Optically Active Amines. 41.[1] Application of the Benzene Chirality Rule to Chiral Ring-Substituted Benzylcarbinamines and Benzylcarbinamine Salts

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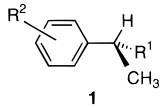
Abstract: The sign of the ^1L_b Cotton effects (CEs) of the benzene chromophore from about 240 to 270 nm in the circular dichroism (CD) of enantiomers of ring-substituted chiral benzylcarbinamines and benzylcarbinamine salts are correlated with their absolute configurations using the benzene sector rule and a consideration of the equilibrium between their two conformers of lowest energy and of oppositely signed rotatory power. These CEs are the result of vibronic borrowing from allowed transitions of the benzene chromophore at shorter wavelength, but an induced rotatory contribution, the sign of which may be predicted using the benzene chirality rule, is small compared to the vibronic contribution and need not be considered when predicting the sign of the ^1L_b CEs.

In an earlier report,[1] an outline was given for the correlation of the sign of the ^1L_b Cotton effects (CEs) from about 240 to 270 nm in the circular dichroism (CD) of enantiomers of chiral benzylcarbinamines and benzylcarbinols with their absolute configurations using the benzene sector rule.[3,4] This rule was initially formulated for the correlation of the sign of the ^1L_b CEs of phenylcarbinamines and phenylcarbinols, such as (*R*)-α-phenylethylamine[5] [(*R*)-**1a**, Table 1] and (*R*)-α-phenylethyl alcohol[6] [(*R*)-**1b**], with their absolute configurations. The CEs are associated with transitions from the lowest energy vibrational mode in the ground state to totally symmetric vibrational modes in the ^1L_b electronically excited state of the benzene chromophore[8,9] and are the result of vibronic borrowing[10,11] from allowed transitions at shorter wavelength. Only the molar absorptivities (ϵ) and molar dichroic absorptions ($\Delta\epsilon$) of the ^1L_b band origin for (*R*)-**1a** and (*R*)-**1b** are shown in Table 1, with complete electronic absorption (EA) and CD data given in references in the table.

For benzene compounds with a contiguous hydrogen-substituted chiral center, empirical potential function and molecular orbital calculations and various diffraction and jet laser spectroscopic measurements indicate that the preferred conformation both in the gas phase and in solution is such that the hydrogen atom at the chiral center eclipses the benzene ring plane (**2**).[3,12] This conformational preference and the CD data for a substantial number of chiral benzene compounds without an additional ring substituent give the quadrant projection **3**, which shows the sign of the rotatory contributions to the ^1L_b CEs by an atom or group attached to the contiguous chiral center and lying in a particular sector. The sector boundaries shown in **3** are defined by the attachment bond of the chiral center and the benzene ring plane. The sum of the rotatory contributions gives the sign to the observed ^1L_b CEs.

Using the CD data for the enantiomers of other benzene compounds with a single chiral substituent, sequences for the

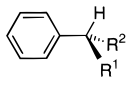
Table 1. ^1L_b Band Origin Maxima for Phenylmethylcarbinamines and Phenylmethylcarbinol in Methanol



1

compd	R^1	R^2	EA λ, nm (ϵ^a)	CD λ, nm ($\Delta\epsilon^b \times 10^2$)	ref[c]
(*R*)-**1a**[d]	NH_2	H	267 (86)	268 (−11)	5
(*R*)-**1b**	OH	H	267 (90)	268 (−17)	6
(*R*)-**1c**	NH_2	*p*-Cl	276 (240)	276 (+6.1)	5
(*R*)-**1d**[d]	NH_2	*p*-CF_3	268 (240)	269 (−18)	5
(*R*)-**1e**[d]	NH_2	*m* -Cl	274 (200)	274 (−24)	7
(*R*)-**1f**[d]	NH_2	*m*-CF_3	271 (550)	271 (−11)	7
(*R*)-**1g**	NH_2	*o*-Cl	273 (160)	273 (+5.8)	7
(*R*)-**1h**[d]	NH_2	*o*-CF_3	271 (950)	270 (−25)	7

[a] Molar absorptivity. [b] Molar dichroic absorption. [c] Report giving complete EA and CD spectra. [d] Enantiomer used.



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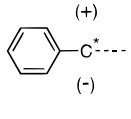
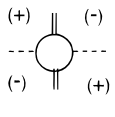


near sectors

3a



all sectors

3b

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rotatory contributions of attached groups and atoms have been established:[3,13]

$$SH, CO_2^-, C(CH_3)_3 > CH_3 > NH_2, {}^+NH_3, {}^+N(CH_3)_3, OH, OCH_3, Cl, F$$

and

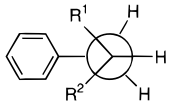
$$CH_3 > CO_2H > {}^+NH_3, OH, OCH_3$$

These sequences, when used in connection with the sector signs in **3**, have a general usefulness for the establishment by CD measurement of the absolute configurations of chiral benzene compounds in which one substituent at a contiguous chiral center is a hydrogen atom, the sign of the ^1L_b CEs depending only on the chirality of the chiral center immediately attached to the benzene ring.[4]

For chiral phenylcarbinamines, -carbinamine salts, and -carbinols with additional ring substituents, an induced rotatory contribution influences the sign of the ^1L_b CEs,[7] and the sign may be the same as or different from that of the nonsubstituted parent, depending on the spectroscopic moment[14] and ring positions of the additional substituents.[5−7] The reversal of the sign for the ^1L_b CEs on para substitution of (*R*)-α-phenylethylamine [(*R*)-**1a**] by an atom or group with a positive spectroscopic moment can be viewed as the overshadowing of the negative vibronic rotational strength by a positive induced contribution, and (*R*)-α-(*p*-chlorophenyl)ethylamine [(*R*)-**1c**] has positive ^1L_b CEs (Table 1). On para substitution by a group with a negative spectroscopic moment, the induced contribution to the ^1L_b rotational strength has the same sign as the vibronic contribution. Thus, (*R*)-α-[(*p*-(trifluoromethyl)phenyl]ethylamine [(*R*)-**1d**] has negative ^1L_b CEs. Meta substitution by an atom or group will result in an induced contribution with an opposite sign from that caused by the same group in the para position. Thus, for (*R*)-α-(*m*-chlorophenyl)ethylamine [(*R*)-**1e**], both the vibronic and induced contributions to the ^1L_b CEs are negative, and (*R*)-**1e** shows strong negative ^1L_b CEs. For meta substitution by a trifluoromethyl group with a negative spectroscopic moment, the induced contribution is of opposite sign to that of the vibronic contribution. Since the latter is more important than the former, the sign of the ^1L_b CEs of (*R*)-**1f** is unchanged from that of (*R*)-**1a**. Ortho substitution again reverses the sense of the induced bond transition moments from that induced by the same meta substitution, and (*R*)-α-(*o*-chorophenyl)ethylamine [(*R*)-**1g**] shows positive ^1L_b CEs, while those of (*R*)-α-[*o*-(trifluoromethyl)phenyl]ethylamine [(*R*)-**1h**] are negative.

If the vibronic and induced contributions to the ^1L_b CEs have the same sign, the sign of a particular ring-substituted benzene compound can be predicted with certainty. When the vibronic and induced contributions to the ^1L_b CEs are of opposite sign, a prediction to the sign of the ^1L_b CEs shown by a particular enantiomer is somewhat ambiguous. However, all of the phenylalkylcarbinamines and -carbinols so far reported that are ortho- and para-substituted with an atom or group having a positive spectroscopic moment (CH_3, Cl, Br, OH, OCH_3) show ^1L_b CEs of opposite sign to that of their unsubstituted parent.[5−7,13,15−21] For phenylalkylcarbinamines and -carbinols having a group with a negative spectroscopic moment (CN, CF_3) in the meta position, the sign of the ^1L_b CEs is not changed from that of the unsubstituted parent.[7]

A chiral center separated by a methylene group from a benzene ring also results in ^1L_b CEs from about 240 to 270 nm in the CD spectra of enantiomers of benzylcarbinamines, -carbinamine salts, and -carbinols, and the sign of these CEs is correlated with the absolute configuration of the respective chiral center using the benzene sector rule.[1] For application of the benzene sector rule to the circular dichroism of phenylcarbinamines, -carbinamine salts, and -carbinols, only conformer **2,** in which the hydrogen atom at the chiral center eclipses the benzene ring plane, need be considered. For benzylcarbinamines, -carbinamine salts, and -carbinols, however, there is greater conformational mobility of the attached group with respect to the benzene ring, and an equilibrium between conformers (−)-**4** and (+)-**4** (Table 2) must be considered when relating the sign of the ^1L_b CEs of such compounds. The two



(±)-**4**

conformers of lowest energy, (−)-**4** and (+)-**4**, follow from the preferred conformation determined by supersonic molecular jet laser[22] and microwave[23] spectroscopy of various alkylbenzenes in the gas phase, including ethylbenzene[22] and 2-phenylethylamine,[23] in which the carbon−carbon bond α,*β* to the benzene ring is orthogonal to the benzene ring plane. Conformer (±)-**4** need not be considered because the gauche interactions of R^1 and R^2 with the benzene ring make it of higher energy than (−)-**4** or (+)-**4**. Since the rotatory contribution of a hydrogen atom attached at the chiral center is insignificant and that of a group in a sector boundary is also small, the benzene sector rule gives the rotatory contributions of (−)-**4** and (+)-**4** as negative and positive, respectively.

