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Correlation of the Circular Dichroism of Unsubstituted and Ring-Substituted Chiral Phenylcarbinamines with Their Absolute Configurations

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The sign of the ${}^1L_b$ Cotton effects (CEs) at about 250—270 nm of the benzene chromophore of unsubstituted chiral phenylcarbinamines and their salts is determined by vibronic borrowing from the ${}^1B_b$-allowed transition at shorter wavelength. For these chiral phenylcarbinamines and their salts of the same generic absolute configuration, the sign of their ${}^1L_b$ CEs is the same. On ring substitution, however, transition moments are induced in the benzene ring bonds adjacent to the attachment bond of the chiral group, resulting in enhanced coupling of the ${}^1L_b$ transition with the chiral group. Since the sign of the induced contribution to the ${}^1L_b$ CEs is determined by the spectroscopic moment of the ring substituent and its position with respect to the chiral group, the sign of the induced contribution may be predicted to be the same or opposite to that of the vibronic contribution. A reversal of the sign of the ${}^1L_b$ CEs with ring substitution is thus the overshadowing of a vibronic contribution by an induced contribution of opposite sign. When both the vibronic and induced contributions have the same sign, the sign of ${}^1L_b$ CEs is unchanged.

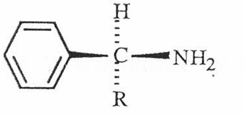
INTRODUCTION

Optical rotatory dispersion (ORD) and circular dichroism (CD) measurements have lead to rules for the correlation of the sign and magnitude of observed Cotton effects (CEs) with the stereoformulas of chiral compounds.[1] Among the best known are the octant rule,[2] the benzoate chirality rule,[3] and the salicylidenamino chirality rule,[4] applied, respectively, to chiral cyclic ketones, the benzoate derivatives of chiral alcohols and glycols, and the *N*-salicylidene derivatives of chiral primary amines. Substantial effort has also been made to correlate the CEs associated with the electronic transitions of aromatic chromophores in various chiral substances.[1,5] Most of this work was focused on utilization of the sign of the easily observed CEs associated with the ${}^1L_b$ transition of the benzene ring at about 250—270 nm,[1] and it was found that in general phenylcarbinamines and phenylcarbinols of the same generic configuration show the same sign for these ${}^1L_b$ CEs.[6,7] On ring substitution, however, the sign of the CEs may be the same or different from that of the unsubstituted parent.[6–9] Only recently, however, have these changes been explained on the basis of the spectroscopic moment[10] and ring position of the additional substituent.[7,9] These considerations have been used to correlate the absolute configurations of a substantial number of unsubstituted and ring-substituted phenylcarbinols with the sign of their respective ^1L_b CEs.[7] The same is now done here for unsubstituted and ring-substituted phenylcarbinamines.

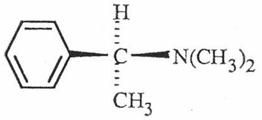
DISCUSSION

1. Unsubstituted Phenylcarbinamines

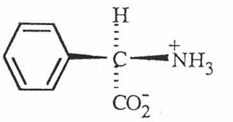
As reported earlier[9] and shown in Figure 1, (*S*)-α-phenylethylamine [(*S*)-*1a*] exhibits a number of positive ^1L_b CEs at about 250—270 nm associated with transitions from the totally symmetric vibrational mode in the ground state to totally symmetric vibrational modes in the excited state.[9] Positive ^1L_b CEs are also observed for its hydrochloride[9] [(*S*)-*1a*·HCl], and the EA and CD maxima for the ^1L_b band for *(S)-1a* and *(S)-1a* · HCl occur at about the same wavelengths with about the same respective magnitudes, the similarities for the EA and CD spectra of *(S)-1a* and *(S)-1b* · HCl being seen by comparison of the respective ^1L_b band origin maxima in Table I.



