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Exciton *Cotton* Effects of Benzoates in the ^{1}B Transition Region. Demonstration and Applications

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Summary. The benzoate ^{1}B region exciton *Cotton* effects, hitherto unexplored, were analyzed for their use in stereochemical assignments in both acyclic (conformationally flexible) and cyclic molecules. It was found that a strong, allowed ^1B_a transition, polarized longitudinally, dominates the ^{1}B region (185–210 nm) both in the UV and the CD spectra. The exciton *Cotton* effects due to this transition have the same sign (but differing magnitude) as those due to the ^1L_a (CT) band. The other component of the nearly degenerate ^{1}B system, i.e. ^1B_b transition, polarized orthogonally to the ^1B_a transition, gives a *Cotton* effect in the case of di- and poly(4-chlorobenzoate) chromophoric system, the sign of which is sensitive to the configuration of di- or polyol. In rigid 5β-steroid skeleton ^1B_b transition couplings appear responsible for strong exciton *Cotton* effects due to nearly parallelly oriented benzoate chromophores. Whereas ^1B_a transition excitation energy appears insensitive to the nature of a substituent in 4-position of the benzoate chromophore, substitution with a donor group (methoxy, dimethylamino) brings about a red shift of the ^1B_b band, although less pronounced than the red shift of the ^1L_a (CT) band.

Keywords. Circular dichroism; Configuration; Exciton coupling; UV/Vis spectroscopy.

Introduction

Exciton coupled CD, ECCD [1–5], has been for many years the most practical and reliable method for determining absolute configuration or conformation of chiral molecules in a non-empirical way. The method is based on the dynamic coupling mechanism applicable to coulombic coupling of the electric dipole transition moments μ_1 and μ_2 in two separate, non-coplanar chromophores. This coupled oscillators mechanism, developed by *Kuhn* [6] and *Kirkwood* [7] and later by *Mason* [8, 9], found widespread use in organic stereochemistry due to its two basic advantages: (i) its theoretical foundations are easily translated to stereochemical models, (ii) many chiral molecules consist of, or can be derivatized to two or more

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chromophoric entities. In a two-chromophoric system one chromophore provides the electric dipole transition moment while the second chromophore provides an external origin for the magnetic dipole transition moment produced by the electric dipole transition moment of the first chromophore and *vice versa*. When the two chromophores are identical (degenerate μ_1–μ_2 mechanism) the CD spectrum is represented by a pair of *Cotton* effects with opposite signs and comparable areas (exciton couplet). The two *Cotton* effects arise from transitions to dimer excited states formed by the symmetric and antisymmetric combination of the two excited configurations. The observable effect in the UV/Vis spectrum due to splitting of the states is either band broadening, or in extreme cases, band splitting. In the CD spectrum the sequence of signs of *Cotton* effects from the lower to the higher energy reveals the helicity of the two edtms system: either positive to negative for *P* helicity ($\omega > 0$) or negative to positive for *M* helicity ($\omega < 0$), Fig. 1.

Due to the seminal work of *Harada* and *Nakanishi* [1] the exciton coupling method found widespread use in organic stereochemical analysis. In their original work [10] they demonstrated the applicability of the method to the analysis of absolute configuration of non-chromophoric diols, after their derivatization as benzoates or 4-substituted benzoates.

In frequently encountered structural applications *syn* orientation of the two benzoate chromophores gives rise to the exciton *Cotton* effect of the sign reflecting the sign of the torsion angle O–C–C–O (Fig. 2).

Note that the electric dipole transition moments in the benzoate chromophores (arrows in Fig. 2) are due to the charge-transfer π–π^* transition and are directed toward the carbonyl oxygen, i.e. they are approximately parallel to the direction of

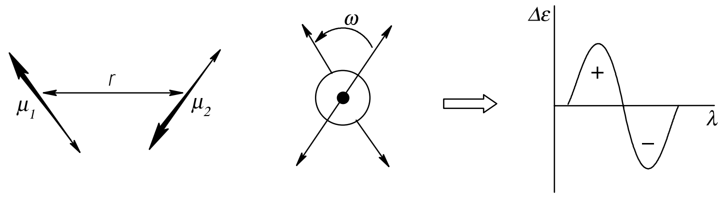
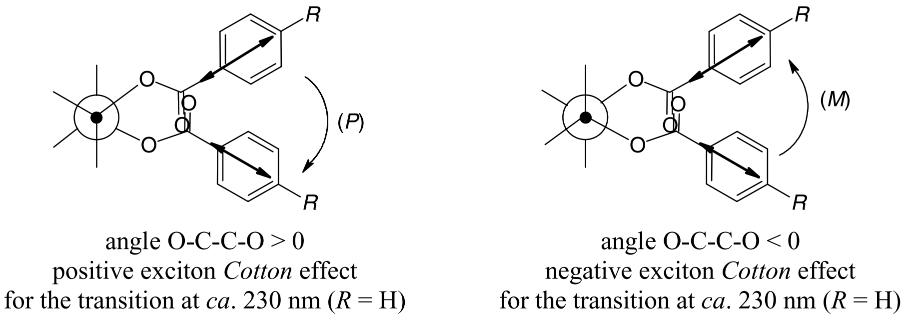