Thus, (*R*)-2-amino-1-phenylpropane [(*R*)-**4a**, Table 2] in methanol shows negative ^1L_b CEs. The negative sign is the result of the greater rotatory contribution of (−)-**4** as compared to (+)-**4**, both the greater rotatory contribution of a methyl group compared to that of an amino group[3] and the respective mole fractions of (−)-**4** and (+)-**4** coming into play. The positive sign for the ^1L_b CEs of (*R*)-**4a** in cyclohexane is the result of a shift in the equilibrium from (−)-**4** to (+)-**4** due to diminished hydrogen bonding of the solvent to the amino group and a stabilizing interaction of the amino group with the benzene ring moiety.[23] (*R*)-2-Amino-1-phenylpropane hydrochloride [(*R*)-**4a**·HCl] in water and methanol and (*R*)-1-phenyl-2-propanol [(*R*)-**4b**] in methanol and cyclohexane show negative ^1L_b CEs, the sign being the result of the greater importance of (−)-**4** as compared to (+)-**4** in these solvents. L-Phenylalaninol (L-**4c**), L-phenylalanine (L-**4d**), and some of the derivatives of L-**4d** in some solvents show both positive and negative maxima in their ^1L_b CD spectra.[1] Thus, L-**4c** in methanol and L-**4d** in water

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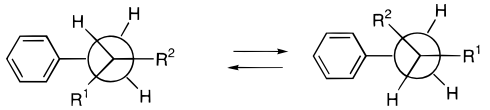
Table 2. ^1L_b Band Origin Maxima for Benzylcarbinamines and Phenylalanine[a]



(-)-**4** (+)-**4**

compd	R^1	R^2	solvent	EA λ, nm (ϵ^b)	CD λ, nm ($\Delta\epsilon^c \times 10^2$)
(*R*)-**4a**	CH_3	NH_2	MeOH	267 (120)	269 (−3.0)
(*R*)-**4a**[d,e]	CH_3	NH_2	cyclohexane	268 (150)	268 (+4.5)
(*R*)-**4a**·HCl	CH_3	N^+H_3	H_2O	*f*	266 (−1.3)
(*R*)-**4a**·HCl	CH_3	N^+H_3	MeOH	267 (77)[g]	267 (−3.3)
(*R*)-**4b**	CH_3	OH	MeOH	267 (120)	268 (−5.5)
(*R*)-**4b**	CH_3	OH	cyclohexane	*f*	269 (−1.7)
L-**4c**	CH_2OH	NH_2	MeOH	267 (130)	269 (−3.3)
L-**4c**	CH_2OH	NH_2	cyclohexane	*f*	271 (−1.4) 267 (+0.91)
L-**4d**	CO_2^-	N^+H_3	H_2O	*f*	265 (+1.1)
L-**4d**	CO_2^-	N^+H_3	MeOH	267 (77)[g]	269 (−0.64) 265 (+0.14)
L-**4d**·NaOH[h]	CO_2^-	NH_2	H_2O	*f*	271 (−0.12) 266 (+1.5)
L-**4d**·KOH[i]	CO_2^-	NH_2	MeOH	268 (110)	270 (−0.64) 266 (+0.82)

[a] Complete EA and CD spectra given in ref 1 except as noted otherwise. [b] Molar absorptivity. [c] Molar dichroic absorption. [d] Complete EA and CD data given in ref 5. [e] Enantiomer used. [f] Data not reported. [g] Shoulder. [h] L-**4d** in 1 M NaOH in H_2O. [i] L-**4d** in 0.1 M KOH in MeOH.

show ^1L_b CEs of only one sign, but L-**4c** in cyclohexane and L-**4d** in methanol show both negative and positive ^1L_b CEs. For L-**4c** in cyclohexane, the two longest wavelength maxima comprise a double CE[24] associated with the band origin maxima at about 267 nm. On changing the solvent from methanol to cyclohexane, the conformational equilibrium of L-**4c** is shifted from (−)-**4** toward (+)-**4**, and the increased amount of (+)-**4** is now detected in the CD spectrum. Thus, the negative and positive CD maxima at 271 and 267 nm, respectively, arise from different wavelength absorption maxima for the two conformers of lowest energy, the negative absorption at a slightly longer wavelength due to the influence of the hydroxymethylene group gauche to the benzene chromophore. A similar interpretation accounts for the observation of the double CEs in the CD spectra of L-**4d** in methanol, in aqueous sodium hydroxide, and in methanolic potassium hydroxide.

For application of the benzene chirality rule as it applies to the correlation of the configurations of ring-substituted chiral benzylcarbinamines, -carbinamine salts, and -carbinols, we have now measured the EA and CD spectra of a number of such compounds (Table 3). These CD data, along with those reported earlier,[5,19,21] were used to correlate the sign of the observed ^1L_b CEs with their absolute configurations.

Results and Discussion

Para-Substituted Benzylmethylcarbinamines. Figure 1 shows the electronic absorption (EA) and circular dichroism (CD) spectra of (*S*)-2-amino-1-(*p*-chlorophenyl)propane hydrochloride in methanol [(*S*)-**5a**·HCl in 0.1 M KOH in methanol]. In the EA spectrum, only transitions to totally symmetric vibrational states are observed, and a positive Cotton effect (CE) is associated with each of these transitions. Although complete EA and CD data are given in the Experimental Section for (*S*)-**5a**·HCl in various solvents, the ^1L_b band origin for its enantiomer (*R*)-**5a**·HCl is compared in Table 4 with the same data for other para-substituted benzylcarbinamines, also with the *R* absolute configuration, regardless of which enantiomer was actually used. Since the negative sign of the ^1L_b CEs for (*R*)-**5a** in methanol is the same as that of the unsubstituted parent (*R*)-**4a** (Table 2) in methanol, the induced rotational contribution for (*R*)-**5a**, predicted to be opposite to that of the vibronic contribution on the basis of the benzene chirality rule,[5−7] must be small compared to the vibronic contribution and need not be considered when predicting the sign of the ^1L_b CEs of chiral ring-substituted benzylcarbinamines and -carbinamine salts. The negative sign for the ^1L_b CEs of (*R*)-**5a** in methanol is the result of the greater rotatory contribution of conformer (−)-**5** as compared to that of (+)-**5**. Since (*R*)-**5a** in cyclohexane has been reported[5] to show negative ^1L_b CEs, whereas for (*R*)-**4a** in cyclohexane these CEs are positive, the *p*-chloro substituent in (*R*)-**5a** results in additional stabilization of conformer (−)-**5** compared to (+)-**5**, perhaps as a result of the positive field (σ_I) effect but a negative resonance (σ°_R) effect of the *p*-chloro substituent.[26] On the other hand, (*R*)-2-amino-1-[*p*-(trifluoromethyl)phenyl]propane [(*R*)-**5b**] in both methanol and cyclohexane shows positive ^1L_b CEs, the *p*-trifluoromethyl group with only a positive field effect[26] stabilizing conformer (+)-**5** compared to (−)-**5**. For 2-(*N*,*N*-dimethylamino)-1-(*p*-chlorophenyl)propane [(*R*)-**5e**], the greater effective bulk size of the dimethylamino group determines its observed negative ^1L_b CEs in both methanol and cyclohexane.

(*R*)-2-Amino-1-(*p*-chlorophenyl)propane hydrochloride [(*R*)-**5a**·HCl] in water gave a CD spectrum too weak to be significant, but in methanol, its CD spectrum has the same sign as that of (*R*)-**5a** in methanol. The ^1L_b CEs for (*R*)-**5b**, as discussed above, are positive, but protonation of the amino group in (*R*)-**5b** shifts the conformational equilibrium from (+)-**5** toward (−)-**5,** so that the observed ^1L_b CEs for (*R*)-**5b**·HCl in methanol are now negative. As expected, the hydrochloride salts (*R*)-**5c**·2HCl, (*R*)-**5d**·HCl, and (*R*)-**5e**·HCl are reported[5,19,21] to show negative ^1L_b CEs in methanol.

