proteins. Many earlier studies[4,43–47] have indicated that 100% nitration of all the accessible tyrosine side chains in the proteins can occur under proper conditions. A previous study[3] on the mechanism of the reaction of 4NM with a series of para-substituted phenoxide ions revealed that the major products consist of nitrite ion and phenol coupling products arising from free-radical oxidation of the phenoxide ion by 4NM. Nitration of phenol occurs not more than 30%. The question then arises in reference to the modification of proteins by 4NM as to why 100% nitration of the tyrosine side chains is apparently occurring. Though protein modifiers on the average use 20–60 molar excess of 4NM in the nitration procedure, our studies have indicated that the use of excess reagent does not lead to 100% nitration. In fact the nitrophenol yields appear lower than expected from our previous study in the presence of excess phenol. Since m-nitrophenol was found to react with 4NM,[3] the 4-methyl-2-nitrophenol derived from p-cresol undoubtedly reacts with 4NM also. Furthermore we have found that the addition of up to 75%

ethanol only increases the nitration of p-cresol about 20%.

The quantitative nitration of accessible tyrosyl residues in proteins may be rationalized as follows: presumably the major reaction is the formation of the phenoxy radical as was found with the model compounds; however, restriction on the spacial freedom of radical species imposed by the protein tertiary structure may prevent intramolecular coupling of the radical species. Intermolecular cross-linking between protein molecules may be possible if the tyrosyl content on the exterior of the protein is sufficiently high. Once radical coupling is hindered, however, the tyrosyl radical may recombine with a nitro radical generated in the oxidation process to form the nitrated tyrosine. Even though 4NM is known to cause cross-linking between tyrosyl residues in such biological materials as collagen and γ-globulin,[43] there has been very little evidence reported for any linked tyrosine residues in the enzymes modified so far.[49]

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Optically Active Amines. XI.[1] Optical Rotatory Dispersion and Circular Dichroism Observations on α- and β-Phenylalkylamine Hydrochlorides[2]

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Abstract: Examination of the uv (isotropic absorption), ORD, and CD spectra from about 225 to 300 nm of a number of optically active α- and β-phenylalkylamine hydrochlorides shows that the sign of the Cotton effects in the range 245–270 nm can be predicted using a quadrant sector rule. This rule applies to and is keyed to the $B_2 \leftarrow A_1$ transitions of the phenyl ring chromophore. For open-chain diphenyl-substituted alkylamine hydrochlorides in which the phenyl rings are connected through at least three σ bonds, there is no vicinal interaction between the phenyl groups. The uv, ORD, and CD spectra are the sum of the contributions of each phenyl chromophore. The quadrant sector rule is useful for the interpretation of both the ORD and CD spectra of these compounds. For diphenyl-substituted alkylamine hydrochlorides in which the phenyl rings are connected through two σ bonds, vicinal interaction (homoconjugation) of the phenyl chromophores is reflected in the uv, ORD, and CD spectra. In both the ORD and CD, a large enhancement of the rotational strength of the multiple Cotton effects from 245 to 270 nm is observed. The sign of these Cotton effects is dependent on the preferred orientation of one phenyl group with respect to the other.

Earlier the ORD curves were reported[4] for (R)-α-phenylethylamine [(R)-1a], (R)-α-phenyl-n-propylamine [(R)-2a], (R)-α-phenylneopentylamine [(R)-

3a], and (S)-α-benzylethylamine [(S)-4a] and their respective hydrochlorides [(R)-1b–(R)-3b and (S)-4b] in methyl alcohol and in isopropyl alcohol from about 225 to 295 nm. As has been noted with similar compounds,[5–13] and in particular with (R)-1a,[6,7] (S)-1a,[11]

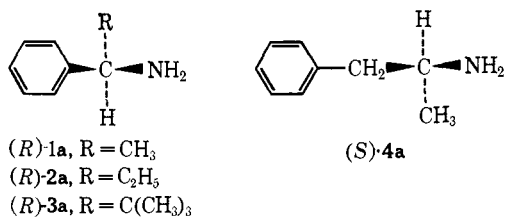(1) Paper X: H. E. Smith and T. C. Willis, *Tetrahedron*, 26, 107 (1970); erratum: *ibid.*, 26, 2258 (1970).
(2) Taken from the Ph.D. dissertation of T. C. W., Vanderbilt University, 1969; presented in part at the Combined Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970, Abstract 376.
(3) Tennessee Eastman Fellow, 1966–1967.

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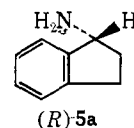(5) L. Verbit, *J. Amer. Chem. Soc.*, 87, 1617 (1965).

(R)-1a, R = CH₃
(R)-2a, R = C₂H₅
(R)-3a, R = C(CH₃)₃

(S)-4a

cluding (R)-α-phenylethylamine [(R)-1a] and (R)-1-indanamine [(R)-5a] and their hydrochlorides [(R)-1b

(R)-5a

(R)-1b,[7] (S)-1b,[11] (S)-2a,[12] (S)-4a,[11] and the sulfate salt of (S)-4a,[11] two contributions to the ORD are found.

One is that of the long wavelength $\pi \to \pi^*$ transition of the phenyl chromophore, designated $^1L_b \leftarrow {}^1A$ by Platt.[14,15] This transition shows multiple Cotton effects in the range 245–270 nm whether the phenyl group is attached directly to the asymmetric center or is separated from it by a methylene group.

Another contribution originates primarily in the two $\pi \to \pi^*$ absorption bands lying below 220 nm,[15] designated $^1L_a \leftarrow {}^1A$ and $^1B \leftarrow {}^1A$ transitions.[14,15] This contribution far overrides in intensity the contribution at 245–270 nm and in general gives the sign to the rotation in the visible part of the spectrum.[4,5,7] For the open-chain amines (1a–4a), the plain ORD curve from about 225 to 245 nm, and the background curves in general, change only slightly with a change in solvent. For a given configuration, however, the plain curve may be of opposite sign.[4] For the open-chain α-phenylalkylamine hydrochlorides (1b–3b), the plain curves from 225 to 245 nm also do not change greatly with a change in solvent, but in the case of (R)-α-phenyl-n-propylamine hydrochloride [(R)-2b], the sign is negative and is opposite to that for the corresponding free base [(R)-2a].[4] For (S)-α-benzylethylamine hydrochloride [(S)-4b] in methyl alcohol, the plain curve is positive whereas in isopropyl alcohol it is negative. For this salt, the sign of rotation at 589 nm ([Φ]D) changes from positive to negative when the solvent is changed from methyl alcohol to isopropyl alcohol.[4,16]

Most significantly, and in agreement with other reports,[6,7,11–13] for the open-chain α- and β-phenylalkyl-amines (1a–4a) and their hydrochlorides (1b–4b), a negative sign for the longest wavelength Cotton effect at about 268 nm correlates with the R configuration. For 1a–3a and 1b–3b, this correlation is in agreement with a recently formulated sector rule for the prediction of the sign of this Cotton effect for a particular enantiomer.[7] The rule was first suggested on the basis of the Cotton effects in the ORD of a series of optically active α-substituted phenylethanes and 1-substituted indans, in-

and (R)-5b]. The rule was later developed as a quadrant sector rule on theoretical grounds for monosubstituted benzene compounds[17] and deduced empirically using the CD spectra of a number of rigid aromatic alkaloids.[18]

