactions since the dicarbonyl ring structures of these isomers possess exact C_s symmetry. Structure (X) has a 3-methyl (equatorial) substituent, and structure (XI) includes a 3-methyl (axial) substituent.

The results presented in Table 2 clearly demonstrate that ring conformation and vicinal effects due to ring substituents contribute significantly to the rotatory strengths associated with the two lowest energy transitions of cyclic α-diketone structures. In some structures these contributions completely dominate the total rotatory strengths, swamping out any contributions attributable to inherent chirality within the α-dicarbonyl moiety. In other structures, the vicinal and ring conformational effects simply reinforce or diminish the stronger contributions made by inherent chirality within the dicarbonyl chromophore. These results strongly suggest that analyses of chiroptical spectra of cyclic α-diketone systems based solely on correlations between spectral observables and torsional distortions within the dicarbonyl group will be incomplete, at best, and unreliable or inaccurate, at worst. Vicinal effects due to substituents and ring conformational influences cannot be neglected.

So far, our discussion has centered on the chiroptical properties calculated for the two lowest energy singlet-singlet transitions of Structures (I)–(XI). Extant spectra-structure relationships for α-diketone systems are based on the observables associated with these transitions, primarily because they lie in an accessible part of the spectrum. Our model is most reliable in calculating the properties of these low lying transitions. Any model for calculating excited state properties based on the virtual orbital-configuration interaction (limited) method of constructing excited states generally becomes progressively less reliable as one goes to higher and higher excited states. The calculations reported here were carried out using a singly-excited configuration basis set of 20. The optical properties calculated for the first four transitions appeared to be quite stable for CI bases $\geqq 16$. The properties of transitions Nos. 5 and 6 appeared to be stable when the CI basis set was expanded to 20. We believe that this CI basis is adequate for calculating reasonably accurate representations of the two lowest energy singlet excited states. Furthermore, within the restrictions imposed by our valence-shell-only atomic orbital basis in the SCF-MO calculations, this CI procedure provides a satisfactory and useful description of the next four singlet excited states.

The oscillator strengths and rotatory strengths calculated for transitions Nos. 3–6 are listed in Table 3. Transition No. 3 is predominantly a dicarbonyl $\pi_+ \rightarrow \pi_-^*$ excitation for each structure. On our model, the excited states in transitions Nos. 4–6 are represented as scrambled combinations of several configurational states and are not easily assigned simple orbital descriptions. However, each of these transitions includes considerable dicarbonyl → ring atom charge transfer character as well as dicarbonyl $\pi_+ \rightarrow \pi_-^*$, $n_+ \rightarrow \pi_+^*$, $n_- \rightarrow \pi_+^*$, and $\pi_+ \rightarrow \pi_+^*$ excitations.

The transition energies computed for transitions Nos. 3–6 lie in the range 8–11 eV (or ~155–110 nm). Although the far and vacuum ultraviolet spectra of cyclic α-diketone systems have not been characterized, it is rather certain that transitions Nos. 3 and 4 in these compounds should fall within the ~225–200 nm spectral region[2]. This suggests that the transition energies for these transitions are computed to be too large by at least 50%. It should be pointed out that our program computes dipole velocity integrals, $\langle\psi_0|\partial/\partial q|\psi_n\rangle$, in atomic units (a.u.) directly from the ground and excited state wave functions. The integrals are then transformed to $\langle\psi_0|eq|\psi_n\rangle$ by the transformation, $69.1584\langle\psi_0|\partial/\partial q|\psi_n\rangle\,(\text{a.u.})/E_n(\text{eV}) = \langle\psi_0|eq|\psi_n\rangle$ Debye, where the E_n(eV) are theoretically computed transition energies to states n. If the computed E_n values are too high (i.e., larger than experimental values), this will tend to lower the values of the integrals $\langle\psi_0|eq|\psi_n\rangle$, the dipole strengths D, the oscillator strengths f, and the reduced rotatory strengths $[R]$ appearing in Tables 2 and 3. This effect should be especially evident in the data of Table 3. The transition energies calculated for transition No. 1 appear to be very close to experimental values, and the calculated values for transition No. 2 are only about 10–20% higher than experiment. The computed optical properties of Table 2 should not, therefore, be distorted significantly by erroneous energy factors.

The electronic rotatory strengths computed for transitions Nos. 3 and 4 have opposite signs for all eleven Structures, (I)–(XI). Furthermore, the signs of the rotatory strengths for these transitions are independent of the conformational and other stereochemical features of the cyclopentanedione systems examined in this study. The magnitudes of the computed rotatory strengths vary from structure to structure, but not the signs. These results suggest that whereas the chiroptical observables associated with transitions Nos. 1 and 2 may be useful as diagnostic probes of α-diketone structure and stereochemistry, the chiroptical observables associated with the higher energy transitions will not be useful for this purpose.

