cleavage is verified to be analogous to that in noncyclic compounds proposed by McLafferty.[18]

This technique of comparing the possible intermediate ions can be extended to other heteroaromatic compounds and will lead to meaningful results when it is applied to various compounds. We believe that the mechanism thus determined will be systematized to establish the generalized fragmentation rules of (hetero) aromatic compounds.

Acknowledgment. We acknowledge Y. Miyaji (Hoshi College of Pharmacy) for helpful discussions. The computations were carried out on a HITAC 5020E computer at the computation center of the Tokyo University.

Optically Active Amines. XIV.[1a] Circular Dichroism of 1-(2-, 3-, and 4-Pyridyl)ethylamine and Some Related Compounds[1b]

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Contribution from the Departments of Chemistry and Molecular Biology, and Center for Population Research and Studies in Reproductive Biology,[2d] Vanderbilt University, Nashville, Tennessee 37235. *Received June 9, 1972*

Abstract: Resolution with tartaric acid gave (*S*)-(−)-1-(2-, 3-, and 4-pyridyl)ethylamine and (*R*)-(+)-1-(3-pyridyl)-ethylamine. As an extension of earlier work, the uv (isotropic absorption) and CD spectra of (*S*)-(+)-*N*-salicylidene-1-(2-pyridyl)ethylamine and (*S*)-(+)-*N*-(5-bromosalicylidene)-1-(4-pyridyl)ethylamine were examined. These are very similar to those of (*S*)-(+)-*N*-salicylidene-α-phenylethylamine, indicating that the CD spectra of such Schiff base derivatives may also be used for the establishment of the absolute configurations of chiral pyridyl-substituted alkylamines. 1-(4-Pyridyl)ethylamine on storage is unstable and forms *N*-[1-(4-pyridyl)ethylidene]-1-(4-pyridyl)ethylamine by way of a light-catalyzed oxidative process. For this reason, the racemic and optically active amines were converted to their respective dihydrochlorides. The uv spectrum of each amine in 0.1 *M* methanolic potassium hydroxide shows an absorption maximum near 260 nm flanked by shoulders near 255 and 265 nm. These extrema are assigned to the $\pi \rightarrow \pi^*$ (^1L_b) transition of the pyridyl chromophore. Corresponding to each of these uv extrema, a positive maximum is found in the CD spectra of (*S*)-(−)-1-(2-pyridyl)ethylamine and (*R*)-(+)-1-(3-pyridyl)ethylamine. For (*S*)-(−)-1-(3-pyridyl)ethylamine the corresponding CD maxima are negative. No CD maximum was found in the spectrum of (*S*)-(−)-1-(4-pyridyl)ethylamine from 240 to 300 nm. In each CD spectrum there is a maximum near 240 nm, negative for (*S*)-(−)-1-(2-pyridyl)ethylamine, (*R*)-(+)-1-(3-pyridyl)ethylamine, and (*S*)-(−)-1-(4-pyridyl)ethylamine and positive for (*S*)-(−)-1-(3-pyridyl)ethylamine. No corresponding absorption maximum near 240 nm was detected in any of the uv spectra. A first-order perturbation treatment of the CD spectra indicates that the $2B_2$ state at 180 nm makes a significant contribution to the rotational strength of the longer wavelength transitions. On the basis of this analysis we suggest that the CD maximum at 260 nm is due to the $1B_2 \leftarrow 1A_1$ ($\pi \rightarrow \pi^*$) transition, that the 240 nm maximum is due to the electric dipole forbidden $1A_2 \leftarrow 1A_1$ ($n \rightarrow \pi^*$) transition, and that the rotational strength of the allowed $1B_1 \leftarrow 1A_1$ ($n \rightarrow \pi^*$) transition near 288 nm is too weak to give an observable CD maximum. As expected, all CD maxima disappear when the pyridine nitrogen lone pair is protonated in strong acid.

Our continuing interest in the chiroptical properties of aromatic chromophores[3-5] and a recent note concerning the preparation and absolute configurations of the optically active isomers of 1-(2-, 3-, and 4-pyridyl)ethylamine[6] prompt us to report our work dealing with the preparation and spectral properties of (*S*)-(−)-1-(2-pyridyl)ethylamine[7] [(*S*)-**1a**], (*S*)-(−)- and (*R*)-(+)-1-(3-pyridyl)ethylamine [(*S*)- and (*R*)-**2a**], and (*S*)-(−)-1-(4-pyridyl)ethylamine [(*S*)-**3a**], the absolute configuration of each established by ozonolysis of the respective (*S*)-*N*-acetyl derivatives to *N*-acetyl-L-alanine.[6] In addition, we report the preparation of the racemic dihydrochlorides [(±)-**1b**–**3b**] and the preparation and spectral properties of the respective optically active dihydrochlorides [(*S*)-**1b**–**3b** and (*R*)-**2b**]. We have also examined the chiroptical properties of the Schiff base derivatives (*S*)-**1c** and (*S*)-**3c** to evaluate the use of such derivatives for the establishment of the absolute configurations of chiral pyridyl-substituted alkylamines.[8]

(1) (a) Paper XIII: H. E. Smith and H. E. Ensley, *Can. J. Chem.*, **49**, 2902 (1971); (b) supported in part by the Agency for International Development under Contract AID/csd 2491 administered by the Population Council.