Fig. 1. Illustration of the geometry of the interacting electric dipole transition moments μ_1 and μ_2 in two chromophores: ω is the torsion angle (here negative) involving the three vectors, μ_1, μ_2, and *r*, and the resulting exciton *Cotton* effect is negative



angle O-C-C-O > 0
positive exciton *Cotton* effect
for the transition at *ca*. 230 nm (*R* = H)

angle O-C-C-O < 0
negative exciton *Cotton* effect
for the transition at *ca*. 230 nm (*R* = H)

Fig. 2. Relation between the benzoate orientation and the sign of the exciton *Cotton* effect

Table 1. UV absorption data for 4-substituted benzoates (in acetonitrile solution)

R	λ_{max}/nm	ε/mol^{-1}dm^3 cm^{-1}
H	228	13000
Cl	241	17000
O*Me*	254	16000
NMe_2	316	30000

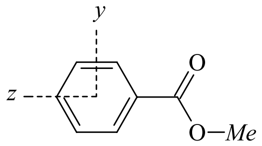
the C–O bond to which the benzoate chromophore is attached. The position of the charge-transfer benzoate band in the UV spectrum is sensitive to the nature of substituent *R* in 4-position of the benzene ring. Typical values are shown in Table 1.

Whereas application of coupling of the benzoate CT transitions to stereochemical problems is well documented, particularly in the carbohydrate field [11–13], other benzoate electronic transitions available for CD/UV measurements have not been yet exploited. We therefore decided to explore the applicability of the benzoate transitions occuring in the range 185–210 nm for stereochemical assignments on the basis of exciton coupling mechanism. Alkyl-substituted benzene derivatives are known to display intense ^{1}B transitions in this region and exciton coupling of these transitions has been studied [14, 15].

Results and Discussion

We first computed the electronic transitions of the model molecule, methyl benzoate, using semiempirical ZINDO and ab initio TDDFT (b3lyp/cc-pvdz) methods. The structure of the methyl benzoate molecule was optimized by DFT (b3lyp/6-311G + (d,p)) method. The results of computations are shown in Table 2. These results are consistent with the appearance of experimental ^1L_b and ^1L_a UV/CD bands in benzoates and indicate the presence of the allowed, nearly degenerate ^{1}B transitions below 200 nm. They are in partial agreement (polarization direction) with the results of earlier semiempirical calculations (CNDO, PPP) on the UV transitions of benzoic acid [16]. According to these data ^1B_a state appears at somewhat lower energy than ^1B_b state.

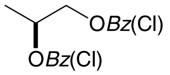
Table 2. Computed singlet electronic transitions (*f* > 0.01) of methyl benzoate



Band assignment	ZINDO λ_{max}/nm (*f*)	Polarization	b3lyp/cc-pvdz λ_{max}/nm (*f*)	Polarization
^1L_b	272 (0.0120)	*y*	248 (0.0133)	*y*
^1L_a (CT)	232 (0.4329)	*z*	224 (0.2420)	*z*
^1B_b	199 (0.3667)	*y*	187 (0.2365)	*y*
^1B_a	194 (0.5667)	*z*	182 (0.5684)	*z*

Our TDDFT results apparently overestimate the transition energies (see experimental data in Tables 3 and 4 below) since no solvent effect is accounted for in the computation. The ^1L_b transition is of forbidden character and therefore of limited applicability to exciton coupling. However, the intense ^1B transitions are of significant interest, since they should be associated with intense exciton *Cotton* effects.

Compounds studied include mostly acyclic di-, tri-, tetra-, penta-, and hexa(4-chlorobenzoates), see data in Table 3, as well as a series of compounds, derived



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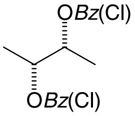

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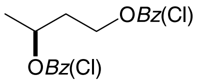

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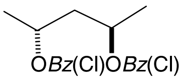

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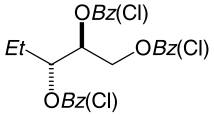

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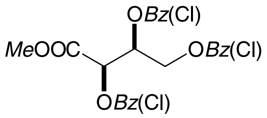

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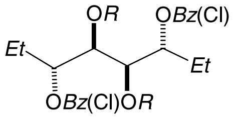
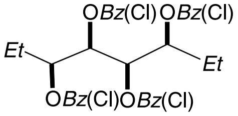


7 *R* = H
8 *R* = *Bz*(Cl)



