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Optically Active Amines. 33.[1] Circular Dichroism of Substituted Phenylcarbinols[2]

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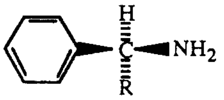
Examination of the isotropic electronic absorption and circular dichroism spectra of unsubstituted and ring-substituted phenylcarbinols indicates that the sign of the ^1L_b Cotton effects (CEs) at about 254–282 nm of the benzene chromophore of the unsubstituted phenylcarbinols is determined by vibronic borrowing from the ^1B_b-allowed transition. On ring substitution by an atom or group with either a positive (Cl, CH_3O, CH_3) or a negative (CF_3, aza) spectroscopic moment, 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*)-α-phenylethyl alcohol, (*R*)-phenylethylene glycol, (*R*)-mandelic acid, methyl (*R*)-mandelate, and (*S*)-β-hydroxy-β-phenylpropionic acid by an atom or group with a positive spectroscopic moment can be viewed as the overshadowing of the positive vibronic rotational strength by a negative induced contribution. On para substitution with an atom or group with a negative spectroscopic moment, bond moments of an opposite sense are induced, and the positive induced contribution to the rotational strength has the same sign as the vibrational contribution. As a result, both (*S*)-α-[*p*-(trifluoromethyl)phenyl]ethyl and (*S*)-α-(4-pyridyl)ethyl alcohol show a positive ^1L_b band origin CE. Meta substitution by a particular group will induce bond moments in an opposite sense from that induced by the same group in the para position. Thus, meta substitution by an atom or group with a positive and a negative spectroscopic moment of the analogues of (*S*)-α-phenylethyl alcohol results in positive and negative ^1L_b CEs, respectively. Ortho substitution again reverses the sense of the induced bond moments from that of the same meta substituent, and the sign of the ^1L_b CEs is reversed from that of the meta isomer.

Examination[3] of the isotropic electronic absorption (EA) and circular dichroism (CD) spectra of unsubstituted, para-substituted, and 3,5-disubstituted α-phenyl- and α-benzylethylamines and their hydrochlorides indicates that, for the unsubstituted compounds, the sign of the ^1L_b Cotton effects (CEs) at 254–282 nm of the benzene chromophore is determined by vibronic borrowing[4,5] from benzene transitions at shorter wavelength. Both (*S*)-α-phenylethylamine [(*S*)-**1a**] and its hydrochloride [(*S*)-**1a**·HCl] show positive CEs associated with transitions from the lowest energy vibrational mode in the ground state to totally symmetric vibrational modes in the first electronically excited state.[6,7] Other phenylalkylcarbinamines,[8,9] such as (*S*)-α-phenyl-*n*-propylamine[8,9] [(*S*)-**1b**] and (*S*)-α-phenylneopentylamine[8] [(*S*)-**1c**] and their hydrochlorides, also show positive ^1L_b CEs, the sign also being determined by vibronic borrowing from benzene transitions at shorter wavelength. On para substitution of (*S*)-**1a** and (*S*)-**1a**·HCl by an atom or group with either a positive (Cl, Br, CH_3, CH_3O) or a negative (CN, CF_3) spectroscopic moment,[10] the sign of the ^1L_b may be different from that of unsubstituted compound,[3,11] but the sign of the CEs can be correlated with the absolute configuration provided the spectroscopic moment of the additional substituent is taken into account.[3] Meta and ortho substitution by similar groups would also influence the sign of the ^1L_b CEs, but only the CD of the 3,5-dimethyl and 3,5-dichloro derivatives of (*S*)-**1a** and its hydrochloride have been reported.[3]



(*S*)-**1a**, R = CH_3

b, R = CH_3CH_2

c, R = $(CH_3)_3C$

Phenylalkylcarbinol analogues of (*S*)-**1a**, such as (*S*)-phenylethyl alcohol[12] [(*S*)-**2a**] and its derivatives for which

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[1] Part 32: Johnson, W. C., Jr.; Fontana, L. P.; Smith, H. E. *J. Am. Chem. Soc.* **1987**, *109*, 3361–3366.

[2] Taken in part from: Fontana, L. P. Ph.D. Dissertation, Vanderbilt University, Dec 1986. To be presented at the 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 30–Sept 4, 1987.