(2) (a) Department of Chemistry; (b) National Science Foundation Undergraduate Summer Fellow, 1971; (c) Department of Molecular Biology; (d) supported by National Institutes of Health Grant HD-05797.

(3) H. E. Smith, M. E. Warren, Jr., and L. I. Katzin, *Tetrahedron*, **24**, 1327 (1968); erratum, *ibid.*, **25**, 4648 (1969).

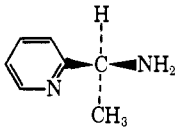
(4) H. E. Smith and A. A. Hicks, *J. Chem. Soc. D*, 1112 (1970).

(5) H. E. Smith and T. C. Willis, *J. Amer. Chem. Soc.*, **93**, 2282 (1971).

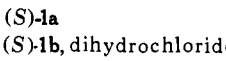
(6) O. Cervinka, O. Belovsky, and P. Rejmanova, *Z. Chem.*, 10, 69 (1970).

(7) Except as noted otherwise, signs in parentheses refer to rotatory powers observed with the sodium D-light for the amines in absolute ethanol, for the amine dihydrochlorides in water, and for the Schiff bases in methanol or absolute ethanol.

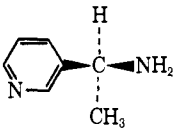
(8) H. E. Smith and T. C. Willis, *Tetrahedron*, **26**, 107 (1970); erratum, *ibid.*, **26**, 2258 (1970).



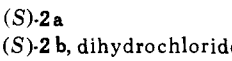
(*S*)-**1a**



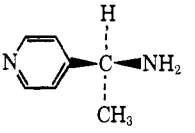
(*S*)-**1b**, dihydrochloride



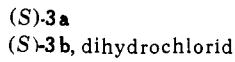
(*S*)-**2a**



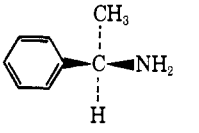
(*S*)-**2b**, dihydrochloride



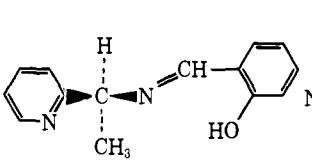
(*S*)-**3a**



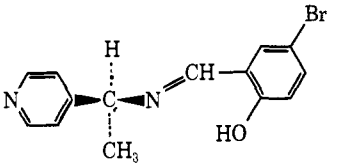
(*S*)-**3b**, dihydrochloride



(*R*)-**4a**



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

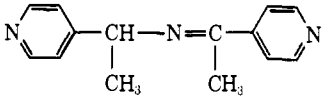


(*S*)-**3c**

Results and Discussion

Resolution, Optical Stability, and Schiff Bases. The racemic free bases were prepared in high yield from the corresponding 2-, 3-, and 4-acetylpyridines by way of the Leuckart reaction.[9,10] As reported earlier without experimental details,[6] the three amines were resolved using tartaric acid. As noted with the racemic amines,[9] the optically active isomers become colored on standing, and optically active **3a** was observed to decrease in rotatory power during a period of months when sealed in vials but without undue precautions to exclude air and sunlight.[11] Under similar conditions of storage, (*R*)-(+)-α-phenylethylamine [(*R*)-**4a**] is optically stable. It and its pyridyl analogs do form reaction products with carbon dioxide[12] and must be protected in sealed vials from the carbon dioxide of the air. In the case of (±)-**4a** the reaction product appears to be a mixture of the carbamate and carbonate salts.[12]

In one sample of (±)-**3a**, during storage, crystalline *N*-[1-(4-pyridyl)ethylidene]-1-(4-pyridyl)ethylamine [(±)-**5**] separated. This same substance is formed by

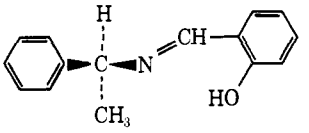


(±)-**5**

the acid-catalyzed reaction of the free base with 4-acetylpyridine in benzene.

De La Mare[13] has found that alkylamines possessing at least one α hydrogen are converted with *tert*-butyl hydroperoxide to the corresponding aldehyde or ketone by way of the aldimine or ketimine. The free base may react directly with the imine and form the Schiff base.[14] Since the rate of loss in rotatory power of a partially racemic form of (*S*)-**3a** increases on exposure to light,[15] the loss in rotatory power probably involves the formation of an optically unstable radical at the chiral center, eventually leading to **5**. Since (*S*)-(−)-1-(4-pyridyl)ethylamine [(*S*)-**3a**] is optically stable on treatment for short periods with sodium methoxide in methanol and as the solid dihydrochloride, the resolved pyridylethylamines were converted to their dihydrochlorides for storage and for use in the CD measurements.