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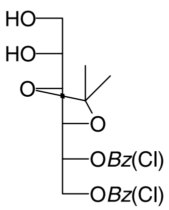

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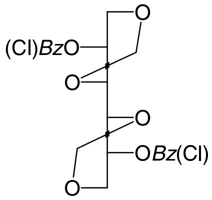

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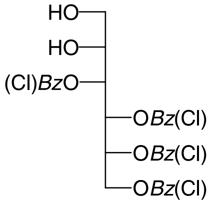

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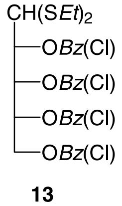

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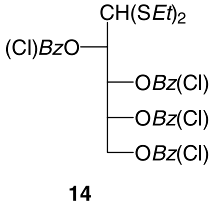

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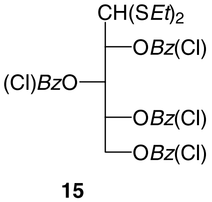

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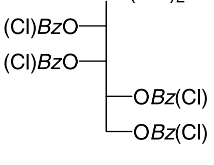

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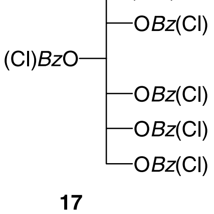

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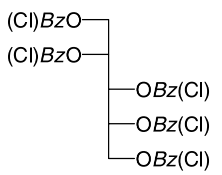

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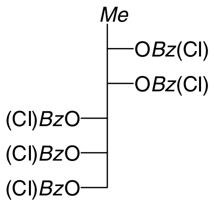

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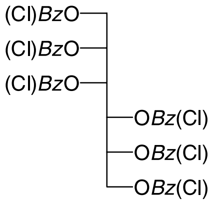

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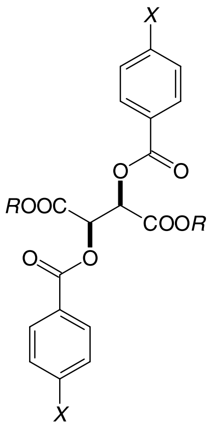
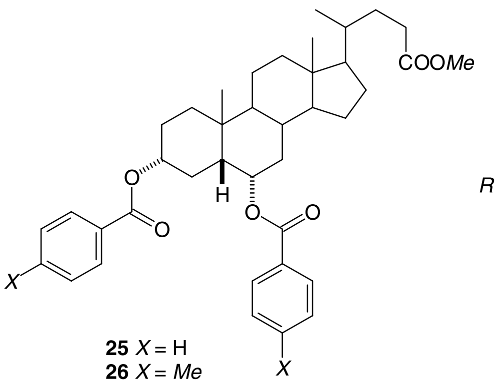
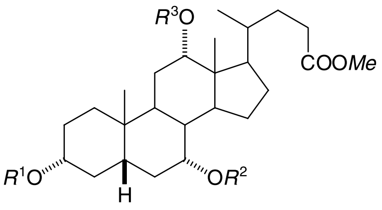


21 $R = Et$, $X = \mathrm{H}$
22 $R = Et$, $X = \mathrm{Cl}$
23 $R = Et$, $X = \mathrm{O}Me$
24 $R = Me$, $X = \mathrm{N}Me_2$



25 $X = \mathrm{H}$
26 $X = Me$
27 $X = \mathrm{Cl}$
28 $X = \mathrm{O}Me$



29 $R^1 = R^2 = Bz$, $R^3 = \mathrm{H}$
30 $R^1 = \mathrm{H}$, $R^2 = R^3 = Bz$
31 $R^1 = R^2 = Bz(\mathrm{O}Me)$, $R^3 = \mathrm{H}$
32 $R^1 = R^3 = Bz(\mathrm{O}Me)$, $R^2 = \mathrm{H}$
33 $R^1 = \mathrm{H}$, $R^2 = R^3 = Bz(\mathrm{O}Me)$
34 $R^1 = R^2 = R^3 = Bz(\mathrm{O}Me)$

from tartaric acid and bile acids, having variously 4-substituted benzoate chromophores (Table 4).

The CD/UV data for 4-chlorobenzoates are due to two types of transitions, the 240 nm ^1L_a band of CT character and 198 nm band of nearly degenerate ^1B transitions. The corresponding exciton *Cotton* effects appear accordingly at 245–257/227–241 nm (241 nm UV band) and at 198–202/186–189 nm (198 nm UV band). To the latter band apparently also belongs the *Cotton* effect appearing in the range 206–210 nm which in several instances is very weak (**3**, **6**, **11**, and **17**). To assign the CD bands of the nearly degenerate ^1B states we use the data of Table 1 according to which the more intense ^1B_a band appears at shorter wavelength compared to ^1B_b band. This means that the intense short-wavelength