[3] Smith, H. E.; Neergaard, J. R.; de Paulis, T.; Chen, F.-M. *J. Am. Chem. Soc.* **1983**, *105*, 1578–1584.

[4] Weigang, O. E., Jr. *J. Chem. Phys.* **1965**, *43*, 3609–3618.

[5] Weigang, O. E., Jr.; Ong, E. C. *Tetrahedron* **1974**, *30*, 1783–1793.

[6] Smith, H. E.; Willis, T. C., *J. Am. Chem. Soc.* **1971**, *93*, 2282–2290.

[7] Smith, H. E.; Burrows, E. P.; Chen, F.-M. *J. Am. Chem. Soc.* **1978**, *100*, 3714–3720.

[8] Smith, H. E.; Warren, M. E., Jr.; Katzin, L. I. *Tetrahedron* **1968**, *24*, 1327–1335.

[9] Ghislandi, V.; La Manna, A.; Vercesi, D. *Farmaco, Ed. Sci.* **1976**, *31*, 561–571.

[10] Platt, J. R. *J. Chem. Phys.* **1951**, *19*, 263–271.

[11] Gottarelli, G.; Samori, B. *J. Chem. Soc. B* **1971**, 2418–2423.

[12] Gillard, R. D.; Mitchell, P. R. *Trans. Faraday Soc.* **1969**, *65*, 2611–2620. The configurational designator for (−)-**2a** in this report is incorrect. The levorotatory isomer of **2a** has the *S* configuration[13] and positive ^1L_b CEs.

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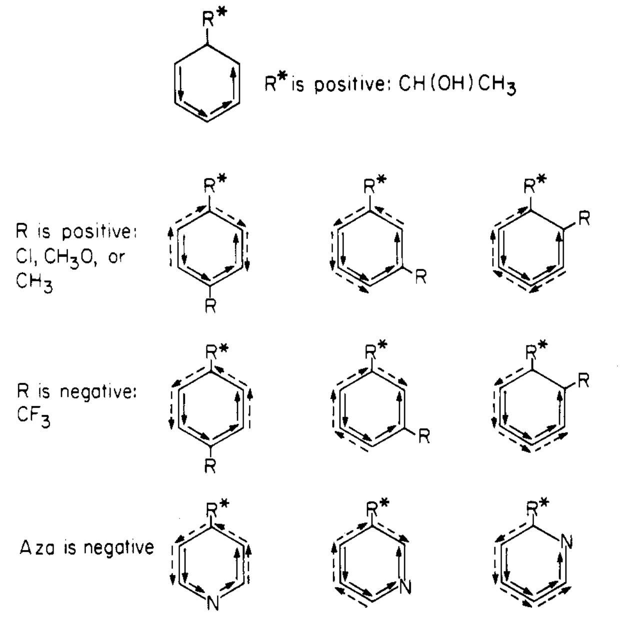
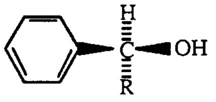


Figure 1. Induced bond moment directions for chiral benzene compounds substituted with groups having positive and negative spectroscopic moments. Solid arrows represent the bond moments induced by the chiral group, whereas the dashed arrows represent those induced by the additional ring substituent.

the alkyl group is in a higher oxidation state[12,14,15] (**2b–d**) or is larger in effective bulk size[16,17] (**2e,f**) than is a methyl group, also show positive ^1L_b CEs, the sign being the same as that of the respective band origin CD maximum shown in Table I.



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

(*R*)-**2b**, $R = CH_2OH$

(*R*)-**2c**, $R = CO_2H$

(*R*)-**2d**, $R = CO_2CH_3$

(*S*)-**2e**, $R = CH_2CO_2H$

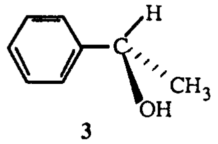
(*S*)-**2f**, $R = C(CH_3)_3$

Table I. Spectral Data for Phenylcarbinols[a]