(*S*)-**1a**, R = CH_3
(*S*)-**1b**, R = $C(CH_3)_3$



(*S*)-**1c**



(*R*)-**1d**

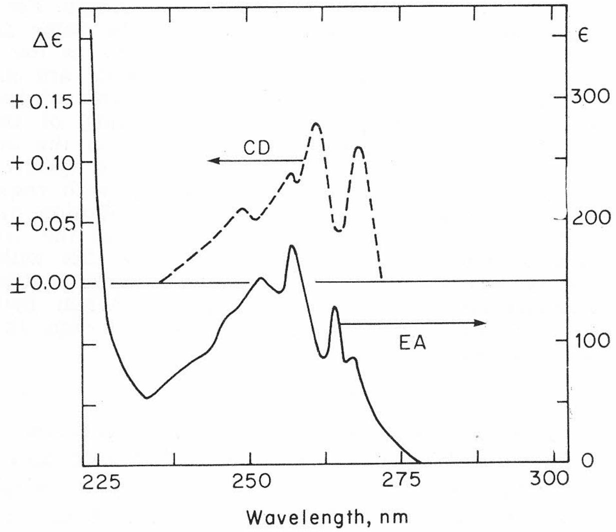
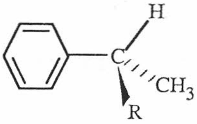


Figure 1. Isotropic electronic absorption (EA) and circular dichroism spectra of (*S*)-α-phenylethylamine [(*S*)-*1a*] in methanol.

Since in the preferred conformation of (*S*)-*1a* (*Ia*), the hydrogen atom at the chiral center essentially eclipses the phenyl ring plane, a change in the effective bulk size of the alkyl group or amino group at the chiral center is predicted not to alter the sign of the ^1L_b CEs from that of (*S*)-*1a* and (*S*)-*1a* · HCl. As predicted, (*S*)-α-phenylneopentylamine [(*S*)-*1b*], (*S*)-*N,N*-dimethyl-α-phenylethylamine [(*S*)-*1c*], and their respective salts all show positive ^1L_b CE, the sign being the same as that of the respective band origin CD maximum (Table I). the alkyl group is changed to a carboxylate [*R-1d*] or carboxyl group [(*R*)-*1d*·HCl], the sign is unchanged from that shown by (*S*)-*1a* (Table I).



Ia, R = NH_2

Ib, R = OH

TABLE I

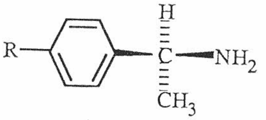
Spectral data for chiral unsubstituted phenylcarbinamines

	Solvent[a]	^1L_b Band origin		Ref.[d]
		λ_{max} [nm] (ε^b)	λ_{max} [nm] ($\Delta\varepsilon^c$)	
(*S*)-*1a*	M	267(86)	267(+0.11)	9
(*S*)-*1a*·HCl	M	267(120)	267(+0.082)	9
(*S*)-*1b*	I	269(50)[e]	268(+0.34)	6
(*S*)-*1b*·HCl	H	266(180)	266(+0.036)	6
(*S*)-*1c*	E	267(85)[e]	268(+0.026)	11
(*S*)-*1c*·HCl	E	268(170)	269(+0.12)	11
(*S*)-*1c*·CH_3I[f]	E	269(280)	269(+0.21)	11
(*R*)-*1d*[g,h]	W	[i]	268(+0.23)	12
(*R*)-*1d*·HCl[g]	E	268(130)	268(+0.22)	13

[a] Solvents: M, methanol; I, isooctane; H, 1,1,1,3,3,3-hexafluoro-2-propanol; E, ethanol; W, water. [b] Molar absorption coefficient. [c] Molar dichroic absorption: $\Delta\varepsilon = [\Theta]/3300$ where $[\Theta]$ is the molar ellipticity. [d] Report of spectral data and assignment of absolute configuration. [e] Shoulder. [f] *N,N,N*-trimethylammonium iodide derivative of (*S*)-*1a*. [g] D-amino acid. [h] Enantiomer used. [i] Not reported.