The quadrant sector rule as applied to α-substituted phenylethanes and 1-substituted indanes may be depicted as 6 and 7 with σ_{xz} and σ_{yz} being symmetry planes

6a   7a   6b and 7b
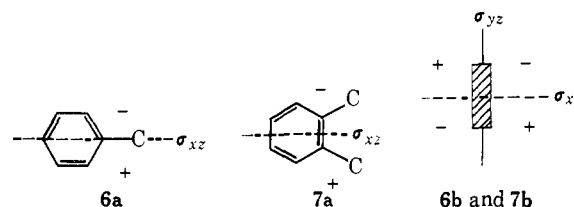
defined by the symmetry axis (C_2 axis) and by the plane of the phenyl ring. The attachments of the carbon substituents are shown in 6a and 7a. In 6a and 7a, the signs refer to the rotatory contributions of groups[19] lying above the phenyl ring plane. For those below this plane, the signs, as shown in 6b and 7b, viewed remotely from the ring substituents, are reversed. Groups lying in the symmetry planes do not contribute to the rotatory perturbation. Also, since no Cotton effect was detected in the ORD of (R)-1-methylindan from 232 to 558 nm,[7] it is concluded that an alkyl group is not capable of a rotationally significant interaction with the phenyl chromophore. For optically active amines, dissymmetric internal hydrogen bonding may be one way by which strong Cotton effects may be produced. For amine salts, the presence of a positive charge may also be important.

The sign of the rotational perturbation of a group lying in a particular sector was deduced empirically. The positive Cotton effect centered near 270 nm shown by (R)-5a and (R)-5b defines the upper left and lower right sectors of 7b as positive. For the open-chain analogs (1a–3a and 1b–3b), the sign follows from a consideration of the preferred conformation of these molecules, the sign of the observed Cotton effect being the algebraic sum of the rotatory contribution of each conformer. Both (R)-1a and (R)-1b show negative longest wavelength Cotton effects at about 268 nm. Their preferred conformation may be depicted as 8. Other conformers are of higher energy due to the nonbonded interactions of the ortho hydrogens of the phenyl ring with the amino (or ammonium chloride) group or with the methyl group. The same preferred conformation is expected regardless of the effective size of the alkyl group (R in 8) at the asymmetric center. As expected,

(6) A. La Manna, V. Ghislandi, P. M. Scopes, and R. J. Swan, *Farmaco, Ed. Sci.*, 20, 842 (1965).

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(8) L. Verbit, *ibid.*, 88, 5340 (1966).

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(12) A. La Manna, V. Ghislandi, P. B. Hulbert, and P. M. Scopes, *Farmaco, Ed. Sci.*, 22, 1037 (1967).

(13) A. La Manna, V. Ghislandi, P. B. Hulbert, and P. M. Scopes, *ibid.*, 23, 1161 (1968).

(14) J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949).

(15) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Chapter 12.

(16) The negative plain curves from 225 to 245 nm for (R)-2b and (R)-3b[4] and the solvent dependence of that of (S)-4b are not in agreement with the conclusion that salts of (S)-α- and (S)-β-phenylethylamines always show a steady descending negative background curve below 240 nm.[11]

(17) J. A. Schellman, *J. Chem. Phys.*, 44, 55 (1966).

(18) G. G. DeAngelis and W. C. Wildman, *Tetrahedron*, 25, 5099 (1969).

(19) At present these groups include carboxyl, amino, N-methyl-and N,N-dimethylamino, and their respective hydrochlorides, N,N,N-trimethylammonium iodide, hydroxyl, and hydroxymethyl.[7] See L. Angiolini and G. Gottarelli, *Tetrahedron*, 26, 421 (1970), for a recent application of the rule to 1-phenyl-1-propanols.
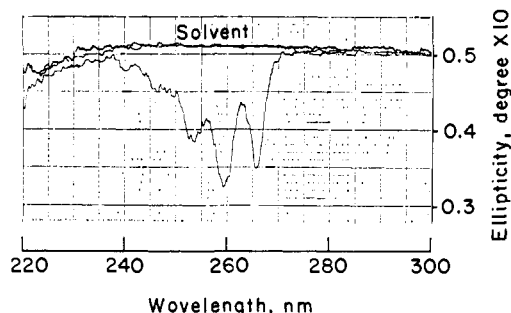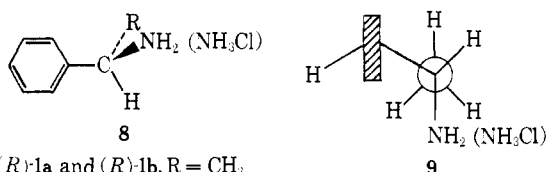
Figure 1. CD record of (R)-α-phenylethylamine hydrochloride [(R)-1b] in water (c 0.105 g/100 ml).

(R)-2a and (R)-3a and their hydrochlorides all show negative longest wavelength Cotton effects at about 268 nm. Similar considerations may be used to predict the observed Cotton effect for (S)-α-benzylethylamine

(R)-1a and (R)-1b, R = CH₃
(R)-2a and (R)-2b, R = C₂H₅
(R)-3a and (R)-3b, R = C(CH₃)₃

[(S)-4a] and (S)-4b. Considering only conformations with the phenyl ring plane eclipsing either hydrogen atom at the carbon atom adjacent to the phenyl ring and for each of these only the two conformations allowed using Brewster's conformational rules,[20] it can be seen that the conformer which probably dominates the rotatory dispersion is **9**. As predicted, the longest wavelength Cotton effect at about 268 nm for both (S)-4a and (S)-4b is positive. For (S)-4a and (S)-4b, the conformational mobility is greater than with the α-phenylalkyl-amines and the amplitude of the positive Cotton effect shown by (S)-4a and by (S)-4b is greatly reduced.

It is noted that the positive sign of the longest wavelength Cotton effect at about 268 nm in the ORD spectrum of (S)-1-phenyl-2-cyclohexylethylamine [(S)-10)] and (S)-1-phenyl-3-cyclohexylpropylamine [(S)-11] in cyclohexane[13] can also be predicted using the sector
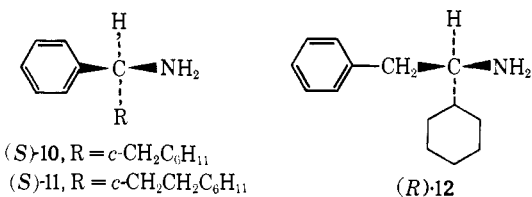
(S)-10, R = c-CH₂C₆H₁₁
(S)-11, R = c-CH₂CH₂C₆H₁₁

(R)-12

rule **6**. For (R)-1-cyclohexyl-2-phenylethylamine [(R)-12] in cyclohexane, the observed negative Cotton effect at 268 nm[13] suggests that a conformation other than one similar to **9** (a cyclohexyl group replacing the methyl group) is the most significant.

