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Circular Dichroism Studies of Optically Active 1,3-Dioxolan-4-ones in the Vacuum Ultraviolet Region

Aharon Gedanken *
Chemistry Department Bar-Ilan University, Ramat-gan, Israel
Tadeusz Połoński *
Department of Organic Chemistry, Technical University, 80-295 Gdansk, Poland

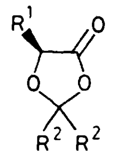
The circular dichroism spectra of substituted 1,3-dioxolan-4-ones in the gas phase from 230–160 nm are reported. The Cotton effect sign in the n–π^* region is dependent of the conformational equilibrium of the five-membered ring. Molecular mechanics (MM2) calculations show that the envelope conformer with bulky substituents in equatorial positions is the most preferred conformation. The circular dichroism corresponding to the Rydberg transitions is less conformationally dependent. Comparison of the dioxolanone (**1**) and the analogous dioxolane (**6**) spectra shows that the Rydberg transitions are mainly due to the promotion of electrons from the diether moiety.

Relationships between chiroptical properties and stereochemical features of lactones and carboxylic acid derivatives have attracted considerable attention over the last few years.[1–3] However, no satisfactory general rules for the correlations of the Cotton effect (CE) sign with the molecular geometry have yet been found. All spectroscopic studies of the above systems were probing the n–π^* transition which is the only absorption band accessible for commercially available circular dichroism (c.d.) instruments. The higher energy transitions were detected in the vacuum ultraviolet (v.u.v.) region by absorption measurements of simple carboxylic acids and esters[2] but no c.d. results have been reported so far.

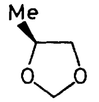
In a previous study, Połoński[3] has reported the results of c.d. measurements for the n–π^* transition of substituted 1,3-dioxolan-4-ones. The c.d. spectra were found to depend on solvent polarity and the size of substituents at positions 2 and 5 of the dioxolanone ring. The spectrum of (*S*)-5-methyl-1,3-dioxolan-4-one (**1**) exhibited bisignate c.d., where a positive CE was observed at lower energies and a negative one at higher energies. These observations were explained as originating from the coexistence of two conformers in solution.

In this study we have extended the measurements of absorption and c.d. spectra for 1,3-dioxolan-4-ones (**1**)–(**5**) to the v.u.v. region. The spectra were recorded in the gas phase down to 160 nm. The gas phase enabled us to probe the conformational equilibrium without solvent perturbations. The extension of the wavelength region to the v.u.v. reveals the higher excited electronic states of the molecule, some of which might be more sensitive to absolute configuration. Such a relation was recently reported for the n(0)–3s Rydberg transition in the oxirane chromophore.[4] The comparison of gas-phase and solution spectra could help in the characterization of the excited states. It is well known that Rydberg transitions undergo blue shifts while valence states are either unaffected or slightly red shifted when a molecule is embedded in a solvent. We have also measured c.d. and absorption spectra of the structurally related 4-methyl-1,3-dioxolane (**6**) which will be compared with the data of compound (**1**).

Since knowledge of preferred conformations is a decisive factor in the interpretation of chiroptical spectra and because previous attempts at conformational analysis of 1,3-dioxolan-4-ones were based mainly on intuition, we have performed molecular mechanics (MM) calculations for compounds (**1**)–(**5**). The MM method has been shown to be a very reliable and efficient way of determining conformations and energies for a wide variety of compounds.[5] The calculations required the development of some new parameters absent in original MM2 parametrization.[6]



(1) R^1 = Me, R^2 = H
(2) R^1 = Me, R^2 = Me
(3) R^1 = Me, R^2 = Et
(4) R^1 = Pr^i, R^2 = H
(5) R^1 = Pr^i, R^2 = Me



(**6**)

Materials and Methods

The syntheses of the 1,3-dioxolane-4-ones (**1**)–(**5**) have been described elsewhere.[3] The dioxolane (**6**) was obtained according to the literature procedure.[7] The v.u.v.c.d. instrument used in this study has been described previously.[8] The monochromator used for the measurements was a McPherson 225 equipped with a 1 200 lines mm^{-1} grating, yielding a spectrum resolution of 0.8 nm mm^{-1}. All absorption and c.d. measurements were carried out in an 18 cm cell using 2 mm slits. The vapour pressure was measured using a Wallace and Tiernan absolute pressure gauge. Torsional parameters V_1, V_2, and V_3 absent in the original MM2 parametrization, for angle types 6-1-3-6 and 3-6-1-6 (atom types assigned according to ref. 6), were obtained following the procedure of Hopfinger and Pearlstein;[9] the potential energy of model $HOCH_2CO_2H$ and $HOCH_2OCHO$ was calculated as a function of corresponding torsional angles by the MNDO method.[10] The following values were obtained: V_1 (6-1-3-6) 0.45, V_2 (6-1-3-6) 0.23, V_3 (6-1-3-6) 0.0 kcal mol^{-1}; V_1 (3-6-1-6) 1.1, V_2 (3-6-1-6) -0.48, and V_3 (3-6-1-6) -1.04 kcal mol^{-1}.