2. *Ring-Substituted Phenylcarbinamines*

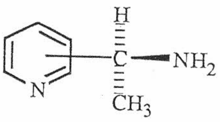
In the unsubstituted phenylcarbinamines (*S*)-*1a-d* and their salts, the sign of the ^1L_b CEs of the benzene chromophore is determined by vibronic borrowing form the allowed ^1B_b-transition at shorter wavelength.[14] On ring substitution by an atom or group with either a positive (CH_3, Cl) or a negative spectroscopic (CF_3) moment,[10] transition moments are induced in the benzene ring bonds adjacent to the attachment bond of the chiral group, resulting in enhanced coupling of the ^1L_b transition with the chiral group. The sign reversal from positive to negative for the ^1L_b CEs on *para* substitution of (*S*)-*1a* and (*S*)-*1a*·HCl by a group or atom with a positive spectroscopic moment[10] as in (*S*)-α-(*p*-methylphenyl)ethylamine [(*S*)-*2a*], (*S*)-α(*p*-chlorophenyl)ethylamine [(*S*)-*2b*], and their hydrochlorides [(*S*)-*2a,b*·HCl] (Table II), is the result of the overshadowing of a positive vibronic contribution as in (*S*)-*1a* and (*S*)-*1a*·HCl by a negative induced contribution in (*S*)-*2a,b* and (*S*)-*2a,b*·HCl. On *para* substitution with a group with a negative spectroscopic moment,[10] as in (*S*)-α-(*p*-(trifluoromethyl)phenyl)ethylamine [(*S*)-*2c*] and its hydrochloride [(*S*)-*2c*·HCl] (Table II), bond moments of an opposite sense are induced in the benzene ring bonds adjacent to the attachment bond of the chiral group. The resulting positive induced contribution to the rotational strength has the same sign as the vibronic contribution. As a result both (*S*)-*2c* and (*S*)-*2c*·HCl show positive ^1L_b CEs (Table II).



(*S*)-**2a**, R = CH_3

(*S*)-**2b**, R = Cl

(*S*)-**2c**, R = CF_3



(*S*)-**3a**, 4-pyridyl

(*S*)-**3b**, 3-pyridyl

(*S*)-**3c**, 2-pyridyl

TABLE II

Spectral data for ring-substituted chiral α-phenylethylamines[a]

Compound	^1L_b Band origin		Ref.[d]
	λ_{max} [nm] (ε[b])	λ_{max} [nm] (Δε[c])	
(*S*)-*2a*	273(310)	273(—0.027)	9
(*S*)-*2a*·HCl	271(170)	271(—0.061)	9
(*S*)-*2b*[e]	276(240)	276(—0.061)	9
(*S*)-*2b*·HCl[e]	274(140)	274(—0.061)	9
(*S*)-*2c*	268(240)	269(+0.18)	9
(*S*)-*2c*·HCl	268(480)	268(+0.16)	9
(*S*)-*3a*	262(1600)[f]	[g]	15
(*S*)-*3b*	267(2100)[f]	268(—0.97)	15
(*S*)-*3c*	267(2900)[f]	267(+0.97)	15

[a] Methanol as solvent. [b] Molar absorption coefficient. [c] Molar dichroic absorption: $\Delta\varepsilon = [\Theta]/3300$ where $[\Theta]$ is the molar ellipticity. [d] Report of spectral data and assignment of absolute configuration. [e] Enantiomer used. [f] Shoulder. [g] No Cotton effect observed.

Similarly, for (*S*)-1-(4-pyridyl)ethylamine [(*S*)-*3a*], the aza group, in a position analogous to substituent *para* to the chiral group and with a negative spectroscopic moment,[10] should result in a positive induced contribution to ^1L_b CEs. This induced contribution, augmenting the positive vibrational contribution, should result in positive ^1L_b CEs for (*S*)-*3a*. No CE associated with the allowed ^1L_b electronic transition at 260—270 nm, however, was observed (Table II).*

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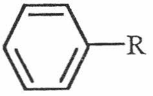
* The CD of several pyridine derivatives has also been described by N. Berova *et al.* at the First International Conference on Circular Dichroism, Sept. 21—25, 1985 in Sofia, p. 303 of Conference Proceedings.

On the other hand, the sign of the observed ^1L_b CEs for *(S)*-1-(3-pyridyl) ethylamine [(*S*)-*3b*] and (*S*)-1-(2-pyridyl)ethylamine [(*S*)-*3c*] are correctly predicted when the spectroscopic moment of the aza group is taken into consideration. Thus a *meta* substitutent with a negative spectroscopic moment, analogous to the aza group in (*S*)-*3b*, will induced bond moments in the opposite sense to that induced by the same group in the *para* position,[9,16] and an *ortho* substitutent with a negative spectroscopic moment, analogous to the aza group in (*S*)-*3c*, again reverses the sense of the induced bond moments from that of the same *meta* substitutent.[16] Assuming also that there is no change in the preferred conformation of the chiral group about its attachment bond to the benzene ring as a result of the change in position of the aza group in the ring, the aza group in (*S*)-*3b* induces a negative contribution to the ^1L_b CEs which overrides the positive vibronic contribution,[7] and the sign of the observed CEs for *(S)*-*3b* is negative (Table II). The induced contribution for (*S*)-*3c* is positive, the same sign as that of the vibronic contribution, and the sign of the observed ^1L_b CEs for (*S*)-*3c* is positive (Table II), the same as that of the parent amine (*S*)-*1a* (Table I).