We have now extended our ORD measurements in the region 225-300 nm, using solvents of different polarities, to the hydrochlorides (5b and 13b-16b) of a number of other phenyl-substituted alkylamines: (S)-1-indan-amine [(S)-5a], (2S)-exo-3-phenyl-endo-2-norbornan-amine [(2S)-13a], (2R)-endo-3-phenyl-endo-2-norborn-

(20) J. H. Brewster, J. Amer. Chem. Soc., 81, 5475 (1959).

anamine [(2R)-14a], (1S,2S)-2,3-diphenyl-1-methyl-propylamine[21] [(1S,2S)-15a], and (S)-1,2,2-triphenyl-ethylamine[22] [(S)-16a]. These amines were characterized earlier as their hydrochlorides[1] (Table I). More

Table I. Rotatory Powers of Some Phenyl-Substituted Alkylamine Hydrochlorides in Methyl Alcohol

Hydrochloride	[φ]D^a	c^b	Ref^c
(R)-α-Phenylethylamine [(R)-1b]	+9.8	2.0	4
(S)-α-Benzylethylamine [(S)-4b]	+12	3.4	4
(S)-1-Indanamine [(S)-5b]	−5.6	5.1	1
(2S)-exo-3-Phenyl-endo-2-norbornanamine [(2S)-13b]	+100	1.0	1
(2R)-endo-3-Phenyl-endo-2-norbornanamine [(2R)-14b]	−89	1.0	1
(1S,2S)-2,3-Diphenyl-1-methylpropylamine [(1S,2S)-15b]	+250	1.0	1
(S)-1,2,2-Triphenylethylamine [(S)-16b]^d	+46	1.5^e	1
(R)-1,2-Diphenylethylamine [(R)-17b]	−299	0.99^e	f

^a Molecular rotation in degrees at 25-27°. ^b Grams per 100 ml of solvent. ^c Source and characterization. ^d Tentative configurational assignment. See ref 1. ^e Absolute ethyl alcohol as the solvent. ^f This work.

importantly we have now examined the CD of these same amine hydrochlorides as well as the CD of (R)-1b,

(2S)-13a   (2R)-14a   (1S,2S)-15a

(S)-16a   (R)-17a
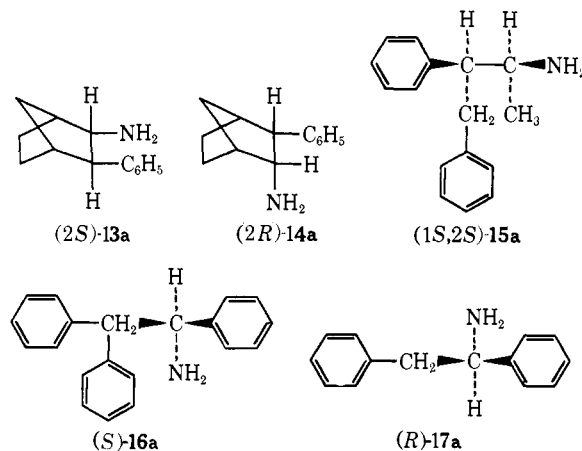
(S)-4b, and the hydrochloride [(R)-17b] of (R)-1,2-di-phenylethylamine[23,24] [(R)-17a] in these same solvents.

Results and Discussion

Monophenyl-Substituted Alkylamine Hydrochlorides in Water. Figure 1 shows the actual record for the CD spectrum from 220 to 300 nm of (R)-α-phenylethyl-amine hydrochloride [(R)-1b] in water. This spectrum, the uv (isotropic absorption) spectrum of (R)-1b, and the uv, ORD, and CD spectra of (S)-α-benzylethyl-amine hydrochloride [(S)-4b], (S)-1-indanamine hydro-chloride [(S)-5b], (2S)-exo-3-phenyl-endo-2-norbornan-amine hydrochloride [(2S)-13b], and (2R)-endo-3-phenyl-endo-2-norbornanamine hydrochloride [(2R)-14b] in water are summarized in Table II. A schematic sum-

(21) The hydrochloride of this amine was provided through the kindness of Dr. Seemon H. Pines, Merck Sharp and Dohme Research Laboratories, Rahway, N. J.
(22) The assigned configuration of this amine and of its hydrochloride is tentative.[1]
(23) This amine was provided through the kindness of Professor Mitchum E. Warren, Jr., Peabody College for Teachers, Nashville, Tenn.
(24) T. Sasaki, K. Kanematsu, Y. Tsuzuki, and K. Tanaka, J. Med. Chem., 9, 847 (1966).

Table II. Spectral Data for Some Monophenyl-Substituted Alkylamine Hydrochlorides in Water

Compd	Extrema				Wavelength, nm (ϵ,[a] [ϕ],[b,c] or [θ][b,d])				
(R)-1b	Uv max	267 (110)	263 (170)	260 (160)	257 (190)		250 (160)	246 (110)[e]	241 (70)[e]
	CD max	266 (−240)		260 (−280)		254 (−180)			
	CD min		263 (−110)		256 (−140)				230 (−20)
(S)-4b	Uv max	267 (70)[e]	263 (130)	260 (90)[e]	257 (170)	252 (140)	247 (100)	242 (60)[e]	237 (40)[e]
	ORD pk	268 (+490)[f]							
	ORD tr	266 (+440)[f]							
	CD max	266 (+40)		259 (+60)		254 (+40)[e]			
	CD min		263 (+30)						
(S)-5b	Uv max	270 (940)		263 (870)	257 (590)	251 (340)[e]			
	ORD tr	271 (−1600)		263 (−1100)		250 (+270)[e]			
	ORD pk	266 (−970)		252 (+300)					
	CD max	270 (−1600)		263 (−1600)	258 (−1100)				
	CD min		268 (−760)		260 (−1000)				
(2S)-13b	Uv max	267 (130)	263 (160)	261 (190)[e]	259 (210)			248 (130)[e]	243 (80)[e]
	ORD	265 (+980)[e]		261 (+940)[e]					
	CD max	266 (+60)		261 (+60)	256 (+60)		250 (+50)		
	CD min		263 (+10)		258 (+40)		253 (+40)		227 (+20)
(2R)-14b	Uv max	268 (130)[e]	265 (170)[e]	262 (200)[e]	259 (220)		253 (180)	249 (140)[e]	243 (90)[e]
	ORD pk	269 (−530)		263 (−680)		257 (−1000)		247 (−1400)[e]	
	ORD tr	266 (−950)[g]		259 (−1200)		252 (−1300)[e]			
	CD max	268 (+410)		262 (+490)		256 (+370)		251 (+210)	
	CD min		266 (+100)		259 (+210)		253 (+180)		

[a] Molar absorptivity. [b] For previously unreported data, temperature 25–28° with c 0.10 g/100 ml except for the CD of (S)-5b for which c was 0.010 g/100 ml. For cutoffs see Table IV. [c] Molecular rotation in degrees. [d] Molecular ellipticity. [e] Shoulder. [f] Data from ref 4. Only two extrema reported. [g] ORD trough also at 280 nm ([ϕ] −670°) as a result of the background curve.

mary of these uv and CD spectra is shown in Figure 2.