(*m*- and (*o*-Chlorobenzyl)methylcarbinamines. As shown in Table 5, (*R*)-2-amino-1-(*m*-chlorophenyl)propane in methanol [(*R*)-**6a**·HCl in 0.1 M KOH in MeOH], its hydrochloride [(*R*)-**6a**·HCl] in water and methanol, 2-(*N*,*N*-dimethylamino)-1-(*m*-chlorophenyl)propane in methanol [(*R*)-**6c**·HCl in 0.1 M KOH in MeOH], and the corresponding *N*-methyl and *N*,*N*-dimethyl-substituted hydrochlorides [(*R*)-**6b**·HCl and (*R*)-**6c**·HCl] in methanol all show negative ^1L_b CEs. As in the EA spectrum of (*S*)-2-amino-1-(*p*-chlorophenyl)propane [(*S*)-**5a**] in methanol (Figure 1), the EA spectra of the *m*-chloro-substituted compounds show only ^1L_b transitions to totally symmetric vibrational modes, and a CE is associated with each of these transitions. Since the benzene chirality rule would predict an induced rotatory contribution of the same sign as that of the vibronic contribution to the ^1L_b CEs, and since conformer (−)-**6** is expected to dominate the CD for these compounds, the *m*-chloro-substituted compounds are predicted, as is observed, to display negative ^1L_b CEs in methanol and water.

The CD spectrum of (*R*)-2-amino-1-(*o*-chlorophenyl)propane in methanol [(*R*)-**6d**·HCl in 0.1 M KOH in MeOH, Table 5] also shows negative ^1L_b CEs, as predicted on the basis of the benzene chirality rule and assuming an insignificant induced rotational contribution. For the hydrochloride [(*R*)-**6d**·HCl] in water, the conformational equilibrium is shifted from (−)-**6**

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Table 3. Substituted Chiral Benzylcarbinamines

compd	name	$[\alpha]^{23}_D$, deg (solvent)[a]	characterization or vendor[b]
(*S*)-**5a**·HCl	(*S*)-2-amino-1-(*p*-chlorophenyl)propane hydrochloride	+22 (H_2O)	ref 25
(*R*)-**5e**·HCl	(*R*)-*N*,*N*-dimethyl-2-amino-1-(*p*-chlorophenyl)propane hydrochloride	−9.0 (H_2O)	ref 19
(*R*)-**6a**·HCl	(*R*)-2-amino-1-(*m*-chlorophenyl)propane hydrochloride	−14 (H_2O)	ref 19
(*R*)-**6c**·HCl	(*R*)-*N*,*N*-dimethyl-2-amino-1-(*m*-chlorophenyl)propane hydrochloride	−5.5 (H_2O)	ref 19
(*R*)-**6d**·HCl	(*R*)-2-amino-1-(*o*-chlorophenyl)propane hydrochloride	−22 (H_2O)	ref 19
L-**7a**	L-*p*-chlorophenylalanine	−21 (H_2O)	A
L-**7b**	L-*p*-iodophenylalanine	+20 (0.5 M HCl)[c]	A
L-**7c** (L-**8d**)	L-*p*-aminophenylalanine	−34 (H_2O)	A
L-**7d**	L-*o*-chlorophenylalanine	−6 (H_2O)	F
L-**8a**	L-tyrosine	−9.8 (1 M HCl)	F
L-**8b**	*O*-methyl-L-tyrosine	−9 (1 M HCl)	A
L-**8c**	methyl L-tyrosinate	+20 (CH_3OH)	F
L-**8e**·HCl	L-tyrosinol hydrochloride	−17 (H_2O)	S

[a] Concentration: 0.71−4.2 g/100 mL of solution. [b] Vendor: S, Sigma; F, Fluka; A, Aldrich. [c] 1 M hydrochloric acid in ethanol, 1:1.

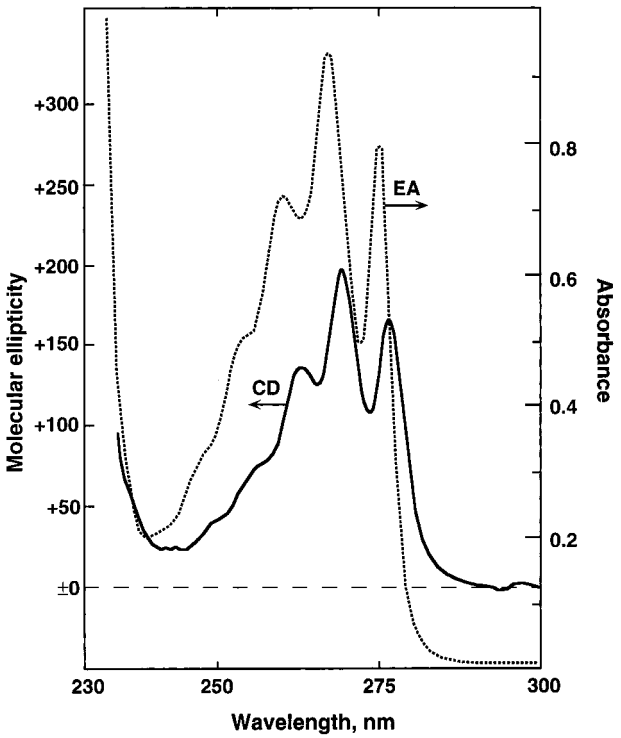


Figure 1. Electronic absorption (EA) and circular dichroism (CD) spectra of (*S*)-2-amino-1-(*p*-chlorophenyl)propane hydrochloride [(*S*)-**5a**·HCl] in 0.1 M KOH in methanol. For the EA spectrum, the concentration was 2.5×10^{-3} M.

toward (+)-**6**, possibly by way of weak hydrogen bonding between the ammonium group and the *o*-chloro substituent, so that, in the CD spectrum of (*R*)-**6d**·HCl, the CD maxima were too weak to be detected. For the hydrochloride in methanol, the equilibrium is shifted even more toward (+)-**6**, and the ^1L_b CEs are now positive.

Ring-Substituted L-Phenylalanines. The CD spectra of L-*p*-chloro- and L-*p*-iodophenylalanine (L-**7a** and L-**7b**) in water and methanol and L-**7a**·HCl and L-*p*-aminophenylalanine dihydrochloride in water (L-**7c** in 1 M HCl in H_2O, Table 6) and in methanol (L-**7c** in 0.1 M HCl in MeOH, Table 6) are similar to those of L-phenylalanine (L-**4d**) in water (Table 2), all showing strong positive ^1L_b CEs as a result of a larger rotational contribution by (+)-**7** and (+)-**4** as compared to that by (−)-**7** and (−)-**4** in these solvents. As discussed above, L-**4d** in methanol also shows negative CEs due to a larger amount of conformer (−)-**4** in methanol. For the sodium salt of L-**7a** in water (L-**7a** in 1 M NaOH in H_2O), the ^1L_b CEs are positive, but the potassium salt of L-**7a** in methanol also shows a weak negative CE at 279 nm (Figure 2) as the longer wavelength component of a double CE[24] associated with the ^1L_b band origin. This CD maximum is the result of a bathochromic shift of the ^1L_b band origin caused by the carboxyl group gauche to the benzene ring in conformer (−)-**7**.[1]

For L-*o*-chlorophenylalanine (L-**7d**) and its hydrochloride (L-**7d**·HCl) in water and methanol, the ^1L_b CEs are negative, the result of a shift in the conformational equilibrium from (+)-**7** toward (−)-**7,** due to an interaction of the carboxyl and carboxylate groups with the *o*-chloro substituent, both the increased mole fraction of (−)-**7** and the greater rotatory contribution of the carboxyl and carboxylate groups as compared to those of the ammonium and amino groups coming into play.[3]

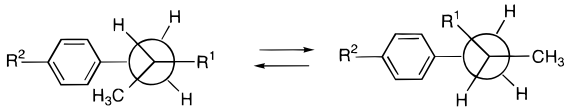
Benzylcarbinamines with Para-Attached Oxygen and Nitrogen Atoms with Lone-Pair Electrons. When an atom having a lone pair of electrons is attached to a benzene ring, the atom can donate a lone pair of electrons to the ring, and this delocalization (resonance) shifts the position of the ^1L_b band to longer wavelength and increases its intensity.[27] Thus, L-tyrosine (L-**8a**, Figure 3) in water and *O*-methyl-L-tyrosine (L-**8b**) in water and methanol show an intense ^1L_b band with an absorption maximum at about 274 nm but without vibrational fine structure. A strong positive CD maximum is associated with this transition, suggesting that, as the result of the greater effective size of a carboxylate group as compared to that of an ammonium group, conformer (+)-**8** (Table 7) is more important than (−)-**8** in determining the sign of this CE. In contrast to the observations with the para-substituted compounds, L-*m*- and L-*o*-hydroxyphenylalanine in water are both reported to show a negative CD maximum.[28]

A positive ^1L_b CE is also observed for the hydrochloride salt of L-**8a** in water and methanol and the hydrochloride salts of L-**8b** and methyl L-tyrosinate (L-**8c**) in water (Table 7). The same is true for the sodium and potassium salts of L-**8a**, L-**8b**, and L-**8c** in these same solvents and for L-**8c** in methanol, dioxane, and tetrahydrofuran. A positive ^1L_b CE is also observed for L-*p*-aminophenylalanine (L-**8d**) in water and methanol, its sodium salt in water, and its potassium salt in methanol, a *p*-amino group having the same effect on the EA and CD spectra as a *p*-hydroxyl, *p*-methoxyl, and *p*-oxy group.