Results

4-Methyl-1,3-dioxolane (**6**).—The absorption and c.d. spectra of 4-methyl-1,3-dioxolane (**6**) are presented in Figure 1. The low-

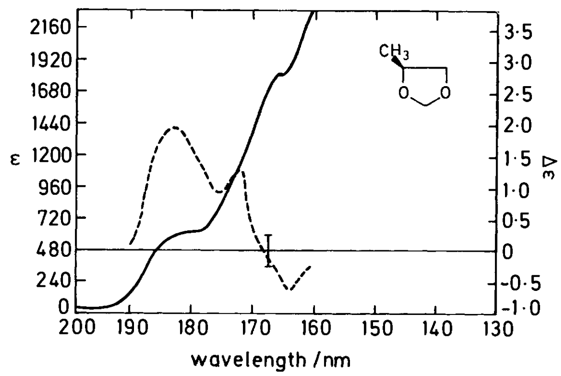


Figure 1. The absorption (——) and c.d. (– – – –) spectra of 4-methyl-1,3-dioxolane in the gas phase. The spectral resolution is 1.6 nm

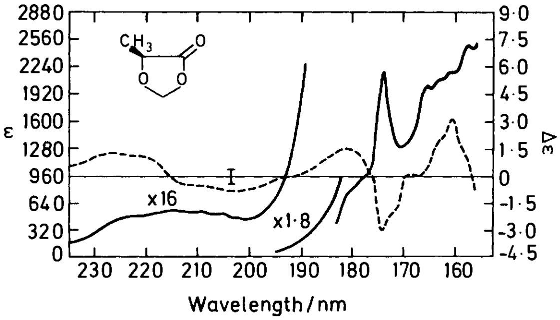


Figure 2. The absorption (——) and c.d. (– – – –) spectra of 5-methyl-1,3-dioxolane-4-one in the gas phase. The spectral resolution is 1.6 nm

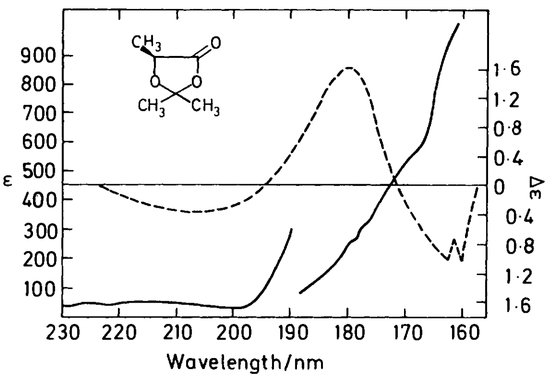


Figure 3. The absorptions (——) and c.d. (– – – –) spectra of 2,2,5-trimethyl-1,3-dioxolane-4-one in the gas phase. The spectral resolution is 1.6 nm

resolution absorption spectrum reveals only two bands, the first appearing at 182.5 ± 1.0 nm and the second as a shoulder near 165 nm. The c.d. spectrum uncovers an extra positive band near 172.5 nm. These three bands can be assigned as 3s, 3p, and 3d Rydberg transitions, respectively. It is well known that in chromophores containing 6–8 atoms, the term value of a 3s Rydberg reaches a limit of 22 000–24 000 cm^{-1}. The term values of 3p and 3d states are 18 000–20 000 and 12 000–14 000 cm^{-1}, respectively.[2] However, if our assignment is correct then the energy spacing between the 3s and 3p and between 3p and 3d Rydbergs should be *ca.* 3 000 cm^{-1}. Indeed, this is the measured energy spacing between the observed bands. The photoelectron spectrum of 1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane[11] shows the first ionization potential of these compounds to be 10.1 and 9.71 eV, respectively. Assuming that the effect of a substitution of a methyl group at position 4 will reduce the ionization potential by *ca.* 0.15 eV the term value for the 3s Rydberg transition of compound (**6**) will be *ca.* 25 000 cm^{-1}. Thus, we assume that the dioxolane (**6**) is close to the limit for a large molecule.