The uv and CD spectra of the monosubstituted benzene compounds (R)-1b, (S)-4b, (2S)-13b, and (2R)-14b resemble those recently reported for L-phenylalanine and a number of its derivatives,[25] as well as those reported for (S)-1,2-dihydroxy-1-phenylethane and a number of related compounds.[26] An analysis of the vibronic transitions in the long wavelength $\pi \rightarrow \pi^*$ absorption system of the phenylalanine compounds, considering phenylalanine to be a derivative of toluene, permitted the identification of the transitions giving rise to most of the CD bands. Since an amine hydrochloride such as (R)-1b, (S)-4b, (2S)-13b, and (2R)-14b may also be considered as derivatives of toluene with C_{2v} symmetry, its uv spectrum[27] may also be used to identify the CD bands in the spectrum of an α- or β-phenylalkylamine hydrochloride.

In the uv spectra of the monosubstituted benzene compounds (R)-1b, (S)-4b, (2S)-13b, and (2R)-14b, the longest wavelength maximum near 268 nm corresponds to the 0–0 transition which in toluene is a $B_2 \leftarrow A_1$ electronic transition.[25,27] This electronic transition has allowed and forbidden components. Only for the former transition for which the electric dipole transition moment is in the plane of the phenyl ring and perpendicular to the substituent attachment[28] (B_2 axis in Figure 3) is a CD maximum observed. These transitions connect the ground state zeroth vibrational level ($^vA_1$) with the zeroth and higher totally symmetric levels (also $^vA_1$) of the ring-breathing vibration in the excited state.[29] The vibronic (total) symmetry of these higher energy states is B_2.[29] For (R)-1b (Figure 3), the excitations to the

first two of these higher totally symmetric vibronic states are seen as CD maxima separated from the band
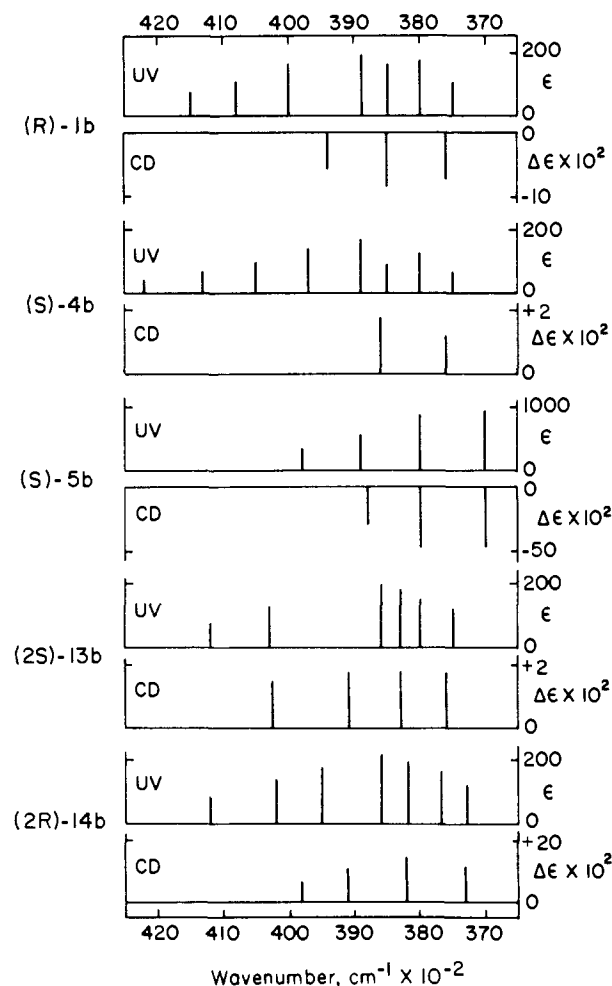
Figure 2. Schematic diagram of the uv and CD maxima observed in the spectra of some monophenyl-substituted alkylamine hydrochlorides in water.

(25) J. Horwitz, E. H. Strickland, and C. Billups, *J. Amer. Chem. Soc.*, **91**, 184 (1969).

(26) R. D. Gillard and P. R. Mitchell, *Trans. Faraday Soc.*, **65**, 2611 (1969).

(27) N. Ginsberg, W. W. Robertson, and F. A. Matsen, *J. Chem. Phys.*, **14**, 511 (1946).

(28) Perturbation by the ammonium chloride group may cause slight distortion in orientation of the electric dipole transition moment.

(29) J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963).
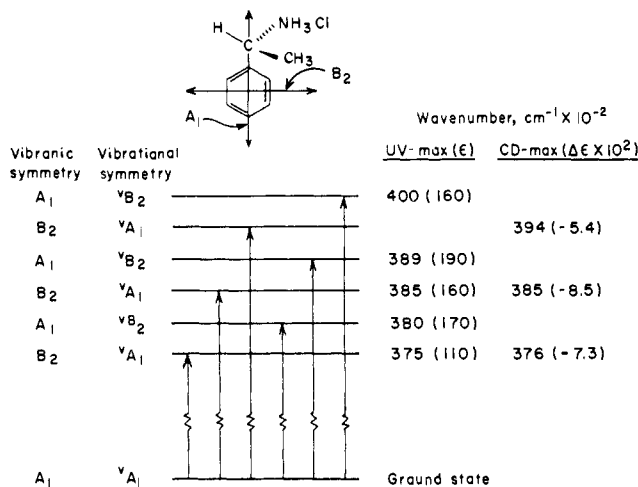
Figure 3. Schematic diagram of the uv and CD maxima observed with (R)-α-phenylethylamine hydrochloride [(R)-1b] in water. The A_1 and B_2 axes are in the plane of phenyl ring.

origin at 376×10^2 cm^{-1} (266 nm) by 9×10^2 and $(9 + 9) \times 10^2$ cm^{-1}. A corresponding uv absorption maximum is observed at $(376 + 9) \times 10^2$ cm^{-1} but one at $(376 + 9 + 9) \times 10^2$ cm^{-1} was not observed. This maximum as well as the corresponding one in the uv spectra of (S)-4b, $(2S)$-13b, and $(2R)$-14b are obscured by other absorption bands (Figure 2). Also, only two CD maxima were observed in the spectrum of (S)-4b since the rotational strength of the CD bands is generally smaller for this compound than for the others. The uv and CD frequencies observed with (R)-1b, (S)-4b, $(2S)$-13b, and $(2R)$-14b correspond in the vapor phase spectrum of toluene to the band origin at 37,477 cm^{-1} and the strongest symmetric vibration at 932 cm^{-1}.[27] In the uv spectrum of toluene in hexane,[30] the band origin is at 372×10^2 cm^{-1}. Excitations to higher totally symmetric vibronic states are separated from the band origin by 9×10^2, $(9 + 10) \times 10^2$, and $(9 + 10 + 10) \times 10^2$ cm^{-1}, respectively.

For the $B_2 \leftarrow A_1$ electronic transition, the forbidden progression combines the ground zeroth vibronic state (A_1) with the first vibrational level of a $^vB_2$ nontotally symmetric ring-deformation vibration, and thence with higher totally symmetric vibrational states. The vibronic symmetry of these excited states is A_1.[29] The electric dipole transition moment is also in the plane of the ring but is parallel to the substituent attachment[28,29] (A_1 axis in Figure 3). In the uv spectrum of (R)-1b, three of these transitions are seen as maxima separated from the band origin by 5×10^2, $(5 + 9) \times 10^2$, and $(5 + 9 + 11) \times 10^2$ cm^{-1}, respectively. Corresponding maxima are present in the uv spectra of (S)-4b, $(2S)$-13b, and $(2R)$-14b (Figure 2). Since near these uv maxima are CD minima (Table II), the Cotton effects associated with these transitions are weak. The uv maxima correspond in the vapor phase spectrum of toluene to the strongest nontotally symmetric vibration at 528 cm^{-1}.[27] In the uv spectrum of toluene in hexane,[30] excitations to higher nontotally symmetric vibrations are separated from the band origin by 5×10^2, $(5 + 8) \times 10^2$, and $(5 + 8 + 8) \times 10^2$ cm^{-1}, respectively. In contrast to the amine hydrochlorides,

however, the intensity of the $B_2 \leftarrow A_1$ transitions for toluene are somewhat greater than that of the $A_1 \leftarrow A_1$ transitions.