L-Tyrosinol hydrochloride (L-**8e**·HCl), its sodium and potassium salts in water and methanol and (*R*)-2-amino-1-(*p*-hydroxyphenyl)propane hydrochloride [(*R*)-**8f**·HCl] and (*R*)-2-amino-1-(*p*-aminophenyl)propane [(*R*)-**8g**·2 HCl in dilute KOH in MeOH] in methanol show a negative ^1L_b CE, conformer (−)-**8** being more important than (+)-**8** in determining the sign of the CE. Protonation of the two amino groups in (*R*)-**8g** [(*R*)-**5c**·2

(27) Jaffe, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; Chapter 12, pp 248−252.
(28) Hooker, T. M., Jr.; Schellman, J. A. *Biopolymers* **1970**, *9*, 1319−1348.

Table 4. ^1L_b Band Origin Maxima for Para-Substituted Benzylmethylcarbinamines and Their Hydrochlorides

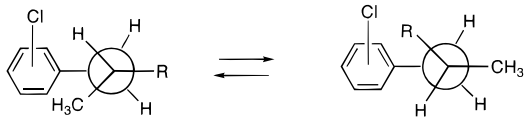


(-)-**5** (+)-**5**

neutral nitrogen				positive nitrogen			
solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]	solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]
(*R*)-**5a**·HCl[c]	$R^1 = NH_2$	0.1 M KOH in MeOH	276 (320)	(*R*)-**5a**·HCl[c]	$R^1 = N^+H_3$	H_2O	[CD too weak to be significant]
	R^2 = Cl		[277 (−4.8)]		R^2 = Cl		
(*R*)-**5a**[c,d]	$R^1 = NH_2$	cyclohexane	277 (420)	(*R*)-**5a**·HCl[c]	$R^1 = N^+H_3$	MeOH	275 (240)
	R^2 = Cl		[278 (−7.9)]		R^2 = Cl		[275 (−1.1)]
(*R*)-**5b**[d]	$R^1 = NH_2$	MeOH	269 (210)	(*R*)-**5a**·HCl[c]	$R^1 = N^+H_3$	0.1 M HCl in MeOH	[275 (−1.2)]
	$R^2 = CF_3$		[269 (+2.0)]		R^2 = Cl		
(*R*)-**5b**[d]	$R^1 = NH_2$	cyclohexane	269 (160)	(*R*)-**5b**·HCl[d]	$R^1 = N^+H_3$	MeOH	269 (310)
	$R^2 = CF_3$		[269 (+3.9)]		$R^2 = CF_3$		[270 (−0.64)]
(*R*)-**5e**·HCl	$R^1 = N(CH_3)_2$	0.1 M KOH in MeOH	276 (310)	(*R*)-**5c**·2 HCl[c,e]	$R^1 = N^+H_3$	dilute HCl in MeOH	268 (120)
	R^2 = Cl		[277 (−7.6)]		$R^2 = N^+H_3$		[268 (−4.2)]
(*R*)-**5e**[c,d]	$R^1 = N(CH_3)_2$	cyclohexane	280 (270)[g]	(*R*)-**5d**·HCl[c,f]	$R^1 = N^+H_2CH_3$	MeOH	276 (230)
	R^2 = Cl		[282 (−15)]		R^2 = Cl		[277 (−4.5)]
				(*R*)-**5e**·HCl[c,f]	$R^1 = N^+H(CH_3)_2$	MeOH	276 (230)
					R^2 = Cl		[277 (−3.6)]

[a] Molar absorptivity. [b] Molar dichroic absorption. [c] Enantiomer used. [d] Complete EA and CD data given in ref 5. [e] Complete EA and CD data in ref 21. [f] Complete EA and CD data in ref 19. [g] Shoulder.

Table 5. ^1L_b Band Origin Maxima for *m*- and *o*-Chlorobenzylmethylcarbinamines and Their Hydrochlorides



(-)-**6** (+)-**6**

neutral nitrogen				positive nitrogen			
solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]	solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]
(*R*)-**6a**·HCl	$R = NH_2$	0.1 M KOH in MeOH	274 (240)	(*R*)-**6a**·HCl	$R = N^+H_3$	H_2O	[273 (−2.9)[c]]
	meta		[275 (−1.7)[c]]		*meta*		
(*R*)-**6c**·HCl	$R = N(CH_3)_2$	0.1 M KOH in MeOH	274 (240)	(*R*)-**6a**·HCl	$R = N^+H_3$	MeOH	274 (200)
	meta		[273 (−6.1)[d]]		*meta*		[274 (−4.5)[c]]
(*R*)-**6d**·HCl	$R = NH_2$	0.1 M KOH in MeOH	273 (190)	(*R*)-**6a**·HCl	$R = N^+H_3$	0.1 M HCl in MeOH	[274 (−5.5)[c]]
	ortho		[276 (−0.82)		*meta*		
				(*R*)-**6b**·HCl[e,f]	$R = N^+H_2CH_3$	MeOH	274 (220)
					meta		[275 (−7.3)]
				(*R*)-**6c**·HCl	$R = N^+H(CH_3)_2$	MeOH	274 (210)
					meta		[274 (−6.6)[d]]
				(*R*)-**6d**·HCl	$R = N^+H_3$	H_2O	[CD too weak to be significant]
					ortho		
				(*R*)-**6d**·HCl	$R = N^+H_3$	MeOH	273 (150)
					ortho		[273 (+1.7)]

[a] Molar absorptivity. [b] Molar dichroic absorption. [c] $\Delta\epsilon$ corrected by a factor of (21/14) for low enantiomer excess. [d] $\Delta\epsilon$ corrected by a factor of (10/5.5) for low enantiomer excess. [e] Complete EA and CD data given in ref 19. [f] Enantiomer used.

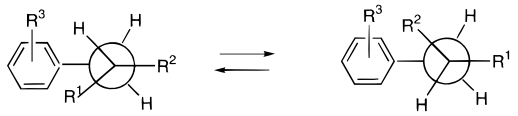
HCl in dilute HCl in MeOH, Table 4] does not cause a change in the sign of the ^1L_b CE but does cause a decrease in its intensity and the appearance of vibrational fine structure.

Experimental Section

The solutes used were characterized or purchased as indicated in Table 3. They were used without further purification and had rotatory powers as shown in Table 1 in agreement with those reported by the vendor or as noted below. Electronic absorption (EA) spectra were measured using a Varian Cary 2300 spectrophotometer. Circular dichroism (CD) were observed with a Jasco J-720 spectropolarimeter, using a 1-cm sample cell. Solutions for these measurements were prepared by diluting 2.7−11.9 mg of substance to 10.0 mL with solvent, and for each CD spectrum, the concentration (*c*) is given in grams per 100 mL of solution. The molar dichroic absorption ($\Delta\epsilon$) equals $[\theta]/3300$, where $[\theta]$ is the molecular ellipticity.