Table 3. Exciton *Cotton* effects of di-, tri-, tetra-, penta-, and hexa(4-chlorobenzoates) **1–20** in acetonitrile solution

Compound no.	Benzoate CT band		Benzoate ^1B_a band		^1B_b CD band
	$\Delta\varepsilon^a$ (λ/nm)	ε^a (λ/nm)	$\Delta\varepsilon^a$ (λ/nm)	ε^a (λ/nm)	$\Delta\varepsilon^a$ (λ/nm)
1	12.0 (247)	33000 (239)	10.7 (199)	64000 (198)	−1.5 (206)
	−4.5 (231)		−7.4 (187)		
2	−9.6 (248)	31700 (239)	−15.5 (199)	60700 (197)	2.8 (206)
	6.0 (230)		10.3 (187)		
3	10.5 (247)	33400 (239)	11.7 (200)	64100 (198)	weak
	−2.0 (228)		−7.2 (187)		
4	−28.4 (245)	32500 (239)	−28.2 (200)	63200 (197)	3.5 (208)
	6.6 (230)		21.0 (187)		
5	−33.5 (249)	51000 (240)	−25.5 (200)	92200 (198)	2.4 (207)
	13.5 (230)		26.6 (186)		
6	−22.4 (248)	50000 (241)	−9.3 (202)	86700 (198)	weak
	4.9 (231)		13.9 (189)		
7	12.7 (247)	34000 (239)	24.9 (201)	65000 (198)	−1.5 (210)
	−3.0 (227)		−14.0 (187)		
8	−51.6 (250)	66000 (241)	−53.7 (199)	114000 (198)	19.3 (208)
	27.0 (232)		55.9 (186)		
9	−20.7 (247)	66000 (240)	−24.5 (199)	115200 (195)	2.9 (207)
			6.5 (187)		
10	20.2 (248)	33200 (240)	17.6 (199)	60500 (198)	−8.4 (207)
	−12.0 (232)		−19.0 (186)		
11	28.6 (248)	34600 (241)	23.9 (200)	60100 (199)	weak
	−6.0 (230)		−22.4 (188)		
12	−8.4 (256)	64800 (242)	−17.5 (198)	111300 (198)	9.1 (208)
	8.8 (236)				
13	43.6 (248)	66200 (242)	35.1 (199)	112900 (198)	−13.5 (208)
	−16.2 (231)		−32.9 (186)		
14	−6.5 (254)	64800 (243)	−11.2 (198)	105500 (198)	12.4 (208)
	12.6 (240)		5.5 (188)		
15	7.7 (253)	66000 (241)	15.8 (198)	107000 (196)	−7.2 (207)
	−8.6 (237)		−11.8 (186)		
16	−33.7 (251)	65500 (242)	−30.5 (199)	105700 (198)	18.6 (208)
	13.3 (234)		36.0 (186)		
17	7.5 (257)	77000 (242)	29.8 (200)	124900 (198)	weak
	−7.4 (241)		−8.8 (186)		
18	−8.9 (253)	79100 (241)	−4.5 (199)	135500 (196)	8.3 (208)
	4.8 (233)		12.6 (186)		
19	28.2 (251)	79800 (242)	20.1 (200)	135000 (197)	−25.1 (209)
	−21.9 (234)		−22.6 (186)		
20	−31.1 (254)	94700 (242)	−21.3 (198)	160300 (195)	37.9 (208)
	23.5 (238)		18.1 (186)		

[a] in $\mathrm{mol^{-1}dm^3cm^{-1}}$

couplet associated with the 198 nm UV band is due to the ^1B_a transition. As an example the CD/UV spectrum of di(4-chlorobenzoate) derivative **2** is shown in Fig. 3.