In the spectra of the amine hydrochlorides, there are transitions to other vibronic states. As in toluene,[27] they are weak, and overlapping is minor in the first uv and CD maxima, which correspond to the $B_2 \leftarrow A_1$ band origin. At shorter wavelengths, however, considerable overlapping of different transitions occurs which broadens both the uv and CD maxima (Figure 1).

The uv spectrum from 225 to 300 nm of (S)-1-indanamine hydrochloride [(S)-5b] is somewhat different from that of the monosubstituted benzene compounds. The uv spectrum of (S)-5b resembles that of indan in petroleum ether,[31] the latter with a band origin at 365×10^2 cm^{-1} and subsequent maxima at $(365 + 9) \times 10^2$ and $(365 + 9 + 9) \times 10^2$ cm^{-1}.

The progression observed in the uv spectrum of indan and of (S)-5b from 245 to 275 nm is assigned to electronic transitions from the ground zeroth vibrational state $(^vA_1)$ to the first electronically excited zeroth vibrational state and to higher totally symmetric vibrational states $(^vA_1)$.[29] Since indan also belongs to the C_{2v} point group and (S)-5b can be considered to be a derivative of indan, the vibronic symmetry of these higher energy states is assigned as B_2 with the electric dipole transition moment in the plane of the phenyl ring and perpendicular to the symmetry axis. This assignment is made in analogy to the "allowed component" for benzene and toluene.[27,29] Owing to the higher symmetry of benzene (D_{6h}) this electronic excitation cannot occur by itself and is not observed.[29] It is different from the assignment $A_1 \leftarrow A_1$ which would be made using a rule derived by Sklar.[32] For indan and (S)-5b, only the $B_2 \leftarrow A_1$ progression is observed in each spectrum since the intensity of this progression has been strengthened[33] to such a degree that it now obscures the transitions to nontotally symmetric vibrational states $(^vB_2)$ with vibronic symmetry A_1.

In the CD spectrum of (S)-5b, only maxima associated with the first three excitations to totally symmetric vibronic states are observed. No other CD maximum was observed in the spectrum.

Sector Rule for Monophenyl-Substituted Alkylamine Hydrochlorides. The sign of the Cotton effects in the 245–270-nm region shown by (R)-α-phenylethylamine hydrochloride [(R)-1b], (S)-α-benzylethylamine hydrochloride [(S)-4b], and (S)-1-indanamine hydrochloride [(S)-5b] can be predicted using the sector rule shown in 6 and 7. This rule applies to and is keyed to the $B_2 \leftarrow A_1$ transitions with the electric dipole transition moment perpendicular to the symmetry axis and in the ring plane. The increased molecular ellipticity of the CD maxima shown by (S)-5b as compared to those of (R)-1b (Table II and Figure 2) accompanies the enhanced intensities of the individual uv transitions. As expected,[34] the optic anisotropy $(\Delta\epsilon/\epsilon)$ (Table IV) for each $B_2 \leftarrow A_1$ band origin is about the same.

The positive CD maxima shown by $(2S)$-exo-3-phenyl-endo-2-norbornanamine hydrochloride [$(2S)$-

(30) "UV Atlas of Organic Compounds," Vol. II, Plenum Press, New York, N. Y., 1966, D2/1.

(31) "UV Atlas of Organic Compounds," Vol. II, Plenum Press, New York, N. Y., 1966, D3/3.

(32) A. L. Sklar, J. Chem. Phys., 10, 135 (1942).

(33) W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, Tetrahedron, 5, 179 (1959).

(34) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, N. Y., 1960, Chapter 12.

Table III. Spectral Data for Some Monophenyl-Substituted Alkylamine Hydrochlorides in Methyl Alcohol and Isopropyl Alcohol

Compd	Extrema[a]								
		Wavelength, nm (ϵ,[b] [ϕ],[c,d] or [θ][c,e])							
		Methyl alcohol				Isopropyl alcohol			
(R)-1b	Uv max	267 (100)[f,g]	263 (170)[f,g]	260 (150)[f,g]	258 (210)[f,g]				
	ORD tr	268 (−50)[f]				269 (+20)[f]			
	ORD pk	265 (+200)[f]				266 (+310)[f]			
	CD max	266 (−210)		260 (−240)		266 (−200)		260 (−230)	
	CD min		264 (−100)		257 (−120)		263 (−80)		256 (−110)
(S)-4b	Uv max	267 (70)	264 (130)	261 (110)[h]	258 (170)	267 (70)	264 (140)	261 (120)[h]	258 (160)
	ORD pk	269 (+380)[f]				268 (+110)		262 (+20)	
	ORD tr	268 (+130)[f]				265 (−140)[i]		258 (−210)	
	CD max	267 (+150)		260 (+160)		267 (+260)		261 (+270)	
	CD min		264 (+30)		258 (+90)		265 (+60)		259 (+140)
(S)-5b	Uv max	272 (1000)		265 (880)		271 (1000)		264 (890)	
	ORD tr	271 (−1400)		265 (−880)		273 (−1400)		266 (−800)	
	ORD pk	268 (−400)		260 (−90)		269 (−400)			
	CD max	271 (−1300)		264 (−1300)		271 (−1100)		265 (−990)	
	CD min		268 (−540)		259 (−830)		268 (−240)		260 (−650)
(2S)-13b	Uv max	267 (120)	263 (150)	260 (170)[h]	258 (200)	267 (140)	264 (160)	260 (180)	258 (200)
	ORD pk	268 (+970)		261 (+1000)		268 (+990)		261 (+1000)	
	ORD tr	265 (+890)		258 (+970)		265 (+890)		259 (+950)	
	CD max	267 (+120)		261 (+140)	259 (+100)[h]	267 (+180)		261 (+170)	
	CD min		265 (+40)				265 (+40)		258 (+80)
(2R)-14b	Uv max	268 (120)[h]	265 (160)	262 (170)[h]	259 (210)	268 (110)[h]	265 (150)		258 (200)
	ORD pk	270 (−400)		264 (−480)		270 (−160)		264 (−160)	
	ORD tr	266 (−690)[i]		260 (−790)		267 (−310)[k]		260 (−320)	
	CD max	268 (+260)		262 (+320)		268 (+180)		262 (+220)	
	CD min		266 (+10)		259 (+110)		266 (+10)		259 (+70)

[a] Extrema below 258 nm usually not shown. [b] Molar absorptivity. [c] For previously unreported data, temperature 25–28° with c 0.010–0.20 g/100 ml. For cutoffs see Table IV. [d] Molecular rotation in degrees. [e] Molecular ellipticity. [f] Data from ref 4. In each ORD spectrum, only two extrema are reported. [g] Absolute ethyl alcohol as the solvent. [h] Shoulder. [i] ORD trough also at 300 nm ([ϕ] −50°) as the result of the background curve. [j] ORD trough also at 278 nm ([ϕ] −490°) as the result of the background curve. [k] ORD trough also at 290 nm ([ϕ] −220°) as the result of the background curve.