parent compd	subst	^1L_b band origin λ_{max}, nm (ϵ[b])	λ_{max}, nm ($\Delta\epsilon$[c])	ref[d]
No Additional Ring Substituent				
(*S*)-**2a**		267 (91)	267 (+0.20)	12[e]
		267 (90)	268 (+0.17)	*f*, *g*
(*R*)-**2b**		267 (70)	267 (+0.11)	12[e,g]
(*R*)-**2c**		266 (100)	267 (+0.11)	14[g,h]
(*R*)-**2d**		*i*	262 (+0.082)[j]	15[e]
(*S*)-**2e**		*i*	268 (+0.11)	16[g]
(*S*)-**2f**		267 (130)	268 (+0.39)	17[e,g]
Para Substitution by a Group with a Positive Spectroscopic Moment				
(*S*)-**2a**	Cl	275 (240)	276 (−0.025)	*f*
(*R*)-**2b**	CH_3O	*i*	274 (−0.28)	18
(*R*)-**2c**	Cl	275 (i)	275 (−0.10)	19
(*R*)-**2d**	Cl	281 (i)	275 (−0.14)	19[k]
(*S*)-**2e**	Cl	*i*	275 (−0.05)	16[g]
Para Substitution by a Group with a Negative Spectroscopic Moment				
(*S*)-**2a**	CF_3	269 (280)	268 (+0.12)	*f*
(*S*)-**2a**	aza[l]	263 (1900)[m]	265 (+0.06)	20[n]
Meta Substitution by a Group with a Positive Spectroscopic Moment				
(*R*)-**2c**	Cl	266 (*i*)	264 (+0.14)	19[g]
(*R*)-**2d**	Cl	275 (*i*)	283 (+0.02)	19[g,k]
(*S*)-**2e**	Cl	*i*	274 (+0.25)	16[g]
Meta Substitution by a Group with a Negative Spectroscopic Moment				
(*S*)-**2a**	aza[o]	266 (2200)[m]	267 (−1.0)	21
Ortho Substitution by a Group with a Positive Spectroscopic Moment				
(*S*)-**2a**	CH_3	270 (150)	273 (−0.040)	22[g,p]
(*R*)-**2c**	Cl	*i*	272 (−0.040)	23
(*R*)-**2d**	CH_3O	281 (*i*)	282 (−0.27)	19[g,k]
(*S*)-**2e**	Cl	*i*	273 (−0.09)	16[g]
Ortho Substitution by a Group with a Negative Spectroscopic Moment				
(*S*)-**2a**	aza[q]	270 (2500)	268 (+0.14)	20[n]

[a] Methanol as solvent or as noted otherwise. [b] Molar absorptivity. [c] Molar dichroic absorption. $\Delta\epsilon = [\theta]/3300$ where $[\theta]$ is the molecular elipticity. [d] Report of spectral data. [e] Ethanol as solvent. [f] This work. [g] Enantiomer used. [h] Water as solvent. [i] Not reported. [j] Center maximum of three ^1L_b CEs. [k] Hexane as solvent. [l] (*S*)-α-(4-Pyridyl)ethyl alcohol [(*S*)-**4a**]. [m] Shoulder. [n] Methanol-glycerol as solvent. [o] (*S*)-α-(3-Pyridyl)ethyl alcohol [(*S*)-**4b**]. [p] Solvent not specified. [q] (*S*)-α-(2-Pyridyl)ethyl alcohol [(*S*)-**4c**].

The absolute configurations of the enantiomers of **2a–f** are well established.[13] It can also be assumed that in each the phenyl ring has a preferred conformation about its attachment bond such that the hydrogen atom at the chiral center essentially eclipses the phenyl ring plane. This preferred conformation was calculated[22] for (*S*)-α-phenylethyl alcohol (**3**) and is suggested by proton magnetic resonance studies with 3,4-dichlorobenzylamine[24] and 3,5-dibromoethylbenzene.[25]



3

The EA and CD spectra of the enantiomers of **2a–e** are of additional interest in that these spectra and those of their ortho-, meta-, and para-substituted derivatives (Table I) can be used to show that when both the spectroscopic moment and position of a ring substituent on **2a–e** are taken into account, the absolute configuration of the chiral

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(13) Klyne, W.; Buckingham, J. *Atlas of Stereochemistry*, 2nd ed.; Oxford: New York, 1978; Vol. 1; Chapman and Hall: London, 1978; Vol. 2.

(14) Verbit, L.; Heffron, P. J. *Tetrahedron* **1968**, *24*, 1231–1236.

(15) Barth, G.; Voelter, W.; Mosher, H. S.; Bunnenberg, E.; Djerassi, C. *J. Am. Chem. Soc.* **1970**, *92*, 875–886.