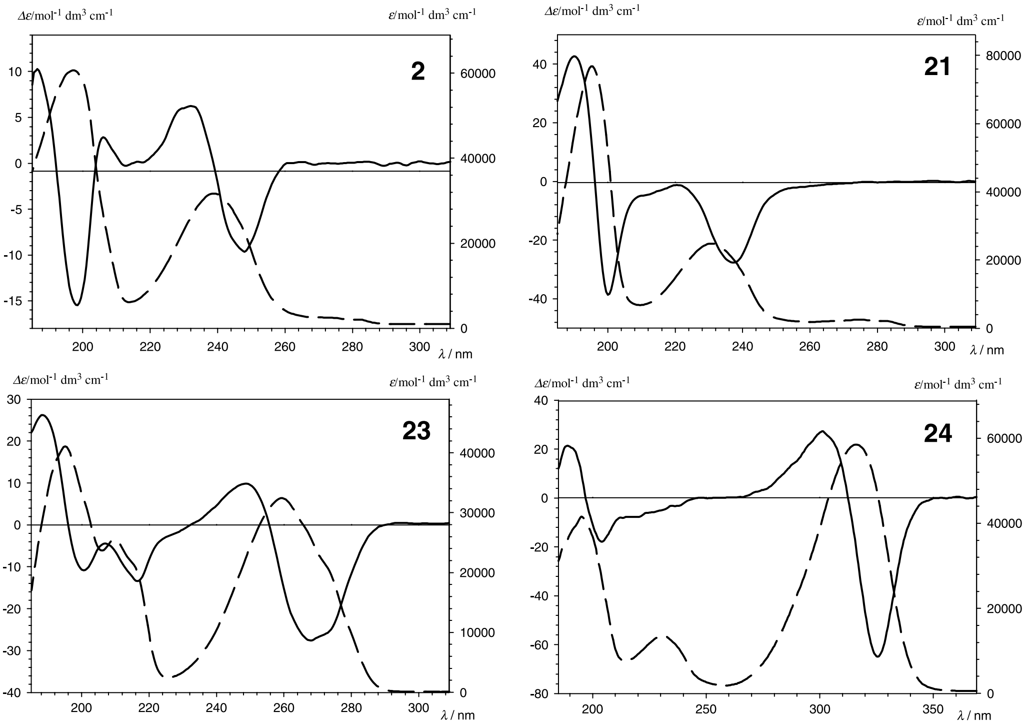
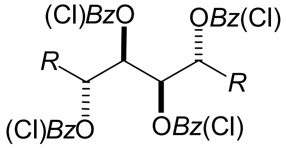


Fig. 3. CD/UV spectra of dibenzoates **2**, **21**, **23**, and **24** in acetonitrile solution

A strong support for the assignment comes from the comparison of 4-chlorobenzoate CT and ^1B_a *Cotton* effects. In all cases (**1**–**20**) the signs of these exciton *Cotton* effects are the same, as expected for chromophoric systems having transitions polarized in the same direction. It should be noted, however, that polarization directions of the CT and ^1B_a transitions are not identical. The former band, due to its charge-transfer character, is polarized into the direction of the carbonyl oxygen whereas in the latter the polarization direction is along the z axis. In very few cases (**9** and **12**) either the CT or ^1B_a *Cotton* effects do not have the appearance of the exciton couplet. This may be due to cancellation of the shorter-wavelength component of the exciton *Cotton* effect. Interestingly, in all cases (**1**–**20**) the sign of the 206–210 nm *Cotton* effect is opposite to that of the long-wavelength component of the exciton couplet of either the CT band or the ^1B_a band. We take it as an evidence of the origin of this *Cotton* effect, arising from interchromophoric coupling of the ^1B_b and ^1B_a transitions. It is expected that coupling of the ^1B_b transitions will not give strong rotational strengths since the oscillator strength of this transition is low compared to the ^1B_a transition. The relation between the CT band *Cotton* effect and the structure of di- and poly(4-chlorobenzoates) has been previously analyzed [12] and is not a subject of this work.

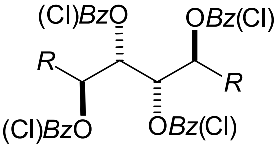
Whereas the signs of the *Cotton* effects due to the 4-chlorobenzoate CT band and ^1B_a band are the same, their amplitudes vary. For example, the amplitudes are comparable, for example in the case of **1**, **5**, and **12**, much higher for the ^1B_a band (**7**, **16**, and **17**), or higher for the CT band (**19** and **20**). Higher amplitudes of the *Cotton* effects can be expected for the ^1B_a band, since the ε value (a measure of the oscillator strength of the transition) of this band is *ca.* 1.6–1.9 times higher compared to the ε value of the CT band. The meaning of these differences is not obvious, as the true intensities of the *Cotton* effects in the range 210–185 nm are affected by overlapping ^1B_b and ^1B_a transitions.

Of interest are the differences in the magnitudes of ^1B_b *Cotton* effects of 4-chlorobenzoates **1**–**20** (Table 2). In many cases (**1**–**7**, **9**, **11**, and **17**) this *Cotton* effect is weak or moderate but in the remaining cases it is strong (**10**, **12**–**15**, and **18**) or very strong (**8**, **16**, **19**, and **20**). The latter four cases are structurally similar and can be represented by *anti*, *syn*, *anti* arrangement of the 4-chlorobenzoate moieties *inside* the polyol carbon chain (**A** or *ent*-**A**).



A, $\Delta\varepsilon_{208} \gg 0$

8, **16**, **20**



ent-**A**, $\Delta\varepsilon_{208} \ll 0$

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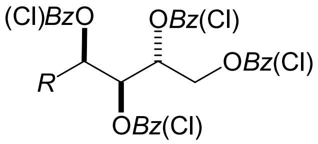
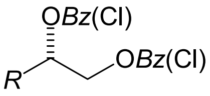
In all these structures at least one *R* group is not a hydrogen atom. The remaining six cases (**10**, **12**–**15**, and **18**) can be classified as *syn*, *anti* (**B**) or terminal (**C**).