3. *Effect of the Spectroscopic Moment of the Chiral Group*

The conclusion that the sign of the ^1L_b CEs for the chiral unsubstituted phenylcarbinamines[9] and phenylcarbinols[7] is determined by vibronic borrowing from the rotational strength of the ^1B_b-allowed transition[14] is supported by the observation that the sign of the ^1L_b CEs in the unsubstituted parent amine, (*S*)-*1a*, and its hydrochloride, (*S*)-*1a*·HCl, does not depend on the respective spectroscopic moments of the chiral groups. These spectroscopic moments may be determined on the basis of the molar absorption coefficient (ε) of the ^1L_b band origins for *(S)*-*1a* and *(S)*-*1a*·HCl, of benzene with a single ring substituent (Table III), and of the corresponding *para*-substituted compound.[18] Thus (*S*)-α-(*p*-methylphenyl)ethylamine [(*S*)-*2a*] and (*S*)-α-(*p*-chlorophenyl) ethylamine [(*S*)-*2b*] have ^1L_b band origins with molar absorption coefficients (Table II) each greater than that of (*S*)-α-phenylethylamine [(*S*)-*1a*] (Table I) and of the respective ring-substituted benzene compound, toluene (*4a*) and chlorobenzene (*4b*) (Table III). Since the positive spectroscopic moments of the methyl group and chlorine atom[10] augment that of the chiral group in (*S*)-*2a* and (*S*)-*2b*, this particular chiral group must also have a positive spectroscopic moment.[18] Also (*S*)-α-(*p*-(trifluoromethyl)phenyl)ethylamine [*(S)*-*2c*] has a molar absorption coefficient (Table II) greater than that of *(S)*-*1a* (Table I) but smaller than that of (trifluoromethyl)benzene (*4c*) (Table III). The negative spectroscopic moment of the trifluoromethyl group[10] is partially cancelled by the positive spectroscopic moment of the chiral group in *(S)*-*2c*.[18]



4a, R = CH_3

4b, R = Cl

4c, R = CF_3

TABLE III

Isotropic absorption data for substituted benzene compounds

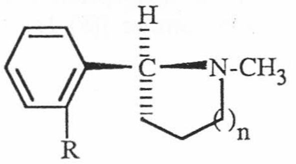
Compound	Solvent[a]	${}^{1}L_{b}$ Band origin, λ_{max} [nm] (ε^{b})	Ref.[c]
4a	C	269(250)	17
4b	M	272(200)	7
4c	M	266(380)	7

[a] Solvent: C, cyclohexane; M, methanol. [b] Molar absorption coefficient. [c] Report of absorption data.

Using the EA spectral data in Tables I—III, it similarly can be shown that the chiral group in the hydrochloride salts of (*S*)-*1a*, (*S*)-*2a*, and (*S*)-*2b* is negative. Thus both (*S*)-*1a* and (*S*)-*1a*·HCl exhibit positive ${}^{1}L_{b}$ CEs despite the fact that their respective chiral grouping has oppositely signed spectroscopic moments.

4. *2-Phenyl Heterocyclic Amines*

As shown in Table IV, the circular dichroism has been reported for a number of chiral unsubstituted and ring-substituted analogues of (*S*)-α-phenylethylamine [(*S*)-*1a*] in which the amino group is part of a heterocyclic ring. For (*S*)-*N*-methyl-2-phenylpyrrolidine [(*S*)-*5a*] and (*S*)-*N*-methyl-2-phenylpiperidine [(*S*)-*5b*], the preferred conformation of each heterocyclic ring about it attachment bond to the benzene ring is such that the tertiary amino atom and the C(3) methylene group are in the same disposition with respect to the benzene ring plane as is the amino group and methyl group in (*S*)-*1a* (*Ia*), the hydrogen atom of the chiral center in (*S*)-*1a*, (*S*)-*5a*, and (*S*)-*5b* eclipsing the benzene ring plane. On this basis, the sign of the ${}^{1}L_{b}$ CEs for both (*S*)-*5a* and (*S*)-*5b* are predicted to be positive as is observed (Table IV).[19,20]