1,3-*Dioxolan*-4-*ones*.—We have examined a series of five 1,3-dioxolan-4-ones (**1**)–(**5**) which are sufficiently volatile for gas-phase studies. The most volatile compound among them is (**1**) the spectra of which are presented in Figure 2. Its absorption spectrum reveals a weak broad band (ε *ca.* 35) centred at 213 nm. The c.d. spectrum at the same energy region shows a bisignate signal with negative CE at long wavelengths changing into a positive sign at shorter wavelengths. This weak electronic transition of n–π^* valence character (n is a non-bonding orbital centred on the carbonyl moiety) is well documented; it is electric-dipole forbidden and magnetic-dipole allowed.[2] This is manifested in the spectrum by the very low intensity of the absorption band whereas the magnitude of the corresponding CE is comparable to other states. The gas-phase c.d. resembles the spectrum observed in cyclohexane solution and differs from those recorded in acetonitrile and methanol solutions where only a positive CE in the n–π^* region was observed.[3] Following the assumptions made by Połoński,[3] we argue that an equilibrium between two conformers exists also in the gas phase.

For compound (**2**) with the C-2 atom substituted with two methyl groups we have obtained only one negative CE corresponding to the n–π^* transition (Figure 3). Since the vapour pressure of this compound is lower than that of compound (**1**) the measurements were repeated in a 75 cm cell. Even so, we have detected only one negative c.d. band at long wavelengths. We believe that the conformational equilibrium for (**2**) is still shifted towards one energetically preferred conformer. The same trend is observed in cyclohexane solution, namely the c.d. of (**2**) shows stronger negative CE than the positive one in the n–π^* region. Analogously, the negative CE for the 5-isopropyl derivatives (**3**) and (**4**) is further enhanced, although a small positive CE can still be detected in cyclohexane solution.

At shorter wavelengths, the dioxolanones (**1**)–(**5**) exhibit the second electronic transition which appears as a shoulder at 182 nm in the absorption spectrum with the positive CE corresponding to it in c.d. spectrum. This c.d. band occurs at almost the same wavelength for all compounds studied and can be attributed to the promotion of a non-bonding electron from the diether moiety to the 3s Rydberg orbital. This transition is similar to the $n(0)$–3s excitation discussed above for dioxolane (**6**) which also shows the same CE sign in this region. It seems probable that the corresponding 'non-bonding' orbital [$n(0)$ is centred on the diether chromophore] contains only very small contributions from the carbonyl group and therefore the $n(0) \longrightarrow 3s$ transition exhibits analogous properties in the diether (**6**) and dioxolanones (**1**)–(**5**). Compound (**1**) shows a second Rydberg transition appearing as a relatively sharp band at 1 730 Å which may be assigned as an n–3p Rydberg excitation. The negative CE corresponding to it in the c.d. spectrum is the opposite of the analogous transition in compound (**6**). However, keeping in mind that the CE sign is determined by the sum of three 3p components it can be responsible for the different CE signs of (**1**) and (**5**). Similarly the c.d. of alkyl-substituted oxiranes shows that although the $n(0) \longrightarrow 3s$ CE sign is determined by the absolute configuration of the molecule, the $n(0) \longrightarrow 3p$ CE sign is rather unpredictable. The $n(0) \longrightarrow 3p$ Rydberg transition for the remaining dioxolanones is more diffuse and occurs at slightly shorter wavelengths; however, it also shows a positive CE. The only exception appears to be compound (**4**), for which the $n(0) \longrightarrow 3p$ CE cannot be observed

Table 1. C.d. data of compounds (**1**)–(**6**). Wavelengths (nm) and c.d. ($\Delta\varepsilon$) of the various transitions ($\Delta\varepsilon$ is in units of mol^{-1} cm^{-1})

	Transition			
Compound	$n\longrightarrow\pi^*$	$n(0)\longrightarrow 3s$	$n(0)\longrightarrow 3p$	$n(0)\longrightarrow 3d$
(**6**)	—	182.5(+2.0)	172.5(+1.5)	165.0(−0.5)
(**1**)	227.0(+1.2)			
	204.0(−0.7)	182.0(+1.6)	173.0(−2.7)	161.0(+3.2)
(**2**)	205.0(−0.4)	181.0(+1.6)	—	163.0(−1.0)
(**4**)	205.0(−0.5)	180.5(+1.6)	—	161.0(−1.2)
(**5**)	205.0(−0.6)	180.5(+2.2)	—	165.0(−1.8)

Table 2. Selected torsion angles (°) for 1,3-dioxolane-4-ones calculated from MM2

Compd.[a]	(2-1-5-4)	(2-3-4-5)	(2-3-4-7)	(3-4-5-6)	Energy/kcal mol^{-1}
(**1**)-eq	29.9	−0.9	−179.0	−139.7	0
(**1**)-ax	−24.5	2.6	−177.6	−106.9	1.3
(**2**)-eq	26.9	0.1	−178.4	−138.3	0
(**2**)-ax	−7.3	2.2	−177.3	−118.8	1.4
(**3**)-eq	29.2	−1.6	−179.8	−140.5	0
(**3**)-ax	−26.7	1.1	180.0	−105.2	1.6
(**4**)-eq	25.5	−0.3	−179.0	−138.9	0
(**4**)-ax	−13.5	0.3	−179.8	−114.7	2.0
(**5**)-eq	26.2	−0.2	−179.0	−136.8	

[a] eq equatorial, ax axial.