B, $\Delta\varepsilon > 0$

12, **14**, **18**



C, $\Delta\varepsilon < 0$

10, **13**, **15**

Putting these data together one can assign the following contributions to the ^1B_b 208 nm *Cotton* effect in the acyclic D-polyol series to qualitatively determine its sign and magnitude (Fig. 4).

It should be added that successful correlation between the sign and approximate magnitude of the 208 nm *Cotton* effect and polyol configuration is due to the fact that this *Cotton* effect does not overlap with the manifold of *Cotton* effects of the ^1B transitions region. Note that lower members of the group (*glycero*, *erythro*, and *threo*) display low intensity *Cotton* effects due to the well-known conformational averaging effect [12, 17]. Compound **10** is an apparent exception, since due to the presence of the acetal ring its conformation is stabilized and the *Cotton* effects are much larger, compared to **1**.

Turning now to the series of 4-substituted benzoate derivatives **21**–**34** collected in Table 4 we note that with few exceptions separation of the *Cotton* effects

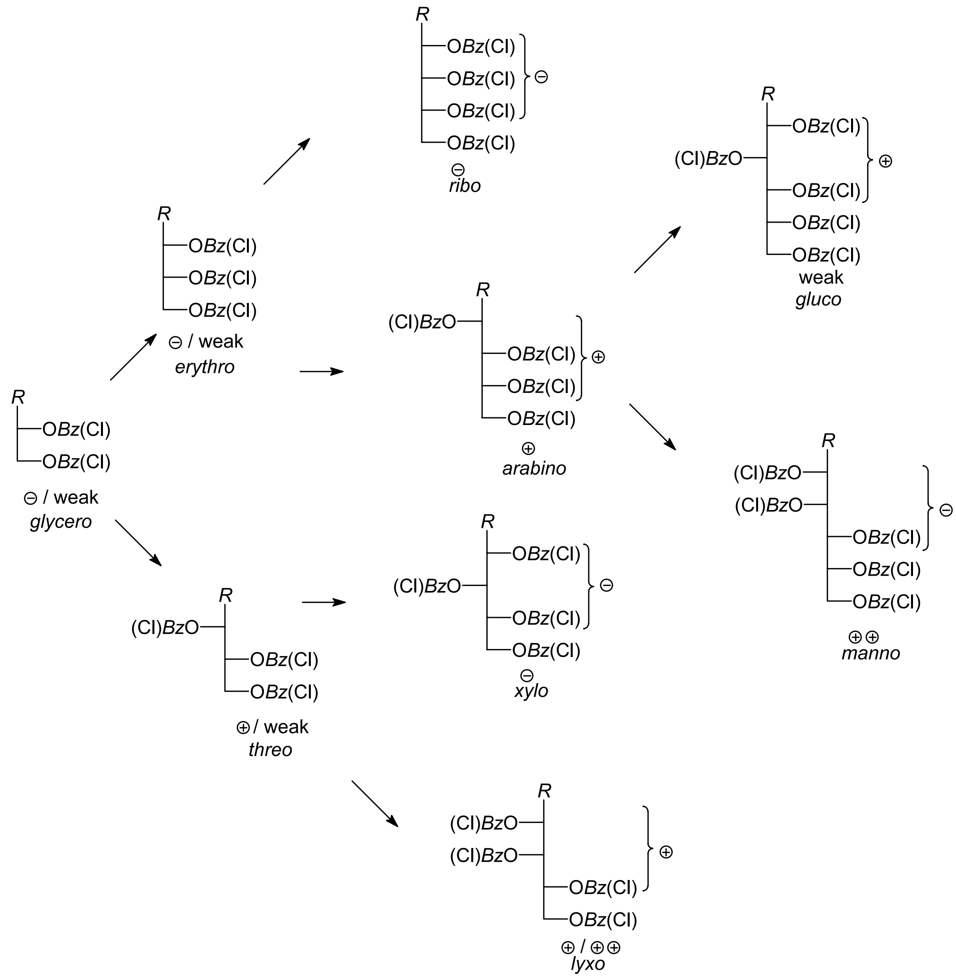


Fig. 4. Evolution of sign and magnitude of the 208 nm *Cotton* effect of D-polyol 4-chlorobenzoates as a function of configuration; the contributions of three-carbon units are marked with brackets

belonging to the ^1B_a and ^1B_b transitions is not possible. In fact, benzoates **21**, **25**, **29**, and **30** as well as 4-methylbenzoate **26** and 4-chlorobenzoates **22** and **27** derived either from (*R*,*R*)-diethyl tartrate or methyl hyodeoxycholate or methyl cholate show only one exciton couplet below 200 nm, associated with a single UV band at 195–199 nm.