(*S*)-2-Amino-1-(*p*-chlorophenyl)propane hydrochloride [(*S*)-5a·HCl] had $[\alpha]^{23}_D$ +22° (*c* 1.2, H_2O) [lit.[5] $[\alpha]^{25}_D$ +22° (*c* 2.01, H_2O),

Table 6. ^1L_b Band Origin Maxima for Ring-Substituted L-Phenylalanines



(-)-**7** (+)-**7**

positive nitrogen				neutral nitrogen			
solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]	solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]
L-**7a**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = p$-Cl	H_2O	[275 (+3.9)]	L-**7a**	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = p$-Cl	1 M NaOH in H_2O	[275 (+4.2)]
L-**7a**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = p$-Cl	MeOH	275 (180) [275 (+3.9)]	L-**7a**	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = p$-Cl	0.1 M KOH in MeOH	276 (260) [279 (−0.33)] [275 (+3.0)]
L-**7a**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = p$-Cl	1 M HCl in H_2O	275 (+4.8)	L-**7d**	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = o$-Cl	1 M NaOH in H_2O	[275 (−1.5)]
L-**7a**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = p$-Cl	0.1 M HCl in MeOH	275 (160) [275 (+3.3]	L-**7d**	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = o$-Cl	0.1 M KOH in MeOH	273 (180) [275 (−2.9)]
L-**7b**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = p$-I	H_2O	277 (320)[c] 278 (+4.5)				
L-**7b**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = p$-I	MeOH	277 (320)[c] [280 (+4.8)]				
L-**7c**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = p$-N^+H_3	1 M HCl in H_2O	261 (130)[c] [265 (+0.76)]				
L-**7c**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = p$-N^+H_3	0.1 M HCl in MeOH	267 (95) [267 (+1.2)]				
L-**7d**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = o$-Cl	H_2O	[274 (−2.1)]				
L-**7d**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = o$-Cl	MeOH	273 (140) [274 (−1.4)]				
L-**7d**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = o$-Cl	1 M HCl in H_2O	[275 (−2.0)]				
L-**7d**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = o$-Cl	0.1 M HCl in MeOH	273 (140) [276 (−1.0)] [272 (+0.67)]				

[a] Molar absorptivity. [b] Molar dichroic absorption; $\Delta\epsilon = [\theta]/3300$, where $[\theta]$ is the molecular ellipticity. [c] Shoulder.

>95% ee]: EA max (0.1 M KOH in MeOH) 276 nm (ϵ 320), 268 (370), 261 (290), 256 (200) (sh), 250 (140) (sh), 244 (88) (sh); CD (*c* 0.068, 0.1 M KOH in MeOH) $[\theta]_{288}$ ±0, $[\theta]_{277}$ +160, $[\theta]_{273}$ +110, $[\theta]_{269}$ +200, $[\theta]_{266}$ +130, $[\theta]_{263}$ +140, $[\theta]_{257}$ +76 (sh), $[\theta]_{250}$ +42 (sh), $[\theta]_{243}$ +24, $[\theta]_{235}$ +95; CD (*c* 0.067, H_2O) spectrum too weak to be significant; EA max (MeOH) 275 nm (ϵ 240), 267 (290), 260 (230), 254 (170) (sh), 249 (120) (sh), 243 (75) (sh); CD (*c* 0.065, MeOH) $[\theta]_{287}$ ±0, $[\theta]_{275}$ +37, $[\theta]_{272}$ +18, $[\theta]_{268}$ +47, $[\theta]_{263}$ +28, $[\theta]_{259}$ +33, $[\theta]_{255}$ +20, $[\theta]_{253}$ +22, $[\theta]_{249}$ +11, $[\theta]_{246}$ +14, $[\theta]_{238}$ +4, $[\theta]_{230}$ +19; CD (*c* 0.062, 0.1 M HCl in MeOH) $[\theta]_{282}$ ±0, $[\theta]_{275}$ +38, $[\theta]_{271}$ +16, $[\theta]_{268}$ +49, $[\theta]_{264}$ +25, $[\theta]_{260}$ +34, $[\theta]_{256}$ +23 (sh), $[\theta]_{251}$ +12, $[\theta]_{249}$ +14, $[\theta]_{240}$ +4, $[\theta]_{232}$ +18.

(*R*)-2-(*N*,*N*-Dimethylamino)-1-(*p*-chlorophenyl)propane hydrochloride [(*R*)-5e·HCl] had $[\alpha]^{23}_D$ −9.0° (*c* 2.0, H_2O) [lit.[19] $[\alpha]^{25}_D$ −9.3° (*c* 2.05, H_2O)]: EA max (0.1 M KOH in MeOH) 276 nm (ϵ 310), 268 (390), 261 (330), 255 (270); CD (*c* 0.059, 0.1 M KOH in MeOH) $[\theta]_{286}$ ±0, $[\theta]_{277}$ −250, $[\theta]_{274}$ −180, $[\theta]_{270}$ −300, $[\theta]_{266}$ −200, $[\theta]_{263}$ −210, $[\theta]_{258}$ −140 (sh), $[\theta]_{243}$ −64.

(*R*)-2-Amino-1-(*m*-chlorophenyl)propane hydrochloride [(*R*)-6a·HCl] had $[\alpha]^{23}_D$ −14° (*c* 1.4, H_2O) [lit.[19] $[\alpha]^{25}_D$ +21° (*c* 2.10, H_2O) for the *S* enantiomer]: EA max (0.1 M KOH in MeOH) 274 nm (ϵ 240), 266 (290), 260 (220), 254 (150) (sh), 248 (92) (sh), 243 (58) (sh); CD (*c* 0.065, 0.1 M KOH in MeOH) $[\theta]_{283}$ ±0, $[\theta]_{275}$ −38, $[\theta]_{272}$ −16 $[\theta]_{268}$ −39, $[\theta]_{264}$ −28, $[\theta]_{261}$ −36, $[\theta]_{240}$ −12, $[\theta]_{231}$ −200; CD (*c* 0.066, H_2O) $[\theta]_{284}$ ±0, $[\theta]_{273}$ −64, $[\theta]_{270}$ −48, $[\theta]_{266}$ −81, $[\theta]_{261}$ -51 (sh), $[\theta]_{238}$ −4.4, $[\theta]_{230}$ −39; EA max (MeOH) 274 nm (ϵ 200), 266 (240), 264 (210) (sh), 260 (190), 254 (130) (sh), 248 (78) (sh), 242 (43) (sh); CD (*c* 0.051, MeOH) $[\theta]_{283}$ ±0, $[\theta]_{274}$ −100, $[\theta]_{271}$ −73, $[\theta]_{267}$ −120, $[\theta]_{262}$ −84 (sh), $[\theta]_{256}$ −51 (sh), $[\theta]_{236}$ ±0, $[\theta]_{230}$ −13; CD (*c* 0.066, 0.1 M HCl in MeOH) $[\theta]_{284}$ ±0, $[\theta]_{274}$ −120, $[\theta]_{271}$ −85, $[\theta]_{267}$ −140, $[\theta]_{263}$ −98, $[\theta]_{261}$ −99, $[\theta]_{254}$ −49 (sh), $[\theta]_{249}$ −23 (sh), $[\theta]_{233}$ −3, $[\theta]_{230}$ −8.

(*R*)-2-(*N*,*N*-Dimethylamino)-1-(*m*-chlorophenyl)propane hydrochloride [(*R*)-6c·HCl] had $[\alpha]^{23}_D$ −5.5° (*c* 0.95, H_2O) [lit.[19] $[\alpha]^{25}_D$ +10° (*c* 2.02, H_2O) for the *S* enantiomer]: EA max (0.1 M KOH in MeOH) 274 nm (ϵ 240), 267 (300), 260 (250), 253 (200); CD (*c* 0.048, 0.1 M KOH in MeOH) $[\theta]_{278}$ ±0, $[\theta]_{273}$ −110, $[\theta]_{270}$ −53, $[\theta]_{266}$ −120, $[\theta]_{263}$ −76, $[\theta]_{260}$ −84, $[\theta]_{255}$ −56 (sh), $[\theta]_{242}$ ±0, $[\theta]_{238}$ +120; EA max (MeOH) 274 nm (ϵ 210), 267 (260), 260 (200), 254 (140) (sh), 248 (87) (sh), 242 (55) (sh); CD (*c* 0.073, MeOH) $[\theta]_{283}$ ±0, $[\theta]_{274}$ −120, $[\theta]_{271}$ −85, $[\theta]_{267}$ −140, $[\theta]_{261}$ −92 (sh), $[\theta]_{254}$ −55, $[\theta]_{233}$ ±0, $[\theta]_{230}$ +37.