(16) Collet, A.; Jacques, J. *Bull. Soc. Chim. Fr.* **1972**, 3857–3862.

(17) Biernbaum, M. S.; Mosher, H. S. *J. Org. Chem.* **1971**, *36*, 3168–3177.

(18) Neilson, D. G.; Zakir, U.; Scrimgeour, C. M. *J. Chem. Soc. C* **1971**, 898–904.

(19) Korver, O. *Tetrahedron* **1970**, *26*, 5507–5518.

(20) Gottarelli, G.; Samori, B. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1462–1465.

(21) Gottarelli, G.; Samori, B. *Tetrahedron Lett.* **1970**, 2055–2058.

(22) Cervinka, O.; Kral, M.; Malon, P. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2406–2421.

(23) Collet, A.; Jacques, J. *Bull. Soc. Chim. Fr.* **1973**, 3330–3334.

(24) Schaefer, T; Danchura, W.; Niemczura, W. *Can. J. Chem.* **1978**, *56*, 2229–2232.

(25) Schaefer, T; Niemczura, W.; Danchura, W. *Can. J. Chem.* **1979**, *57*, 355–359.

center correlates with the sign of the ^1L_b CEs.

Discussion

For benzene, the ^1L_b transition is both electrically and magnetically forbidden with its EA intensity coming from the $^1B_{ab}$-allowed transition. On substitution, an electric transition moment normal to the substituent attachment bond and concomitantly a magnetic transition moment perpendicular to the ring are induced in the ^1L_b transition. These induced transition moments can give rise to ^1L_b CEs in chiral benzene compounds through coupling with dissymmetric substituents.[3] Further, as in the EA, the rotational strengths of the CEs can be influenced by the $^1B_{ab}$ transitions by vibronic interaction.[4,5] The magnitude of the induced electronic transition moment is related to the spectroscopic moment[10] of the substituent of the benzene ring. This moment can be decomposed into bond transition moments[26,27] as shown in Figure 1. The direction of the induced magnetic transition moment can be determined by the sense of rotation of the bond transition moments, pointing up for the bond transition moments in the counterclockwise sense.

The relative importance of the induced effect can be rationalized by using Figure 1. The chiral substituent (R*) does not induce transition moments in bonds adjacent to its attachment bond, and thus there is negligible chiral interaction by the ^1L_b transition moment with the chiral substituent. The positive ^1L_b CEs for the enantiomers of **2a**–**f** in Table I are dominated by vibronic borrowing from the ^1B_b-allowed transition and do not depend on the spectroscopic momentof the chiral group. The chiral group for **2a** is shown in Figure 1 with a positive spectroscopic moment, deduced on the basis of the molar absorptivity (ϵ) of the ^1L_b band origin for the parent compound (**2a**), for benzene with a single ring substituent, and for the para-substituted parent compound. Thus α-(p-chlorophenyl)ethyl alcohol has an ^1L_b band origin with an ϵ of 240, higher than those for α-phenylethyl alcohol (ϵ 91) or for chlorobenzene (ϵ 200) (see the Experimental Section), the positive spectroscopic moment of the chlorine atom[10] augmenting that of the chiral group.[28] Also, α-[p-(trifluoromethyl)phenyl]ethyl alcohol has an ϵ of 280, higher than that of **2a** but smaller than that of (trifluoromethyl)benzene (ϵ 380) (see the Experimental Section), the negative spectroscopic moment of the trifluoromethyl group[10] being partially canceled by the positive spectroscopic moment of the chiral group.[28] That the chiral group in mandelic acid (**2c**) has in fact a negative spectroscopic moment is suggested by the ^1L_b band origin intensities reported[29] for **2c** (ϵ 78, 265 nm) and p-chloromandelic acid (ϵ 180, 274 nm), the latter slightly smaller than that for chlorobenzene.