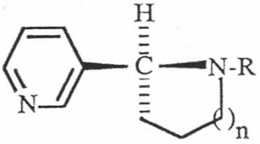


(*S*)-**5a**, n = 1; R = H

(*S*)-**5b**, n = 2; R = H

(*S*)-**5c**, n = 1; R = CH$_3$

(*S*)-**5d**, n = 2; R = CH$_3$



(*S*)-**6a**, n = 1; R = H

(*S*)-**6b**, n = 1; R = CH$_3$

(*S*)-**6c**, n = 2; R = H

(*S*)-**6d**, n = 2; R = CH$_3$

Substitution of the benzene ring at the *ortho* position by a methyl group causes a negative induced contribution to the ${}^{1}L_{b}$ CEs, and the observed ${}^{1}L_{b}$ CEs for (*S*)-*N*-methyl-2-(*o*-methylphenyl)pyrrolidine [(*S*)-*5c*] and (*S*)-*N*-methyl-2-(*o*-methylphenyl)piperidine [(*S*)-*5d*] are positive (Table IV).[19,20]

A similar analysis explains the negative ${}^{1}L_{b}$ CEs for (*S*)-nornicotine [(*S*)-*6a*], (*S*)-nicotine [(*S*)-*6b*], (*S*)-anabasine [(*S*)-*6c*], and (*S*)-*N*-methylanabasine

TABLE IV

Circular dichroism data fo chiral 2-phenyl heterocyclic Amines

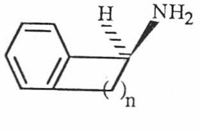
Compound	Solvent[a]	^1L_b Band origin, λ_{max} [nm] ($\Delta\varepsilon^b$)	Ref.[c]
(S)-5a	C	266(+0.030)	19
(S)-5b	C	273(+0.079)	20
(S)-5c	C	270(—0.052)	19
(S)-5d	C	273(—0.027)	20
(S)-6a	W	261(—1.3)[d]	21
(S)-6b	W	263(—1.6)[d]	21
(S)-6c	W	263(—1.1)[d]	21
(S)-6d	W	264(—1.2)[d]	21

[a] Solvent: C, cyclohexane; W, water, pH 11.5. [b] Molar dichroic absorption: $\Delta\varepsilon = [\Theta]/3300$ where $[\Theta]$ is the molar ellipticity. [c] Report of CD data and assignment of absolute configuration. [d] Only one ^1L_b CD maximum reported.

[(*S*)-*6d*]. In each of these (*S*)-3-pyridylcarbinamine analogous of (*S*)-*1a*, the amino atom and the methyl group have a disposition with respect to the aromatic ring as that in (*S*)-*1a* (*Ia*). This arrangement results in a positive vibronic contribution to the ^1L_b CE which is overshadowed by a negative induced contribution by the aza group, with a negative spectroscopic moment in a position equivalent to the *meta* position of a benzene ring substitutent. Thus the observed ^1L_b CEs for (*S*)-*6a-d* are all negative (Table IV).[21]

5. *Chiral 1-Aminobenzocycloalkenes*

The sign of the ^1L_b CEs shown by the bicyclo analogues (*S*)-*8a-c* of (*S*)-α-phenylethylamine [*(S)-1a*] (Table V) can also be related to that of the ^1L_b CEs of (*S*)-*1a*. Since 1-aminobenzocyclobutene [(*S*)-*8a*], (*S*)-1-aminohydrindan [(*S*)-*8b*], and 1-amino-1,2,3,4-tetrahydronaphthalene [(*S*)-*8c*] can be considered to be *ortho*-substituted phenylcarbinamines, the negative sign of the respective ^1L_b CEs (Table V) is the result of an overriding negative induced contribution