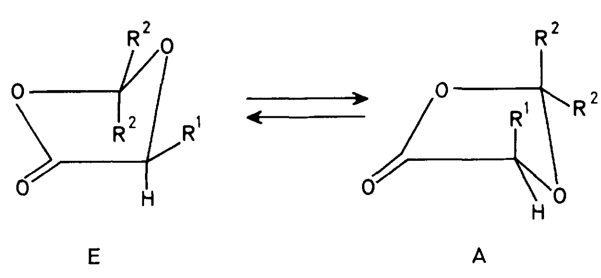


Figure 4. Conformations of 1,3-dioxolane-4-ones

directly from the spectrum. However, the minimum on the c.d. spectrum corresponding to the shoulder at 170 nm in the absorption spectrum probably reflects the existence of the small negative CE in this region which is overshadowed by neighbouring strong positive c.d. bands overlapping it. The further confirmation of this effect comes from the non-Gaussian band shape of the close $n(0)\longrightarrow 3s$ c.d. band.

The third Rydberg transition [$n(0)$–3d] occurs for (**1**) at 161 nm and shows a positive CE sign. It can be also observed in compounds (**3**) and (**4**) but for the remaining compounds it occurs in an inaccessible v.u.v. region. In Table 1 we present the transition energies and the c.d. sign of compounds (**1**)–(**6**).

Molecular-mechanics Calculations and Conformational Considerations.—The results of calculations (at selected torsional angles) for compounds (**1**)–(**5**) obtained with the extended Allinger MM2 force field are presented in Table 2. The MM2 method showed that the dioxolanone ring assumes an envelope conformation with the O=C–O group and the neighbouring C-2 and C-4 atoms lying in one plane and the O-1 atom being out of this plane. There are two energy-minima conformers: the envelope form with the bulky 5-substituent in either the equatorial (E) or axial (A) position (Figure 4). Bulky substituents, owing to the transannular steric 2,5-interactions, favour the equatorial conformer, which is more stable by *ca.* 1.3–2.0 kcal mol^{-1} than the axial one. In the case of strong interactions, as in compound (**5**), the only energy minimum is the E form. It is noteworthy that in some cases [(**2**) and (**4**)] the A conformer is considerably flattened in comparison with the E. These results agree well with *X*-ray data for 5-phenyl-1,3-dioxolan-4-one[12] and structurally analogous γ-lactones[13] in which five-membered rings exist in envelope conformations in the crystalline state. The bisignate c.d. in the 230–200 nm region exhibited by compound (**1**) reflects the conformational equilibrium between the E and A forms. It is generally accepted that the chirality of the lactone ring determines its n–π^* CE sign; however, the vicinal effect of substituents cannot be neglected. According to the Weigang's sector rule[14] for n–π^* transitions and bearing in mind the Snatzke doctrine of spheres[15] which assumes that the contribution of the chiral ring outweighs the contributions of alkyl substituents, the positive CE can be assigned to the A conformer and the negative CE to the E. The only negative CE at 205.0 nm shown by (**2**) and (**4**) points to the predominance of the E form in the equilibrium in the gas phase in agreement with the MM2 results. The positive c.d. corresponding to the $n(0)\longrightarrow 3s$ Rydberg transition exhibited by all the dioxolanones (**1**)–(**5**) may result from the predominant contribution of the E conformer to the CE sign. However, the diether (**6**), which is a highly flexible compound and in which, at room temperature, at least three conformers coexist in equilibrium owing to easy pseudorotation of the five-membered ring,[16] also exhibits a positive $n(0)$–3s CE. Yet another explanation seems possible, namely, that the $n(0)$–3s CE is determined by the vicinal effect of unsymmetrically placed substituents whose relative orientation to the ether chromophore governs the CE sign. Analogously, the c.d. sign of the $n(0)$–3s Rydberg transition in alkyl-substituted oxiranes was found to be directly dependent on the spatial location of the substituents and the positive CE was obtained for *S*- and negative for *R*-enantiomers. Early results indicated the same correlation holds for oxetanes[17] and perhaps also for five- and six-membered-ring ethers.[18]

Conclusions

In the near u.v. region, 1,3-dioxolane-4-ones show c.d. spectra characteristic of the γ-lactone chromophore. The CE corresponding to the *n*–π* transition appears to be strongly dependent on conformational equilibria. However, the c.d. in the v.u.v. region is less sensitive to conformational changes. Comparison with the diether (**6**) indicates that dioxolanones, despite being a combination of the two functional groups, show the Rydberg transitions due mainly to the promotion of the electron from the diether moiety.

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