Table IV. Spectral Data for Some Monophenyl-Substituted Alkylamine Hydrochlorides

Compd	Solvent	Band origin					Cutoff			
		Uv		CD			ORD		CD	
		ν,[a] cm^{-1} × 10^{-2}	ϵ[b]	ν,[a] cm^{-1} × 10^{-2}	$\Delta\epsilon$[c] × 10^2	$\Delta\epsilon/\epsilon$[d] × 10^4	λ,[e] nm	[ϕ][f]	λ,[e] nm	[θ][g]
(R)-1b	H₂O	375	110	376	−7.3	−6.6	h		220	−50
	MeOH	375[i,j]	100[i,j]	376	−6.4	−6.4	219[i]	+1000[i]	220	−70
	2-PrOH	h		376	−6.1	−6.1[k]	236[i]	+690[i]	220	−30
(S)-4b	H₂O	375[l]	70	376	+1.2	+1.7	223[i]	+1700[i]	225	±0
	MeOH	375	70	375	+4.5	+6.4	223[i]	+440[i]	225	±0
	2-PrOH	375	70	375	+7.9	+11	220	−930	220	−270
(S)-5b	H₂O	370	940	370	−48	−5.1	225	−2300	220	−3400
	MeOH	368	1000	369	−39	−3.9	225	−1900	220	−1600
	2-PrOH	369	1000	369	−33	−3.3	225	−2300	220	−1800
(2S)-13b	H₂O	375	130	376	+1.8	+1.4	235	+1900	225	+60
	MeOH	375	120	375	+3.6	+3.0	230	+2200	225	+40
	2-PrOH	375	140	375	+5.4	+3.9	230	+2100	225	±0
(2R)-14b	H₂O	373[l]	130	373	+12	+9.2	230	−2500	225	−760
	MeOH	373[l]	120	373	+7.9	+6.6	230	−1600	225	−470
	2-PrOH	373	110	373	+5.4	+4.9	230	−350	225	−400

[a] Wave number. [b] Molar absorptivity. [c] Differential circular dichroic absorption. [d] Optic anisotropy. [e] Wavelength. [f] Molecular rotation in degrees. [g] Molecular ellipticity. [h] Not measured. [i] Data from ref 4. [j] Absolute ethyl alcohol as the solvent. [k] Calculated using ϵ 100. [l] Shoulder.

13b] can be predicted assuming a preferred conformation such that the plane of the phenyl ring eclipses the hydrogen atom at C-3. For (2R)-endo-3-phenyl-endo-2-norbornanamine hydrochloride [(2R)-14b], inspection of models indicates that a conformation with the plane of the phenyl ring eclipsing the hydrogen atom at C-3 is sterically crowded by the endo-hydrogen atom at C-5. Models also indicate that in its preferred conformation, the plane of the phenyl ring is at about a right angle to the hydrogen atom at C-3. Thus, positive CD maxima are predicted for (2R)-14b using the sector rule 6.

Solvent Effects for Monophenyl-Substituted Hydrochlorides. Table III summarizes the uv, ORD, and

CD spectra of (R)-α-phenylethylamine hydrochloride [(R)-1b], (S)-α-benzylethylamine hydrochloride [(S)-4b], (S)-1-indanamine hydrochloride [(S)-5b], (2S)-exo-3-phenyl-endo-2-norbornanamine hydrochloride [(2S)-13b], and (2R)-endo-3-phenyl-endo-2-norbornanamine hydrochloride [(2S)-14b] in methyl alcohol and in isopropyl alcohol. For each spectrum, only extrema from about 258 to 300 nm are recorded in Table III. Table IV records the wavelength, molecular absorptivity (ϵ), the differential circular dichroic absorption ($\Delta\epsilon$), and the optic anisotropy ($\Delta\epsilon/\epsilon$) for the B₂ ← A₁ band origins for each hydrochloride in water, in methyl alcohol, and in isopropyl alcohol. For each salt in each solvent are shown the molecular rotation

Table V. Spectral Data for Some Di- and Triphenyl-Substituted Alkylamine Hydrochlorides in Water

Compd	Extrema				Wavelength, nm (ϵ,[a] $[\phi]$,[b,c] or $[\theta]$[b,d])					
(1S,2S)-	Uv max	267 (190)	263 (290)	260 (300)[e]	257 (370)	252 (300)	248 (220)[e]	242 (140)[e]	
15b	ORD pk	267 (+4200)		259 (+4800)					
	ORD tr	265 (+3900)		257 (+4700)					
	CD max 269 (−140)[f]	266 (+390)		260 (+600)		253 (+550)	248 (+400)[e]		
	CD min		263 (+190)		257 (+530)				232 (+120)
(S)-16b	Uv max	266 (480)		260 (700)	257 (720)	252 (610)	248 (500)		
	ORD tr 271 (−5600)		263 (−3300)		256 (−1500)		248 (−2600)[e]		
	ORD pk 267 (−1500)		259 (−300)		253 (−1400)				
	CD max 269 (−5000)		262 (−4600)		256 (−2600)		248 (−1200)[e]		
	CD min	266 (−2500)		258 (−2300)				243 (−800)	
(R)-17b	Uv max	266 (220)	262 (330)	259 (340)[e]	256 (410)	251 (320)	247 (230)[e]		
	CD max 268 (+130)	266 (−450)		259 (−660)		252 (−510)		246 (−300)	
	CD min		262 (−150)		255 (−330)		249 (−280)		232 (−70)

[a] Molar absorptivity. [b] Temperature 25–28°. For cutoffs see Table VII. [c] Molecular rotation in degrees with c 0.010 g/100 ml. [d] Molecular ellipticity with c 0.10 g/100 ml. [e] Shoulder. [f] CD maximum also at 285 nm ($[\theta]$ +120) as the result of the background curve.

and molecular ellipticity at cutoff. The latter indicate the shape of the apparent plain ORD and CD curves below 245 nm.
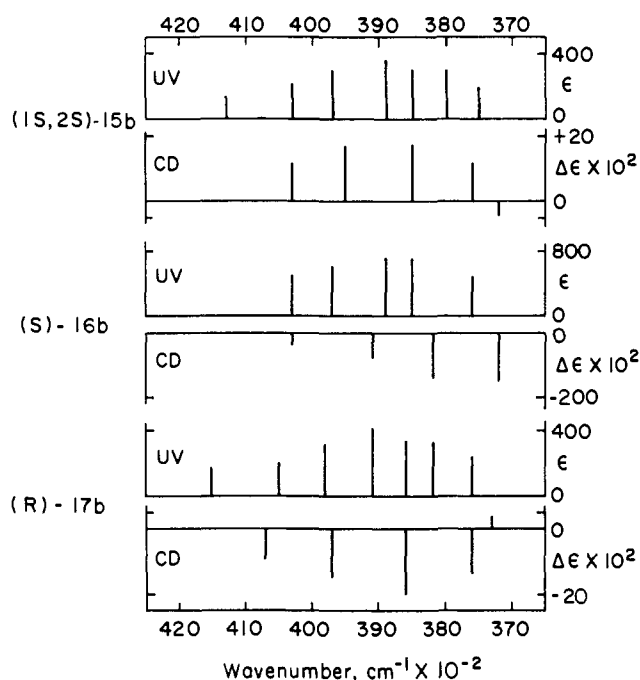

Figure 4. Schematic diagram of the uv and CD maxima observed in the spectra of some di- and triphenyl-substituted alkylamine hydrochlorides in water.