(*R*)-2-Amino-1-(*o*-chlorophenyl)propane hydrochloride [(*R*)-6d·HCl] had $[\alpha]^{23}_D$ −22° (*c* 1.2, H_2O) [lit.[19] $[\alpha]^{25}_D$ −26° (*c* 1.96, H_2O)]: EA max (0.1 M KOH in MeOH) 273 nm (ϵ 190), 266 (240), 263 (210) (sh), 260 (190) (sh), 253 (130) (sh), 247 (82) (sh), 242 (53) (sh); CD (*c* 0.062, 0.1 M KOH in MeOH) $[\theta]_{283}$ ±0, $[\theta]_{276}$ −27, $[\theta]_{273}$ −5.6, $[\theta]_{269}$ −38, $[\theta]_{266}$ −23, $[\theta]_{263}$ −40, $[\theta]_{259}$ −23, $[\theta]_{256}$ −27, $[\theta]_{249}$ −16, $[\theta]_{230}$ −530; CD (*c* 0.070, H_2O) too weak to be significant; EA max (MeOH) 273 nm (ϵ 150), 268 (170) (sh), 265 (200), 263 (190) (sh),

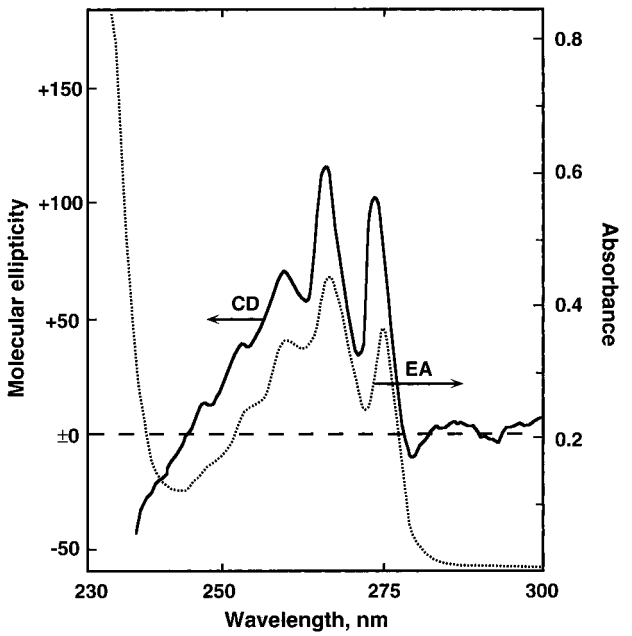


Figure 2. Electronic absorption (EA) and circular dichroism (CD) spectra of L-*p*-chlorophenylalanine (L-**7a**) in 0.1 M KOH in methanol. For the EA spectrum, the concentration was 1.4×10^{-3} M.

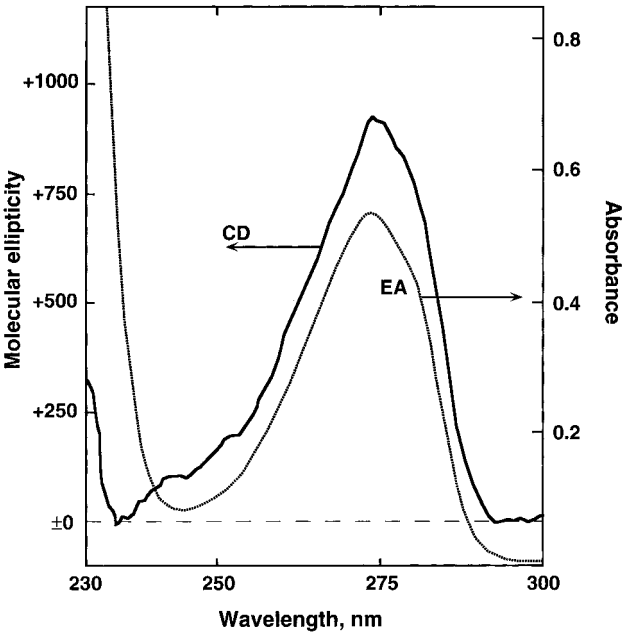


Figure 3. Electronic absorption (EA) and circular dichroism (CD) spectra of L-tyrosine (L-**8a**) in water. For the EA spectrum, the concentration was 4.0×10^{-4} M.

259 (170) (sh), 253 (120) (sh), 249 (88) (sh), 241 (44) (sh); CD (*c* 0.064, MeOH) $[\theta]_{280}$ ±0, $[\theta]_{273}$ +55, $[\theta]_{269}$ +33, $[\theta]_{266}$ +53, $[\theta]_{260}$ +31 (sh), $[\theta]_{247}$ +6, $[\theta]_{244}$ +7, $[\theta]_{239}$ ±0, $[\theta]_{230}$ +13; CD (*c* 0.056, 0.1 M HCl in MeOH) $[\theta]_{280}$ ±0, $[\theta]_{273}$ +57, $[\theta]_{270}$ +37, $[\theta]_{265}$ +56, $[\theta]_{260}$ +35 (sh), $[\theta]_{237}$ ±0, $[\theta]_{230}$ +13.

L-*p*-Chlorophenylalanine (L-7a) had $[\alpha]^{23}_{D}$ −21° (*c* 0.95, H_2O): CD (*c* 0.030, H_2O) $[\theta]_{290}$ ±0, $[\theta]_{275}$ +130, $[\theta]_{271}$ +81, $[\theta]_{267}$ +140, $[\theta]_{263}$ +81, $[\theta]_{261}$ +84, $[\theta]_{256}$ +53 (sh), $[\theta]_{250}$ +31, $[\theta]_{232}$ +740; EA max (MeOH) 275 nm (ϵ 180), 267 (230), 260 (190), 255 (140) (sh), 249 (89) (sh); CD (*c* 0.044, MeOH) $[\theta]_{285}$ ±0, $[\theta]_{275}$ +130, $[\theta]_{272}$ +71, $[\theta]_{268}$ +130, $[\theta]_{263}$ +76, $[\theta]_{262}$ +79, $[\theta]_{257}$ +51 (sh), $[\theta]_{247}$ +24, $[\theta]_{233}$ +780; CD (*c* 0.040, 1 M HCl in H_2O); $[\theta]_{282}$ ±0, $[\theta]_{275}$ +160, $[\theta]_{271}$ +110, $[\theta]_{267}$ +180, $[\theta]_{263}$ +110, $[\theta]_{261}$ +120, $[\theta]_{256}$ +68, $[\theta]_{254}$ +71, $[\theta]_{252}$ +65, $[\theta]_{233}$ +3300; EA (0.1 M HCl in MeOH) 275 nm (ϵ 160), 266 (210), 259 (170), 255 (120) (sh), 249 (83) (sh); CD (*c* 0.054, 0.1 M HCl in MeOH) $[\theta]_{284}$ ±0, $[\theta]_{275}$ +110, $[\theta]_{272}$ +70, $[\theta]_{268}$ +130, $[\theta]_{264}$ +83, $[\theta]_{261}$ +94, $[\theta]_{256}$ +61, $[\theta]_{253}$ +72 (sh), $[\theta]_{233}$ +4300; CD (*c* 0.044, 1 M NaOH in H_2O) $[\theta]_{284}$ ±0, $[\theta]_{275}$ +140, $[\theta]_{271}$ +84, $[\theta]_{267}$ +150, $[\theta]_{263}$ +87, $[\theta]_{261}$ +96, $[\theta]_{254}$ +51 (sh), $[\theta]_{248}$ +24, $[\theta]_{235}$ +220; EA max (0.1 M KOH in MeOH) 276 nm (ϵ 260), 268 (320), 261 (250), 256 (180) (sh), 249 (120) (sh); CD (*c* 0.027, 0.1 M KOH in MeOH) $[\theta]_{283}$ ±0, $[\theta]_{279}$ −11, $[\theta]_{278}$ ±0, $[\theta]_{275}$ +100, $[\theta]_{272}$ +32, $[\theta]_{267}$ +120, $[\theta]_{264}$ +57, $[\theta]_{261}$ +70, $[\theta]_{254}$ +39 (sh), $[\theta]_{245}$ ±0, $[\theta]_{235}$ −46.

L-*p*-Iodophenylalanine (L-7b) had $[\alpha]^{23}_{D}$ +20° (*c* 1.1, 0.5 M HCl in 1:1 $H_2O-C_2H_5OH$): EA (H_2O) 277 nm (ϵ 320) (sh), 266 (620) (sh), 257 (860) (sh); CD (*c* 0.0088, H_2O) $[\theta]_{300}$ ±0, $[\theta]_{278}$ +150, $[\theta]_{242}$ ±0; EA (MeOH) 277 nm (ϵ 320) (sh), 266 (620) (sh), 253 (880) (sh); CD (*c* 0.0078, MeOH) $[\theta]_{298}$ ±0, $[\theta]_{280}$ +160, $[\theta]_{266}$ ±0, $[\theta]_{244}$ −100.