Glyoxals. The purpose of our calculations on structural isomers of glyoxal was to ascertain how the spontaneous emission spectra of α-dicarbonyl systems might be influenced by non-planarity of the $X{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C$ ($X = H$ or C) groups in the emitting states. These calculations were carried out by performing SCF-MO calculations (in the INDO-MO approximation) on structures having the assumed geometries of the emitting states (thermally equilibrated, lowest energy singlet excited states), then constructing the terminal states of the emission processes by use of the virtual orbital-configuration interaction method. The terminal states are, of course, unrelaxed molecular ground states reached by Franck-Condon transitions. They have the geometries of the respective emitting states.

Among the glyoxal structures studied, the $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C$ moieties are planar only in (*G*1) and (*G*2). In these structures, the dicarbonyl group is twisted [$\phi = 5°$ for (*G*1) and $\phi = 10°$ for (*G*2)], but the $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C$ groups remain planar. In structures

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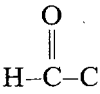
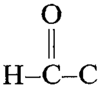
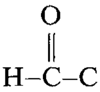
[2] The CD spectrum of camphorquinone exhibits two bands of opposite signs adjacent to one another at ~225 nm and ~205 nm. The absorption spectrum in this region shows no peaks, but from ~250 nm to 200 nm there is the onset of a very strong band centered somewhere below 200 nm.

(*G*3)–(*G*10), however, the  $\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}C}$ groups take on nonplanar geometries. The results displayed in Table 4 reveal that nonplanarity in the  $\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}C}$ groups leads to significant red-shifting of the transition wavelengths for the fluorescent processes. Additionally, the dipole strengths and the rotatory strengths exhibit a strong dependence upon the relative values of the structure parameters ϕ, α, and β (see Section 3) and are sensitive to nonplanarity in the  $\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}C}$ groups.

Our calculations on the cyclopentanedione Structures, (I)–(XI), revealed that glyoxal may not be a suitable model for studying the chiroptical properties of α-diketones (specifically, cyclic α-diketones). However, it is expected that glyoxal *should* be a useful model for examining the *relative* values of the optical properties associated with α-dicarbonyl chromophores subjected to local distortions or alterations in geometry.

6. Summary

Direct calculations of the electronic rotatory strengths of transitions in various structural isomers of cyclopentanedione, 3-methylcyclopentane-1,2-dione, and glyoxal were performed in this study. These calculations were based on the semiempirical INDO-MO model for obtaining ground state wave functions and on the virtual orbital-configuration interaction method for constructing electronic excited states.

The principal results obtained for the cyclopentanedione structures (substituted and unsubstituted) can be summarized as follows:

(a) The splitting energies between the α-dicarbonyl localized n_- and n_+ orbitals in Structures (I)–(XI) lie in the range 1.6–2.2 eV.

(b) The ordering of the highest occupied orbitals in energy is $n_+ > \pi_+ > n_-$.

(c) The lowest energy singlet-singlet transition can be described as a nearly pure $n_+ \rightarrow \pi_-^*$ excitation localized on the α-dicarbonyl group.

(d) The second singlet excited state can be described as an admixture of $n_-\pi_-^*$ and $n_+\pi_+^*$ configurational states localized on the α-dicarbonyl group, with $n_-\pi_-^*$ making the dominant contribution.

(e) The two lowest energy transitions (to singlet excited states) are only weakly allowed in electric dipole radiation, but both are computed to have moderately strong magnetic dipole transition moments (>0.50 Bohr magnetons).

(f) The sign patterns and relative magnitudes of the rotatory strengths associated with the two lowest energy singlet-singlet transitions are extraordinarily sensitive to ring substituents and ring conformational parameters as well as to inherent chirality within the α-dicarbonyl moiety. That is, vicinal effects play a significant role in determining the signs and magnitudes of the electronic rotatory strengths.

(g) For structures which lack asymmetric centers and which derive their optical activity from inherent dissymmetry within the α-dicarbonyl and carbocyclic ring moities, a *negative* rotatory strength for the lowest energy transition is associated with a right-handed screw sense (***P*** configuration) in the twisted dicarbonyl group. A *positive* rotatory strength is associated with left-handed screw sense (***M*** configuration).

These latter results are in direct conflict with those obtained from calculations on cisoid glyoxal structures [2, 24] and suggest that glyoxal may not provide a suitable model for cyclic α-dicarbonyl molecules (particularly those which include strained ring systems). Additionally, our results suggest quite strongly that vicinal effects cannot be ignored in developing spectra-structure relationships applicable to the chiroptical observables of cyclic α-diketone systems.

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