As noted previously the benzoate CT exciton *Cotton* effect in several cases is monosignate rather than bisignate (**21**, **29**, and **31**), the short-wavelength ^1B_a CD couplet is of the same sign as the CT *Cotton* effect and the presence of ^1B_b band in most cases can only be inferred from the appearance of a weak shoulder on the CD curve at *ca.* 210 nm (see Fig. 3, **21**). The benzoate CT and ^1B_a bands of tartrates **21**–**24** are negative, due to the extended conformation of the tartrate four-carbon chain [18].

In the case of 4-methoxy- (**23**, **28**, and **31**–**34**) and 4-dimethylaminobenzoates (**24**) the CT bands are significantly red-shifted (see Table 1 and Fig. 3, **23** and **24**). The short-wavelength ^1B bands evidently split into presumably ^1B_b and ^1B_a

Table 4. Exciton *Cotton* effects of (4-substituted) benzoates **21–34** in acetonitrile solution

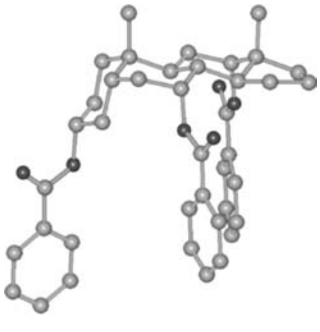
Compound no.	Benzoate CT band		Benzoate ^{1}B bands	
	$\Delta\varepsilon^a$ (λ/nm)	ε^a (λ/nm)	$\Delta\varepsilon^a$ (λ/nm)	ε^a (λ/nm)
21	−27.7 (238)	24800 (231)	−38.7 (200)	76800 (195)
			42.6 (190)	
22	−34.0 (250)	30000 (242)	−14.0 (202)	55200 (198)
	5.1 (232)		26.6 (188)	
23	−27.6 (268)	32400 (260)	−13.4 (217)	sh (210)
	9.8 (249)		−10.8 (200)	41100 (195)
			26.1 (189)	
24	−64.9 (326)	58500 (316)	−7 sh (230)	13500 (230)
	27.3 (301)		−17.9 (204)	41600 (195)
			21.3 (189)	
25	−18.5 (235)	25100 (229)	−16.2 (200)	78500 (195)
	2.2 (220)		14.8 (191)	
26	−23.5 (245)	30700 (237)	−16.7 (202)	67300 (199)
	4.4 (228)		14.5 (191)	
27	−27.8 (246)	34600 (239)	−13.7 (200)	61100 (198)
	6.5 (230)		11.4 (187)	
28	−22.9 (262)	33200 (255)	−13.0 (200)	40300 (196)
	8.7 (243)		11.8 (189)	
29	−4.4 (222)	23900 (228)	−55.2 (199)	77600 (194)
			18.4 (189)	
30	5.9 (237)	23400 (228)	21.1 (199)	73000 (195)
	−4.1 (229)		−13.7 (186)	
31	−6.3 (254)	34100 (253)	−35.1 (208)	43600 (196)
			11.2 (197)	
			−1.9 (188)	
32	6.5 (258)	34500 (254)	24.4 (207)	44300 (196)
	−1.5 (232)		−1.5 (195)	
			4.0 (186)	
33	4.4 (262)	32000 (254)	19.1 (201)	39100 (195)
	−3.5 (243)		−9.9 (188)	
34	1.1 (267)	46700 (252)	21.4 (199)	60000 (193)
	−4.1 (242)		−2.6 (187)	

[a] in $\mathrm{mol^{-1}dm^{3}cm^{-1}}$

components. In the case of **23** (Fig. 3 and Table 4) a shoulder appears in the UV spectrum at 210 nm (^1B_b band) and the ^1B_a band peaks at 195 nm, whereas the corresponding UV maxima for **24** appear at 230 and 195 nm. An important observation is that 4-methoxy and 4-dimethylamino substituents have no effect on the excitation energy of the benzoate ^1B_a band. However, there is a batochromic effect determining the position of the ^1B_b band, up to 30 nm in the case of 4-dimethylamino substituent. In addition, these substituents evidently reduce the oscillator strength of the ^1B_a transition. In consequence, the ε_{max} and the corresponding amplitudes of the *Cotton* effects fall in the sequence of benzoate 4-substituents: $\mathrm{H} > Me > \mathrm{Cl} > OMe > \mathrm{N}Me_2$. This observation is in agreement with the results derived by *Sagiv* [19] from linear dichroism measurements, *i.e*. the strong, allowed ^{1}B system is much less sensitive to benzene substitution pattern than the forbidden ^1L_a and ^1L_b transitions. The splitting of ^{1}B systems into a pair of components with orthogonal polarization could only be observed in the LD spectra in the case of benzene derivatives, 1,4-disubstituted with a strong donor–acceptor pair.