The data in Tables III and IV show that a change in solvent has no great effect on the molecular absorptivity of the uv maxima. Larger changes in the differential circular dichroic absorption are observed. A rather large increase in the optic anisotropy is observed with (S)-α-benzylethylamine hydrochloride [(S)-4b] when the polarity of the solvent is decreased. This change may be related to the greater range of conformational possibilities for this compound. For the other compounds in which intramolecular hydrogen bonding may be present, (R)-1b, (S)-5b, and (2R)-14b, the optic anisotropy decreases in absolute value as the polarity of the solvent is decreased. For (2S)-exo-3-phenyl-endo-2-norbornanamine hydrochloride [(2S)-13b] in which intramolecular hydrogen bonding is not involved, the optic anisotropy increases with a decrease

in solvent polarity. Operative in this latter case, as well as the others, may be a change in the ionization of the ammonium hydrochloride group and small changes in the conformational equilibrium.

As seen in Table IV, only for (S)-α-benzylethylamine hydrochloride [(S)-4b] does the plain ORD curve from 245 nm to cutoff at about 220 nm change sign when the solvent is changed from water to isopropyl alcohol.

As has been noted earlier,[4] two contributions to this far-uv component of the ORD are recognizable in the case of (R)-α-phenyl-n-propylamine hydrochloride [(R)-2b] and (R)-α-phenylneopentylamine hydrochloride [(R)-3b]. For each of the compounds in methyl alcohol or isopropyl alcohol, the sign of the longest wavelength Cotton effect at about 268 nm is negative, the plain curve in the 225–245-nm region is also negative, but the rotatory power in the visible region, which sums the rotatory contributions throughout the spectrum, is positive. It is presumed then that for these compounds the Cotton effects associated with the two intense $\pi \rightarrow \pi^*$ absorption bands lying below 220 nm are of opposite sign. This is clearly seen in ORD and CD spectra of (R)-α-phenylethylamine hydrochloride [(R)-1b]. The plain ORD curve below 245 nm is positive, but below 245 nm to cutoff at 220 nm a plain negative CD curve is observed. For (S)-4b, the change in sign of the plain ORD curve, and the change in sign of rotatory power at 589 nm ($[\alpha]D$) may be the result of a change in the relative intensities of the Cotton effects associated with the two intense $\pi \rightarrow \pi^*$ electronic transitions below 220 nm.

Di- and Triphenyl-Substituted Alkylamine Hydrochlorides. Table V summarizes the extrema observed in the uv, ORD, and CD spectra of (1S,2S)-2,3-diphenyl-1-methylpropylamine hydrochloride [(1S,2S)-15b], (S)-1,2,2-triphenylethylamine hydrochloride [(S)-16b], and (R)-1,2-diphenylethylamine hydrochloride [(R)-17b] in water from about 225 to 300 nm. The uv and CD spectra are shown graphically in Figure 4. Table VI summarizes the uv, ORD, and CD spectra of these same compounds in isopropyl alcohol. Only extrema from 256 to 300 nm are presented in Table VI. Table VII records the wavelength, molecular absorptivity (ϵ), the differential circular dichroic absorption ($\Delta\epsilon$), and the optic anisotropy ($\Delta\epsilon/\epsilon$) for the absorption band origins for each hydrochloride in water and in isopropyl alcohol.

The intensity of the individual bands observed in the

Table VI. Spectral Data for Some Di- and Triphenyl-Substituted Alkylamine Hydrochlorides in Isopropyl Alcohol

Compd	Extrema^a	Wavelength, nm (ϵ,^b [φ],^c,d or [θ]^c,e)				
(1S,2S)-15b	Uv max		267 (180)	264 (300)	261 (280)^f	258 (380)
	ORD pk		267 (+4500)		261 (+4900)	
	ORD tr		265 (+3900)		258 (+4400)	
	CD max	271 (+60)^g	267 (+1100)		260 (+1300)	
	CD min			264 (+540)		258 (+910)
(S)-16b	Uv max	270 (360)^f	268 (430)^f		258 (660)	
	ORD tr	272 (−4300)		265 (−2500)		257 (−1200)
	ORD pk	268 (−930)		262 (±0)		256 (−770)
	CD max	270 (−3400)		264 (−2800)		257 (−1100)
	CD min		267 (−1200)		260 (−620)	
(R)-17b	Uv max		267 (190)	263 (300)	259 (290)^f	256 (380)
	CD max	270 (+60)	267 (−650)		259 (−910)	
	CD min			263 (−340)		256 (−490)

^a Extrema below 256 nm not shown. ^b Molar absorptivity. ^c Temperature 25-28° with c 0.10 g/100 ml except for (S)-16b for which c was 0.010 g/100 ml. For cutoffs see Table VII. ^d Molecular rotation in degrees. ^e Molecular ellipticity. ^f Shoulder. ^g This is a negative CD maximum but the sign of the molecular ellipticity is positive due to the background curve. A positive CD maximum also at 287 nm ([θ] +160) due to the background curve.

Table VII. Spectral Data for Some Di- and Triphenyl-Substituted Alkylamine Hydrochlorides

Compd	Solvent	Band origin				$\Delta\epsilon/\epsilon^d \times 10^4$	Cutoff			
		Uv		CD			ORD		CD	
		ν,^a cm^{-1} × 10^{-2}	ϵ^b	ν,^a cm^{-1} × 10^2	$\Delta\epsilon^c$ × 10^2		λ,^e nm	[φ]^f	λ,^e nm	[θ]^g
(1S,2S)-15b	H₂O	375	190	376	+12	+6.3	225	+24,000	225	+1,000
	2-PrOH	375	180	375	+33	+18	226	+24,000	225	+1,400
(S)-16b	H₂O	h		372	−150		230	−20,000	230	−12,000
	2-PrOH	370^i	360	370	−100	−28	230	−11,000	230	−11,000
(R)-17b	H₂O	376	220	376	−14	−6.4	j		225	−370
	2-PrOH	375	190	375	−20	−11	j		225	−800

^a Wave number. ^b Molar absorptivity. ^c Differential circular dichroic absorption. ^d Optic anisotropy. ^e Wavelength. ^f Molecular rotation in degrees. ^g Molecular ellipticity. ^h Band origin not located ^i Shoulder. ^j Not measured.

uv spectrum of (1S,2S)-2,3-diphenyl-1-methylpropyl-amine hydrochloride [(1S,2S)-15b] suggests that the maxima are the result of two isolated, but superimposed absorption systems, one system associated with each of the phenyl chromophores. The molar absorptivities for corresponding maxima in the uv spectrum of (1S,2S)-15b are about the sum of those of (R)-1b and (S)-4b. This conclusion is supported by recent ORD and CD studies of a number of 1-benzyltetrahydroisoquino-lines.[35] Each of these compounds contains two phenyl chromophores connected through three σ bonds. The analysis of the spectra was best accomplished using the assumption that the two phenyl chromophores do not interact with each other.