The importance of the vibronic coupling mechanism in **2a**–**f** is underscored by the everpresence of a nontotally symmetric vibrational progression in their EA spectra.[6,12] The dominance of a vibronic contribution to the ^1L_b CEs also affords a rationale for the observation of positive ^1L_b CEs for both (S)-α-phenylethylamine [(S)-**1a**] and its hydrochloride [(S)-**1a**·HCl] despite the difference in sign of the spectroscopic moment, positive and negative, respectively, for their chiral groups.[3]

On additional ring substitution, transition moments are induced in ring bonds adjacent to the attachment bond of the chiral group (Figure 1), resulting in enhanced coupling of the ^1L_b transition with the chiral group. Since a substituent at the para position does not change the preferred conformation of the phenyl group about its attachment bond, the reversal of the sign of the ^1L_b CE on para substitution of **2a**–**e** with an atom or group with a positive spectroscopic moment[10] (Cl, CH_3O) results from the overshadowing of the positive vibrational rotational strength by a negative induced contribution. On para substitution with a group with a negative spectroscopic moment[10] (CF_3, aza), bond moments of an opposite sense are induced in the ring bonds adjacent to the attachment bond of the chiral group (Figure 1). The positive induced contribution resulting from enhanced chiral interaction of the ^1L_b transition moment with the chiral group has the same sign as the vibrational rotational strength. These derivatives of (S)-**2a** show positive ^1L_b band origins.

As has been noted earlier,[3] the lack of correlation of the magnitude of the molar absortivity (ϵ) with that of the molar dichroic absorption ($\Delta\epsilon$) suggests that the contribution from the induced electric transition moment is less important than that of the induced magnetic transition moment. This is in agreement with a similar conclusion reached by Schoenfelder and Snatzke[30] from CD studies of benzene derivatives with several identical chiral substituents.

On meta and ortho substitutions of (S)-**2a**–**e** it can also be assumed that there is no change in the preferred conformation of the phenyl ring about its attachment bond, and the hydrogen atom at the chiral center still eclipses an ortho hydrogen atom. As shown in Figure 1, however, meta substitution by a particular group will induce bond moments in the opposite sense from that induced by the same group in the para position.[3,31] Thus, meta substitution of a phenylcarbinol by an atom or group with a positive (Cl) and a negative spectroscopic moment (aza) results in positive and negative ^1L_b CEs, respectively (Table I). Ortho substitution again reverses the sense of the induced bond moments from that of the same meta substituent (Figure 1), and ortho-substituted analogues of (S)-**2a** have negative and positive ^1L_b CEs when the ortho substituents have, respectively, positive and negative spectroscopic moments (Figure 1).

Other examples of the reported CD spectra of substituted phenylcarbinols could be used to illustrate the effect of substituent position and spectroscopic moment on the sign of the ^1L_b CEs. Thus, the absolute configuration of various para-, meta-, and ortho-substituted fluoro, bromo, and methoxy derivatives of (R)-mandelic acid[18,19,23,32] [(R)-**2c**], methyl (R)-mandelate[19] [(R)-**2d**], and (S)-β-hydroxy-β-phenylpropionic and[16] [(S)-**2e**] are also correlated with the sign of the ^1L_b CE. The absolute configurations of these phenylcarbinols were established by various means, including Horeau's method of asymmetric synthesis,[16] chemical conversion,[16,18] ORD correlations with chromophoric derivatives,[18] ^1H NMR spectra using (+)-α-(1-naphthyl)ethylamine as a chiral solvent,[19] and Fredga's method of quasi-racemates.[23] In one report,[32] the sign of the ^1L_b band origin CD maximum for the o-Br derivative of (R)-**2a** in methanol was corrected from that reported earlier[18] so that the negative sign now agrees with prediction. Other inconsistencies, however, remain. The CD of the m-F derivative of (R)-**2c** in methanol was also cor-

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[26] Mason, S. F. *J. Chem. Soc., Chem. Commun.* **1973**, 239–241.

[27] Sagiv, J. *Tetrahedron* **1977**, *33*, 2315–2320.

[28] Matsen, F. A. In *Chemical Applications of Spectroscopy*; West, W., Ed.; Interscience: New York, 1956; Chapter V, Part 2.

[29] Collopy, T. J.; Klingenberg, J. J. *J. Inorg. Nucl. Chem.* **1961**, *18*, 184–191.

[30] Schoenfelder, W.; Snatzke, G. *Isr. J. Chem.* **1980**, *20*, 142–149.

[31] Snatzke, G.; Kajtar, M.; Werner-Zamojska, F. *Tetrahedron* **1972**, *28*, 281–288.