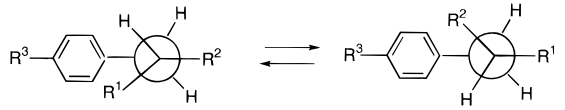
L-*p*-Aminophenylalanine (L-7c and **L-8d)** had $[\alpha]^{23}_{D}$ −34° (*c* 2.6, H_2O): EA max (H_2O) 284 nm (ϵ 1400); CD (*c* 0.0067, H_2O) $[\theta]_{313}$ ±0, $[\theta]_{284}$ +780, $[\theta]_{261}$ ±0, $[\theta]_{251}$ −760; EA max (MeOH) 288 nm (ϵ 1400); CD (*c* 0.00102, MeOH) $[\theta]_{328}$ ±0, $[\theta]_{291}$ +690, $[\theta]_{265}$ ±0; EA max (1 M HCl in H_2O) 261 nm (ϵ 130) (sh), 257 (160), 253 (140) (sh); CD (*c* 0.0096, 1 M HCl in H_2O) $[\theta]_{274}$ ±0, $[\theta]_{265}$ +25, $[\theta]_{262}$ +7.1, $[\theta]_{259}$ +27, $[\theta]_{256}$ +5.7, $[\theta]_{252}$ +26 (sh), $[\theta]_{230}$ +3100; EA max (0.1 M HCl in MeOH) 267 nm (ϵ 95) (sh), 263 (140), 258 (180), 253 (160) (sh), 249 (130) (sh), 244 (98) (sh); CD (*c* 0.059, 0.1M HCl in MeOH) $[\theta]_{274}$ ±0, $[\theta]_{267}$ +39, $[\theta]_{264}$ +32, $[\theta]_{260}$ +51, $[\theta]_{257}$ +40, $[\theta]_{252}$ +69 (sh), $[\theta]_{230}$ +5400; EA max (1 M NaOH in H_2O) 284 nm (ϵ 1400); CD (*c* 0.0064, 1 M NaOH in H_2O) $[\theta]_{312}$ ±0, $[\theta]_{285}$ +760, $[\theta]_{256}$ ±0, $[\theta]_{249}$ −110; EA max (0.1 M KOH in MeOH) 288 nm (ϵ 2200); CD (*c* 0.0068, 0.1 M KOH in MeOH) $[\theta]_{315}$ ±0, $[\theta]_{287}$ +520, $[\theta]_{264}$ ±0, $[\theta]_{256}$ −480.

L-*o*-Chlorophenylalanine (L-7d) had $[\alpha]^{23}_{D}$ −6° (*c* 1.0, H_2O): CD (*c* 0.054, 1 M NaOH in H_2O) $[\theta]_{283}$ ±0, $[\theta]_{275}$ −50, $[\theta]_{271}$ −26, $[\theta]_{268}$ −46, $[\theta]_{263}$ −30 (sh), $[\theta]_{250}$ ±0, $[\theta]_{232}$ +400; EA max (0.1 M KOH in MeOH) 273 nm (ϵ 180), 266 (230), 260 (190) (sh), 253 (140) (sh), 248 (98) (sh); CD (*c* 0.039, 0.1 M KOH in MeOH) $[\theta]_{284}$ ±0, $[\theta]_{275}$ −97, $[\theta]_{272}$ −72, $[\theta]_{268}$ −100, $[\theta]_{264}$ −84, $[\theta]_{262}$ −86, $[\theta]_{250}$ −35, $[\theta]_{232}$ −690; CD (*c* 0.044, H_2O) $[\theta]_{283}$ ±0, $[\theta]_{274}$ −70, $[\theta]_{270}$ −43, $[\theta]_{266}$ −58, $[\theta]_{261}$ −28 (sh), $[\theta]_{254}$ −8.0, $[\theta]_{253}$ −11, $[\theta]_{248}$ ±0, $[\theta]_{230}$ +680; EA max (MeOH) 273 nm (ϵ 140), 269 (160) (sh), 265 (200), 263 (190) (sh), 259 (160) (sh), 253 (120) (sh), 247 (80) (sh); CD (*c* 0.057, MeOH) $[\theta]_{281}$ ±0, $[\theta]_{274}$ −47, $[\theta]_{271}$ −34, $[\theta]_{266}$ −43, $[\theta]_{260}$ −20, $[\theta]_{258}$ −21, $[\theta]_{254}$ −7.0, $[\theta]_{252}$ −11, $[\theta]_{249}$ ±0, $[\theta]_{230}$ +670; CD (*c* 0.068, 1 M HCl in H_2O) $[\theta]_{285}$ ±0, $[\theta]_{275}$ −67, $[\theta]_{271}$ −34, $[\theta]_{267}$ −53, $[\theta]_{260}$ −15 (sh), $[\theta]_{255}$ ±0, $[\theta]_{253}$ +8.5 (sh), $[\theta]_{230}$ +4100; EA max (0.1 M HCl in MeOH) 273 nm (ϵ 140), 266 (190), 263 (180), 248 (87) (sh); CD (*c* 0.055, 0.1 M HCl in MeOH) $[\theta]_{283}$ ±0, $[\theta]_{276}$ −33, $[\theta]_{274}$ ±0, $[\theta]_{272}$ +22, $[\theta]_{269}$ ±0, $[\theta]_{265}$ +27, $[\theta]_{262}$ +19, $[\theta]_{260}$ +32, $[\theta]_{256}$ +22, $[\theta]_{253}$ +47 (sh), $[\theta]_{230}$ +6000.

L-Tyrosine (L-8a) had $[\alpha]^{23}_{D}$ −9.8° (*c* 4.2, 1 M HCl): EA max (H_2O) 278 nm (ϵ 1200) (sh), 274 (1300); CD (*c* 0.0072, H_2O) $[\theta]_{292}$ ±0, $[\theta]_{276}$ +850 (sh), $[\theta]_{273}$ +930, $[\theta]_{252}$ +190 (sh), $[\theta]_{244}$ +110 (sh), $[\theta]_{235}$ ±0, $[\theta]_{233}$ +50; EA max (1 M NaOH in H_2O) 292 nm (ϵ 2400); CD (*c* 0.0070, 1 M NaOH in H_2O) $[\theta]_{318}$ ±0, $[\theta]_{292}$ +1200, $[\theta]_{266}$ ±0, $[\theta]_{256}$ −460; EA max (0.1 M KOH in MeOH) 294 nm (ϵ 2400); CD (*c* 0.0069 in 0.1 M KOH in MeOH) $[\theta]_{312}$ ±0, $[\theta]_{293}$ +650, $[\theta]_{288}$ +560 (sh), $[\theta]_{267}$ ±0, $[\theta]_{257}$ −810; EA max (1 M HCl in H_2O) 278 nm (ϵ 1200) (sh), 273 (1300); CD (*c* 0.0080, 1 M HCl in H_2O) $[\theta]_{292}$ ±0, $[\theta]_{279}$ +850 (sh), $[\theta]_{275}$ +1000, $[\theta]_{270}$ +920 (sh), $[\theta]_{263}$ +610 (sh), $[\theta]_{250}$ +190, $[\theta]_{234}$ +4200; EA max (0.1 M HCl in MeOH) 281 nm (ϵ 1600) (sh), 277 (1700); CD (*c* 0.0083, 0.1 M HCl in MeOH) $[\theta]_{296}$ ±0, $[\theta]_{282}$ +760 (sh), $[\theta]_{277}$ +880, $[\theta]_{273}$ +780 (sh), $[\theta]_{258}$ +220 (sh), $[\theta]_{252}$ +150, $[\theta]_{237}$ +5300.

***O*-Methyl-L-tyrosine (L-8b)** had $[\alpha]^{23}_{D}$ −9° (*c* 0.71, 1 M HCl): EA max (1 M NaOH in H_2O) 278 nm (ϵ 1200) (sh), 273 (1300); CD (*c* 0.0068, 1 M NaOH in H_2O) $[\theta]_{290}$ ±0, $[\theta]_{279}$ +700 (sh), $[\theta]_{274}$ +850, $[\theta]_{244}$ ±0, $[\theta]_{236}$ ±0, $[\theta]_{234}$ +42; EA max (H_2O) 279 nm (ϵ 1100) (sh), 273 (1200); CD (*c* 0.0057, H_2O) $[\theta]_{291}$ ±0, $[\theta]_{277}$ +750 (sh), $[\theta]_{273}$ +880, $[\theta]_{268}$ +680 (sh), $[\theta]_{256}$ +230 (sh), $[\theta]_{249}$ +94, $[\theta]_{246}$ +120, $[\theta]_{241}$ ±0, $[\theta]_{235}$ −73, $[\theta]_{233}$ −56; EA max (MeOH) 282 nm (ϵ 1300), 276 (1500), 269 (1100) (sh); CD (*c* 0.0073, MeOH) $[\theta]_{288}$ ±0, $[\theta]_{282}$ +540, $[\theta]_{280}$ +520, $[\theta]_{276}$ +690, $[\theta]_{271}$ +550 (sh), $[\theta]_{262}$ +290 (sh), $[\theta]_{249}$ ±0, $[\theta]_{242}$ ±0, $[\theta]_{235}$ +290; EA max (1 M HCl in H_2O) 278 nm (ϵ 1200) (sh), 273 (1300); CD (*c* 0.0097, 1 M HCl in H_2O) $[\theta]_{291}$ ±0, $[\theta]_{278}$ +910 (sh), $[\theta]_{273}$ +1100, $[\theta]_{251}$ +180, $[\theta]_{236}$ +3200.