With (1S,2S)-2,3-diphenyl-1-methylpropylamine hy-drochloride [(1S,2S)-15b], inspection of models sug-gests that the phenyl group at C-2 dominates the ORD and CD spectra and gives rise to positive Cotton effects for the B₂ ← A₁ transitions. These same transitions for the phenyl group at C-3 give rise to much weaker, nega-tive Cotton effects. One of these is detected as a nega-tive CD maximum in water and in isopropyl alcohol near 270 nm (Figure 5). The others are obscured by the more intense, positive differential circular dichroic ab-sorption of the C-2 phenyl group. As seen in Table VII, no great changes in the uv, ORD, and CD spectra were observed with a change in solvent. Analogous to the changes observed with (S)-α-benzylethylamine hy-drochloride [(S)-4b], the optic anisotropy for the B₂ ← A₁ band origin of the C-2 phenyl group is substantially more positive with isopropyl alcohol as the solvent than with water.
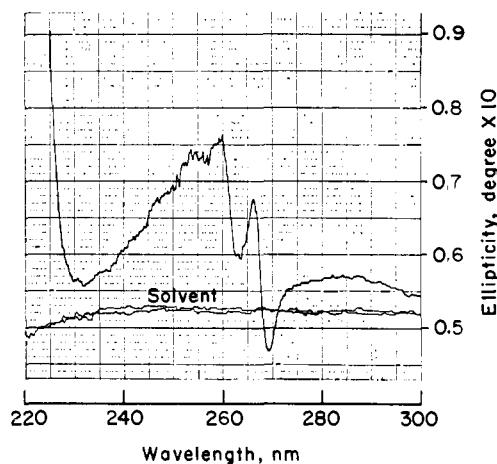

Figure 5. CD record of (1S,2S)-2,3-diphenyl-1-methylpropyl-amine hydrochloride [(1S,2S)-15b] in water (c 0.101 g/100 ml).

In the case of (S)-1,2,2-triphenylethylamine hydro-chloride [(S)-16b], there are intensity enhancements of the maxima in both the uv and CD spectra. The large amplitudes of the ORD Cotton effects reflect the en-hancement of the differential circular dichroic absorp-tion. It is assumed that these enhancements are due to a vicinal interaction (homoconjugation) of the two C-2 phenyl groups connected through two σ bonds.

(35) G. Snatzke, G. Wollenberg, J. Hrbek, Jr., F. Šantavý, K. Bláha, W. Klyne, and R. J. Swan, Tetrahedron, 25, 5059 (1969).

There are two conflicting reports concerning interactions of this type. It was concluded,[36] using Raman spectral data, that the connecting atom (X) of the two phenyl groups in **18** prevents inter-ring conjugation.

18, X = NH, CO, S, O, or CH₂
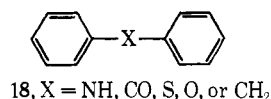
The other report,[37] based on uv data, indicates that inter-ring interaction through a heteroatom (S, O, or NH_2) is weak but not absent.

It is to be noted, however, that uv maxima in the spectrum of (S)-1,2,2-triphenylethylamine hydrochloride [(S)-**16b**] associated with the intense Cotton effects are generally not observed. Only for (S)-**16b** in isopropyl alcohol was an associated uv maximum detected. CD minima were found at the wavelengths at which uv maxima generally occur.

Since the ORD and CD spectra are dominated by the vicinal interaction of the *gem*-diphenyl group, the sign of the observed Cotton effects is dependent on the orientation of one phenyl group with respect to the other, much the same as is found for optically active biphenyls.[38] For (S)-**16b**, the chirality of the asymmetric center at C-1 fixes the preferred orientation of the two phenyl groups to each other at C-2.

The uv and CD spectra of (R)-1,2-diphenylethylamine hydrochloride [(R)-**17b**] again indicate that there is no great vicinal interaction between the two phenyl groups connected through three σ bonds. The uv spectrum is the superimposition of two discrete spectra due to isolated chromophores. The molar absorptivities for corresponding uv maxima in the spectrum of (R)-**17b**

(36) Z. Alaune, *Liet. TSR Mokslu Akad. Darb. Ser. B*, 91 (1964); *Chem. Abstr.*, **62**, 422h (1965).

(37) R. S. Tsekhanskii, *Zh. Org. Khim.*, **1**, 1905 (1965); *Chem. Abstr.*, **64**, 9548b (1966).

(38) K. Mislow in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," G. Snatzke, Ed., Sadtler Research Laboratories Inc., Philadelphia, Pa., 1967, Chapter 10.

are about the same as those in the spectrum of (1S,2S)-**15b** and roughly the sum of those of (R)-**1b** and (S)-**4b**. Each phenyl group gives rise to a set of Cotton effects associated with its $B_2 \leftarrow A_1$ transitions. Application of sector rule **6** predicts negative Cotton effects for these transitions of the phenyl group at C-1. Positive Cotton effects are predicted for the phenyl group at C-2. As seen in Tables V and VI and Figure 4 in the CD spectrum of (R)-**17b**, a positive maxima near 269 nm as well as other negative maxima at shorter wavelength are observed. As expected, the negative differential circular dichroic absorption due to the C-1 phenyl group obscures the positive CD maxima of C-2 phenyl group at shorter wavelength. Only a small change in the optic anisotropy was observed for the C-1 phenyl group $B_2 \leftarrow A_1$ band origin when the solvent was changed from water to isopropyl alcohol.

Experimental Section

Spectral Measurements. Uv (isotropic absorption) spectra were measured with a Cary Model 14 spectrophotometer using 1-cm cells and the normal, variable slit. ORD and CD spectra were measured at 25–28° using a Cary Model 60 spectropolarimeter equipped with a CD Model 6001 accessory. The slit width was programmed for a spectral band width of 1.5 nm and a 1-cm cell was used. Cutoff was indicated when the dynode voltage reached 800 V for ORD measurements and 400 V for CD measurements.

(R)-1,2-Diphenylethylamine Hydrochloride [(R)-**17b**]. An excess of concentrated hydrochloric acid was added to a solution of (R)-1,2-diphenylethylamine[23] [(R)-**17a**], $[\alpha]^{25}D -45°$ (c 2.0, absolute EtOH), in ethanol. The resulting crystalline precipitate was redissolved in hot water to which was then added concentrated hydrochloric acid. On cooling of this solution, the salt recrystallized. After drying at 55° (3 mm), (R)-**17b** had mp 257–261° dec (sealed capillary tube, corrected), $[\alpha]^{25}D -128°$ (c 0.99, absolute EtOH) [lit.[24] mp 259–260°, $[\alpha]^{25.5}D -125.5°$ (c 0.97, EtOH)].

Anal.[39] Calcd for $C_{11}H_{16}ClN$: Cl, 15.17. Found: Cl, 15.06.

(39) Done by Galbraith Laboratories, Inc., Knoxville, Tenn.