[32] Korver, O.; De Jong S.; van Soest, T. C. *Tetrahedron* **1976**, *32*, 1225–1229.

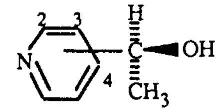
rected from that reported earlier[19] so that the negative sign now assigned to the ^1L_b CEs[32] does not agree with prediction. The respective CD spectra of *o*-Br, *o*-Cl, *m*-Br, and *m*-F derivatives of (*R*)-**2c** were also measured in EPA (ether–isopentane–ethanol) at 25 °C and −185 °C.[32] At 25 °C, the sign of ^1L_b CEs for each derivative was the same as that in methanol. On cooling however, the ^1L_b CEs for the *o*-Br and *o*-Cl derivatives change sign, while those of the *m*-Br and *m*-F derivatives do not. This reversal in sign for the ortho-substituted derivatives was suggested as being the result of conformational change for the ortho-substituted compound[32] and certainly is worthy of additional investigation.

In connection with CD spectra of the aza-substituted derivatives of (*S*)-α-phenylethyl alcohol [(*S*)-**2a**], another report[33] for the CD spectra of α-(2-, 3-, and 4-pyridyl)ethyl alcohols in methanol or cyclohexane is in general agreement with the data in Table I except that the CD maximum for ^1L_b band origin for the 4-pyridyl isomer was not observed. The same is true for the three aza derivatives of (*S*)-α-phenylethylamine [(*S*)-**1a**)].[34] The 2- and 3-pyridyl analogues of (*S*)-**1a** in methanol show, as predicted, positive and negative ^1L_b band origin CEs, respectively,[34] but a similar ^1L_b CE for the 4-pyridyl compound in methanol was not observed. The pyridyl CD spectra, however, are sometimes complicated by substantial vibrational fine structure within the ^1L_b band[20] and by dichroic absorption with a maximum at about 240 nm.[34] This dichroic absorption is generally of opposite sign to that of the ^1L_b band origin CD maximum and can make the identification of the ^1L_b band origin CD maximum difficult. The 240-nm band is assigned to an $n \rightarrow \pi^*$ transition of the aza group[34,35] or to the ^1L_b transition as a result of strong vibronic coupling.[36]

Similar to the CD observations for (*S*)-(3-pyridyl)ethyl alcohol [(*S*)-**4b**], nicotine [(*S*)-**5a**], nornicotine [(*S*)-**5b**], anabasine [(*S*)-**6a**], and *N*-methylanabasine [(*S*)-**6b**] all show, as predicted, a negative CD maximum corresponding to the ^1L_b absorption maximum,[37] but multiple ^1L_b CEs are reported only for (*S*)-**5a**.[38]

Experimental Section

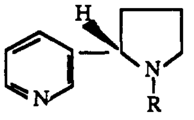
Rotatory powers at the sodium D line were measured with a Rudolph Research Autopol III automatic polarimeter and 1-dm sample tube. Electronic absorption (EA) spectra were measured with a Cary Model 14 spectrometer with matched 1-cm cells and the normal variable slit. Circular dichroism (CD) spectra were obtained at 25–28 °C with a Cary Model 60 spectropolarimeter with a CD Model 6001 accessory. The sample cell length was 1 cm, and the slit was programmed for a spectral band width of 1.5 nm. Cutoff was indicated when the dynode voltage reached 400 V. Spectral measurements began at 300 nm, and the molecular ellipticity values are corrected to 100% enantiomeric excess (ee).



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

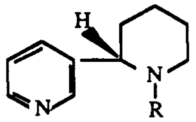
b , 3-pyridyl

c , 2-pyridyl



(*S*)-**5a**, R = CH$_3$

b, R = H



(*S*)-**6a**, R = H

b, R = CH$_3$

(*R*)-α-Phenylethyl alcohol:[39] $[\alpha]^{25}_D$ +41° (*c* 1.44, CH_3OH), d^{20}_4 1.01, and $[\alpha]^{25}_D$ +39.1° (neat) [lit.[40] α_D +45.7° (neat, 1 dm), 100% ee], 87% ee; EA_{max} (CH_3OH) 267 nm (ϵ 90), 264 (150), 261 (150) (sh), 257 (210), 255 (170) (sh), 252 (220), 250 (200) (sh), 247 (210), 243 (190), 207 (8900); CD (CH_3OH, *c* 0.0576) $[\theta]_{275}$ ±0, $[\theta]_{268}$ −550, $[\theta]_{265}$ −180, $[\theta]_{261}$ −620, $[\theta]_{258}$ −290, $[\theta]_{255}$ −390, $[\theta]_{252}$ −180, $[\theta]_{250}$ −190, $[\theta]_{247}$ −110 (sh), $[\theta]_{230}$ ±0.