Another point of interest is high intensity of the ^{1}B band *Cotton* effects in cholic acid derivatives **29**–**34**. In these structures the C–O bonds are nearly parallel (3α *equatorial*, 7α and 12α *axial*, see structure **D**) and consequently the exciton *Cotton* effect of the benzoate derivatives should be small, if any. Indeed, this is the case with the benzoate and 4-methoxybenzoate CT band *Cotton* effects (Table 4), as previously observed [20]. Surprisingly, the *Cotton* effects of **29**–**34** in the ^{1}B bands region are intense (compare $\Delta\varepsilon$ $-4.4\,\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ at 222 nm with $A = -73.6$ at 199–189 nm for **29**), despite the unfavorable geometry of the chromophoric system. These high intensity *Cotton* effects apparently originate from strong contributions of the ^1B_b transitions, polarized orthogonally to either ^1L_a (CT) or ^1B_a transitions. In derivatives **29**–**34** at least one benzoate substituent is axial and therefore of restricted rotational freedom. Consequently, rotational averaging of the ^1B_b couplings in axial benzoates is less pronounced than in diequatorial benzoate derivatives **25**–**28**. The *Cotton* effects in the benzoate ^{1}B region of **29**–**34** are thus due to multiple $^1B_b/^1B_a$ (homo and hetero) couplings and the separation of component *Cotton* effects cannot be readily accomplished.

According to the additivity rule the CD spectrum of tri(4-methoxybenzoate) **34** should be the sum of the pair contributions, represented by di(4-methoxybenzoates) **31**–**33**. This is an exemplary case, since the steroid skeleton is rigid and the 4-methoxybenzoate chromophores are well separated. Therefore no significant anisoate groups' conformational changes are expected for variously substituted derivatives. Indeed, the CD spectrum of **34** matches satisfactorily the CD curve obtained by summation of the individual CD curves of **31**–**33** (Fig. 5).



D

In conclusion we have shown that unexplored until now the region of ^{1}B benzoate transitions can provide stereochemical information complementary to that obtained from the exciton *Cotton* effect of the benzoate CT transition. In particular, the lower energy *Cotton* effect of the 4-chlorobenzoate ^1B_a couplet

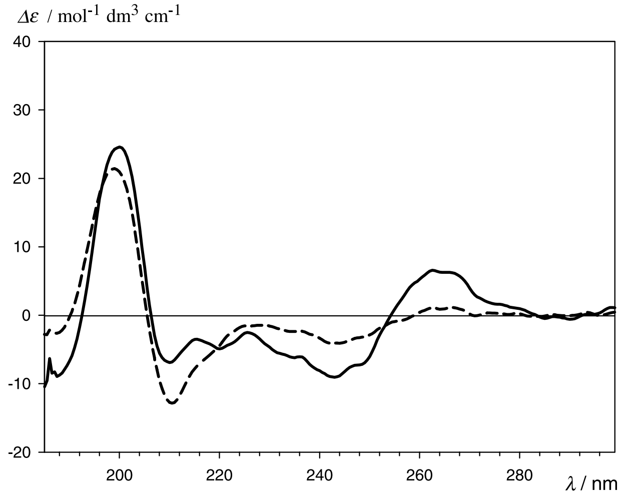


Fig. 5. Comparison of CD curves of **34**: ----- experimental, —— reconstructed by addition of CD curves of **31–33**

changes the sign and magnitude with polyol configuration, providing a tool for configurational assignment. Large exciton *Cotton* effects of 4-methoxybenzoates in the ^{1}B region were obtained for diols and triols having nearly parallel C–O bonds in the 5β-steroidal skeleton, whereas the corresponding ^1L_a region *Cotton* effects were weak. We also observed significant batochromic shift of the ^1B_b CD band in the case of benzoates having a donor methoxy or dimethylamino substituent, whereas the position of the ^1B_a band did not change upon substitution of the benzoate group. Low sensitivity to substitution of the strong benzoate ^1B_a band offers a possibility for using heterochromophoric coupling of this transition in the benzoate and the (substituted) benzene chromophores for stereochemical assignments. This application appears attractive since both the benzene ring and the hydroxy group (to which benzoate chromophores can be attached) are frequently encountered in chiral molecules. Last but not least, a high intensity of ^1B_a transitions in the benzene and benzoate chromophores assures large amplitudes of the exciton *Cotton* effects and consequently high sensitivity of the CD measurement.

Materials and Methods

Compounds references: **1**, **2**, **6**, **7**, **10**, **11**, and **25**–**34** [21]; **3** and **4** [22]; **5**, **8**, **9**, and **12**–**20** [12]; **21**–**24** [18]; **25** and **28**–**34** [20]. The CD and UV spectra were measured with a JASCO 810 spectropolarimeter. The computations were performed with the use of Gaussian 03 suite of programs [23].

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