Table 7. ^1L_b Absorption Maxima for Benzylcarbinamines with Para-Attached Oxygen and Nitrogen Atoms with Lone-Pair Electrons



(-)-**8** (+)-**8**

phenylalanines								phenylalaninols and 1-phenyl-2-aminopropanes			
positive nitrogen				neutral nitrogen							
solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]	solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]	solute	substituents	solvent	λ, nm (ϵ^a) [λ, nm ($\Delta\epsilon^b \times 10^2$)]
L-**8a**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = OH$	H_2O	274 (1300) [273 (+28)]	L-**8a**	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = O^-$	1 M NaOH in H_2O	292 (2400) [292 (+36)]	L-**8e**·HCl	$R^1 = CH_2OH$ $R^2 = N^+H_3$ $R^3 = OH$	H_2O	274 (1400) [274 (−11)]
L-**8a**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = OH$	1M HCl in H_2O	273 (1300) [275 (+30)]	L-**8a**	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = O^-$	0.1 M KOH in MeOH	294 (2400) [293 (+20)]	L-**8e**·HCl	$R^1 = CH_2OH$ $R^2 = N^+H_3$ $R^3 = OH$	MeOH	275 (1600) [279 (−12)]
L-**8a**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = OH$	0.1 M HCl in MeOH	277 (1700) [277 (+27)]	L-**8b**	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = OCH_3$	1 M NaOH in H_2O	273 (1300) [274 (+26)]	L-**8e**·HCl	$R^1 = CH_2OH$ $R^2 = NH_2$ $R^3 = O^-$	1 M NaOH in H_2O	293 (2400) [295 (−20)]
L-**8b**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = OCH_3$	H_2O	273 (1200) [273 (+27)]	L-**8c**	$R^1 = CO_2CH_3$ $R^2 = NH_2$ $R^3 = OH$	H_2O	274 (1400) [274 (+33)]	L-**8e**·HCl	$R^1 = CH_2OH$ $R^2 = NH_2$ $R^3 = O^-$	0.1 M KOH in MeOH	294 (2300) [294 (−16]
L-**8b**	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = OCH_3$	MeOH	276 (1500) [276 (+21)]	L-**8c**	$R^1 = CO_2CH_3$ $R^2 = NH_2$ $R^3 = OH$	MeOH	273 (1200) [277 (+18)]	(*R*)-**8f**·HCl[d]	$R^1 = CH_3$ $R^2 = N^+H_3$ $R^3 = OH$	MeOH	277 (1600) [277 (−11)]
L-**8b**	$R^1 = CO_2H$ $R^2 = N^+H_3$ $R^3 = OCH_3$	1 M HCl in H_2O	273 (1300) [273 (+33)]	L-**8c**	$R^1 = CO_2CH_3$ $R^2 = NH_2$ $R^3 = OH$	dioxane	278 (2000) [275 (+15)]	(*R*)-**8g**·2 HCl[c−e]	$R^1 = CH_3$ $R^2 = NH_2$ $R^3 = NH_2$	dilute KOH in MeOH	289 (1500) [289 (−11)]
L-**8c**	$R^1 = CO_2CH_3$ $R^2 = N^+H_3$ $R^3 = OH$	1 M HCl in H_2O	273 (1300) [274 (+29)]	L-**8c**	$R^1 = CO_2CH_3$ $R^2 = NH_2$ $R^3 = OH$	THF	278 (1800) [278 (+18)]				
L-**8d**[f]	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = NH_2$	H_2O	284 (1400) [284 (+24)]	L-**8c**	$R^1 = CO_2CH_3$ $R^2 = NH_2$ $R^3 = O^-$	1 M NaOH in H_2O	293 (2400) [292 (+39)]				
L-**8d**[f]	$R^1 = CO_2^-$ $R^2 = N^+H_3$ $R^3 = NH_2$	MeOH	288 (1400) [291 (+21)]	L-**8d**[f]	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = NH_2$	1 M NaOH in H_2O	284 (1400) [285 (+23)]				
				L-**8d**[f]	$R^1 = CO_2^-$ $R^2 = NH_2$ $R^3 = NH_2$	0.1 M KOH in MeOH	288 (2200) [287 (+16)]				

[a] Molar absorptivity. [b] Molar dichroic absorption. [c] Enantiomer used. [d] Complete EA and CD data given in ref 21. [e] Also identified as (*R*)-**5c**·2HCl in Table 4. [f] Also identified as L-**7c** in Table 6.

Methyl L-tyrosinate (L-8c) had $[\alpha]^{23}_D$ +20° (*c* 3.5, CH_3OH): EA max (H_2O) 278 nm (ϵ 1300) (sh), 274 (1400); CD (*c* 0.0079, H_2O) $[\theta]_{296}$ ±0, $[\theta]_{278}$ +950 (sh), $[\theta]_{274}$ +1100, $[\theta]_{268}$ +840 (sh), $[\theta]_{261}$ +500 (sh), $[\theta]_{249}$ +170, $[\theta]_{234}$ +3400; EA max (MeOH) 284 nm (ϵ 950) (sh), 273 (1200); CD (*c* 0.0093, MeOH) $[\theta]_{301}$ ±0, $[\theta]_{283}$ +480 (sh), $[\theta]_{277}$ +600, $[\theta]_{269}$ +430 (sh), $[\theta]_{247}$ +75, $[\theta]_{236}$ +2000; EA max (dioxane) 285 nm (ϵ 1700), 278 (2000), 273 (1700 (sh); CD (*c* 0.0064, dioxane) $[\theta]_{297}$ ±0, $[\theta]_{284}$ +340, $[\theta]_{282}$ +310, $[\theta]_{275}$ +480, $[\theta]_{270}$ +410 (sh), $[\theta]_{261}$ +170 (sh), $[\theta]_{255}$ ±0, $[\theta]_{248}$ −230; EA max (THF) 284 nm (ϵ 1500) (sh), 278 (1800), 266 (910) (sh), 259 (460) (sh), 253 (240), 246 (200) (sh); CD (*c* 0.0087, THF) $[\theta]_{292}$ ±0, $[\theta]_{285}$ +410 (sh), $[\theta]_{278}$ +610, $[\theta]_{271}$ +480 (sh), $[\theta]_{263}$ +250 (sh), $[\theta]_{254}$ ±0, $[\theta]_{246}$ −310, $[\theta]_{243}$ ±0, $[\theta]_{239}$ +1200; EA max (1 M HCl in H_2O) 278 nm (ϵ 1200) (sh), 273 (1300); CD (*c* 0.0068, 1 M HCl in H_2O) $[\theta]_{294}$ ±0, $[\theta]_{280}$ +820 (sh), $[\theta]_{274}$ +970, $[\theta]_{267}$ +690 (sh), $[\theta]_{251}$ +170, $[\theta]_{233}$ +4700; EA max (1 M NaOH in H_2O) 293 nm (ϵ 2400); CD (c 0.0079, 1 M NaOH in H_2O) $[\theta]_{321}$ ±0, $[\theta]_{292}$ +1300, $[\theta]_{266}$ ±0, $[\theta]_{256}$ −420.

L-Tyrosinol hydrochloride (L-8e·HCl) had $[\alpha]^{23}_D$ −17° (*c* 2.0, H_2O): EA max (H_2O) 280 nm (ϵ 1200) (sh), 274 (1400); CD (*c* 0.0087, H_2O) $[\theta]_{294}$ ±0, $[\theta]_{281}$ −300 (sh), $[\theta]_{274}$ −360, $[\theta]_{245}$ −30, $[\theta]_{231}$ −500; EA max (MeOH) 281 nm (ϵ 1400) (sh), 275 (1600); CD (*c* 0.0097, MeOH) $[\theta]_{292}$ ±0, $[\theta]_{284}$ −300 (sh), $[\theta]_{279}$ −380, $[\theta]_{253}$ ±0, $[\theta]_{234}$ +90; EA max (1 M NaOH in H_2O) 293 nm (ϵ 2400); CD (*c* 0.0093, 1 M NaOH in H_2O) $[\theta]_{319}$ ±0, $[\theta]_{295}$ −670, $[\theta]_{267}$ −180, $[\theta]_{254}$ −320; EA max (0.1 M KOH in MeOH) 294 nm (ϵ 2300); CD (*c* 0.0077, 0.1 M KOH in MeOH) $[\theta]_{319}$ ±0, $[\theta]_{298}$ −500 (sh), $[\theta]_{294}$ −530, $[\theta]_{264}$ −100, $[\theta]_{255}$ −520.

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