(*S*)-α-(*p*-Chlorophenyl)ethyl alcohol:[39] $[\alpha]^{27}_D$ −47° (*c* 2.13 $(CH_3CH_2)_2O$), d^{25}_4 1.16, and $[\alpha]^{24}_D$ −54.0° (neat) [lit.[41] +49.9° (*c* 2, $(CH_3CH_2)_2O$) for the enantiomer, 100% ee], 94% ee; EA_{max} (CH_3OH) 275 nm (ϵ 240), 272 (160) (sh), 270 (230) (sh), 267 (290), 264 (240) (sh), 262 (230), 259 (250), 254 (190), 248 (130); CD (CH_3OH, *c* 0.130) $[\theta]_{285}$ ±0, $[\theta]_{276}$ −83, $[\theta]_{273}$ ±0, $[\theta]_{269}$ −62, $[\theta]_{266}$ +52, $[\theta]_{262}$ ±0, $[\theta]_{259}$ +42, $[\theta]_{255}$ +21, $[\theta]_{252}$ +42, $[\theta]_{235}$ ±0.

(*S*)-α-[*p*-(Trifluoromethyl)phenyl]ethyl alcohol:[39] $[\alpha]^{25}_D$ −29° (*c* 1.69, CH_3OH) and α^{24}_D −41.0 (neat, 1 dm), 90% ee;[39] EA_{max} (CH_3OH) 269 nm (ϵ 280), 266 (210) (sh), 263 (370), 258 (350), 253 (260) (sh), 245 (170) (sh), 238 (120) (sh), 213 (10000); CD (CH_3OH), *c* 0.0518) $[\theta]_{275}$ ±0, $[\theta]_{268}$ +390, $[\theta]_{265}$ +200, $[\theta]_{262}$ +360, $[\theta]_{258}$ +240, $[\theta]_{255}$ +280, $[\theta]_{246}$ +150, $[\theta]_{234}$ ±0.

Chlorobenzene: EA_{max} (CH_3OH) 272 nm (ϵ 200), 267 (170), 264 (280), 261 (220), 258 (220), 255 (180), 252 (150), 249 (110), 246 (95), 240 (50).

(Trifluoromethyl)benzene: EA_{max} (CH_3OH) 266 nm (ϵ 380), 263 (180), 259 (450), 256 (240), 253 (310), 250 (190), 248 (180).

Registry No. (*R*)-α-Phenylethyl alcohol, 1517-69-7; (*S*)-α-(*p*-chlorophenyl)ethyl alcohol, 3391-10-4; (*S*)-α-[*p*-(trifluoromethyl)phenyl]ethyl alcohol, 99493-93-3.

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(33) Cervinka, O.; Malon, P. *Collect. Czech. Chem. Commun.* **1978**, *43*, 278–287.

(34) Smith, H. E.; Schaad, L. J.; Banks, R. B.; Wiant, C. J.; Jordan, C. F. *J. Am. Chem. Soc.* **1973**, *95*, 811–818.

(35) Salvadori, P.; Rosini, C.; Bertucci, C.; Pini, D.; Marchetti, M. *J. Chem. Soc., Perkin Trans. 2* **1983**, 399–402.

(36) Yeh, C.-Y.; Richardson, F. S. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 331–350.

(37) Testa, B.; Jenner, P. *Mol. Pharmacol.* **1973**, *9*, 10–16.

(38) Tomita, A.; Ochiai, E.; Hirai, H.; Markishima, S. *J. Org. Chem.* **1966**, *31*, 4307–4308.

(39) Polavarapu, P. L.; Fontana, L. P.; Smith, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 94–99.

(40) Okamoto, K.; Kinoshita, T.; Takemura, Y.; Yoneda, H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1426–1433.

(41) Ishizaki, T.; Miura, H.; Nohira, H. *Nippon Kagaku Kaishi* **1980**, 1381–1384.