(*S*)-8a, n = 1

(*S*)-8b, n = 2

(*S*)-8c, n = 3

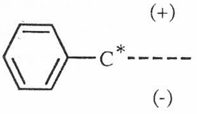
to the CEs by the methylene substituent with its positive spectroscopic moment. Since the vibronic contribution for such an *ortho*-substituted phenylcarbinamine (Table IV) is of opposite sign to that of the induced contribution, a positive vibronic contribution requires the signs shown on quadrant projection II. These signs give the circular dichroism contribution by groups lying in the four quadrants to the vibronic contribution to the ^1L_b CEs. The algebraic sum of these contributions give the sign to the vibronic contribution, and the signs for the quadrants follow from the assumption that the contribution of the amino group in (*S*)-*8a-c* is larger than that of the hydrogen atom, thus resulting in a positive vibronic contribution to the ^1L_b CEs. In

TABLE V

Sepctral data for chiral 1-aminobenzocycloalkenes[a]

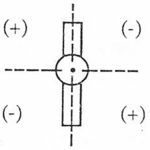
Compound	^1L_b Band origin		Ref.[d]
	λ_{max} [nm] (ε[b])	λ_{max} [nm] ($\Delta\varepsilon$[c])	
(*S*)-*8a*	273(1300)[e]	274(—)[f]	22
(*S*)-*8b*	273(800)[g]	274(—0.06)[h]	22
(*S*)-*8b*·HCl	272(1000)	271(—0.39)	23
(*S*)-*8c*	274(320)[i]	274(—0.14)	22

[a] Methanol as solvent. [b] Molar absorption coefficient. [c] Molar dichroic absorption: $\Delta\varepsilon = [\Theta]/3300$ where $[\Theta]$ is the molecular ellipticity. [d] Report of CD data and assignment of absolute configuration. [e] An additional inflection at 280 nm (ε 410) assumed not to be the ^1L_b band origin. [f] A negative maximum observed only as an inflection on a strong positive background curve. [g] An additional shoulder at 280 nm (ε 290) assumed not to be the ^1L_b band origin. [h] Shoulder. [i] An additioal shoulder at 281 nm (ε 68) assumed not to be the ^1L_b band origin.



upper quadrants

IIa



all quadrants

IIb

agreement with this analysis and on the basis of a larger contribution by a methyl group than by an hydroxyl group, positive ^1L_b CEs are predicted and are observed[7] for (*S*)-α-phenylethyl alcohol (*Ib*). The relative magnitude of the contribution by a methyl group as compared to that by an hydroxyl group is probably related to the effective bond transition moments of their attachment bonds to the chiral center, that of a carbon-carbon bond greater than that of a carbon-oxygen bond.[24] Assuming that the effective bond transition moment of a carbon-carbon bonds is also larger than that of a carbon-nitrogen bond, the sign od the ^1L_b CEs for the unsubstituted chiral phenylcarbinamine (*S*)-*1a-d* and their salts (Table I) and the unsubstituted chiral 2-phenyl heterocyclic amines (*S*)-*5a,b* (Table IV) are also correctly predicted to be positive using quadrant projection II.

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SAŽETAK

Korelacija cirkularnog dikroizma nesupstituiranih i u prstenu supstituiranih kiralnih fenilkarbinamina i njihove apsolutne konfiguracije

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Predznak $^{1}L_b$ Cottonova efekta (CE) benzenskog kromofora 250—270 nm za nesupstituirane kiralne fenilkarbinamine i njihove soli određen je vibronskom »posudbom« od $^{1}B_b$-dozvoljenog prijelaza kod kraćih valnih duljina. Za ove kiralne fenilkarbinamine i njihove soli iste generičke apsolutne konfiguracije, predznak $^{1}L_b$ CE je jednak. Nakon supstitucije prstena dolazi međutim do indukcije prijelaznih momenata u cezama benzenskog prstena koje su u susjedstvu veze prema kiralnoj skupini, što rezultira povećanim sprezanjem $^{1}L_b$ prelaza s kiralnom skupinom. Budući da je predznak induciranog doprinosa $^{1}L_b$ vrijednosti CE određen spektroskopskim momentom i položajem supstituenata na prstenu s obzirom na kiralnu skupinu, predznak induciranog doprinosa može biti isti ili suprotan od onoga za vibronski doprinos. Promjena predznaka za $^{1}L_b$ CE tako je rezultat prekrivanja (zasjenjenja) vibronskog doprinosa s induciranim doprinosom suprotnog predznaka. Kada i vibronski i inducirani doprinos imaju isti predznak, tada predzna $^{1}L_b$ CE ostaje nepromijenjen.