(*S*)-(+)-*N*-Salicylidene-1-(2-pyridyl)ethylamine [(*S*)-**1c**] and (*S*)-(+)-*N*-(5-bromosalicylidene)-1-(4-pyridyl)-ethylamine [(*S*)-**3c**] were prepared and their CD spectra compared with that of (*S*)-(+)-*N*-salicylidene-α-phenylethylamine [(*S*)-**4b**] (Table I). In contrast to (*S*)-**4b** which



(*S*)-**4b**

Table I. Spectral Data for *N*-Salicylidene Derivatives in Methanol

Compd	Isotropic absorption λ_{max}, nm (log ϵ^a)	Circular dichroism λ_{max}, nm ($[\theta]^b$)
(*S*)-**1c**	319 (4.08)[c]	312 (+57,000)[d]
	256 (4.69)	262 (+93,000)
	214 (4.88)	
(*S*)-**3c**		410 (+3.4)[f]
	328 (3.61)[e]	328 (+10,000)[g]
		274 (−5200)[g]
	256 (4.16)	254 (+26,000)[h]
	224 (4.57)	
(*S*)-**4b**[i]	404 (2.78)[j]	405 (+1100)
	315 (3.61)	315 (+18,000)
	283 (3.35)[k]	
		274 (−3000)
	256 (4.14)	253 (+34,000)

[a] Molar absorptivity. [b] Molecular ellipticity; temp 25–28°. [c] This spectrum at 7.07×10^{-6} mol/l. [d] *c* 1.60×10^{-4} g/100 ml for this spectrum. Molecular ellipticity corrected to optical purity. [e] This spectrum at 2.11×10^{-5} mol/l. [f] *c* 5.41 g/100 ml. [g] *c* 5.28×10^{-3} g/100 ml. [h] *c* 1.38×10^{-3} g/100 ml. [i] From H. E. Smith and R. Records, *Tetrahedron*, **22**, 813 (1966); erratum, *ibid.*, **22**, 2400 (1966). [j] 95% ethanol as the solvent for this spectrum. [k] Shoulder.

is optically stable on heating and on treatment with strong bases, (*S*)-**1c** is racemized on heating.[9] When formed in methanol it has $[\alpha]^{25}D$ +140°. Removal of the solvent and recrystallization from *n*-hexane gave a head crop with $[\alpha]^{25}D$ +66.4° (absolute ethanol) and a foot crop with $[\alpha]^{25}D$ +128° (absolute ethanol). The *N*-salicylidene derivatives of both (±)-**3a** and (*S*)-**3a** were obtained as oils, but (*S*)-**3c** is a crystalline solid. Since *N*-5-bromosalicyclidene derivatives of optically active α- and β-phenylalkylamines have essentially the same uv (isotropic absorption) and ORD spectra from about 275 to 600 nm as the *N*-salicylidene derivatives,[16] (*S*)-**3c** was used for the CD studies. (*S*)-**3c** is optically stable on recrystallization from *n*-

(9) H. E. Smith and V. Rajevsky, *J. Heterocycl. Chem.*, **5**, 715 (1968).
(10) We thank Mr. F. A. Karnatz, Reilly Tar and Chemical Corp., for a generous gift of (±)-1-(4-pyridyl)ethylamine.
(11) During 10 months of storage, the rotatory power of partially resolved (*S*)-**3a** changed from $\alpha^{24}D$ −10.1° (neat) to −2.8° (neat).
(12) H. B. Wright and M. B. Moore, *J. Amer. Chem. Soc.*, 70, 3865 (1948).
(13) H. E. De La Mare, *J. Org. Chem.*, **25**, 2114 (1960).
(14) R. G. R. Bacon, W. J. W. Hanna, D. J. Munro, and D. Stewart, *Proc. Chem. Soc., London*, 113 (1962).
(15) A sample of partially racemic (*S*)-**3a**, $\alpha^{24}D$ −4.3 (neat), was exposed to strong sunlight in a Vycor test tube. After 14 days it had $\alpha^{24}D$ −0.9° (neat) as compared to $\alpha^{24}D$ −2.8° (neat) for a portion of the same material in the dark.
(16) H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, 29, 2265 (1964).

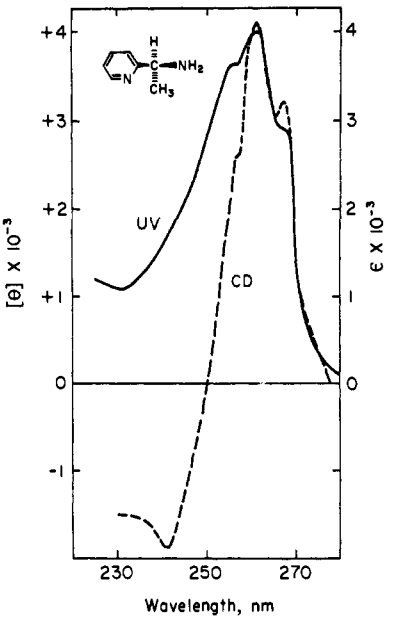


Figure 1. Uv and CD spectra of (*S*)-(−)-1-(2-pyridyl)ethylamine [(*S*)-**1a**] in 0.1 *M* methanolic potassium hydroxide.

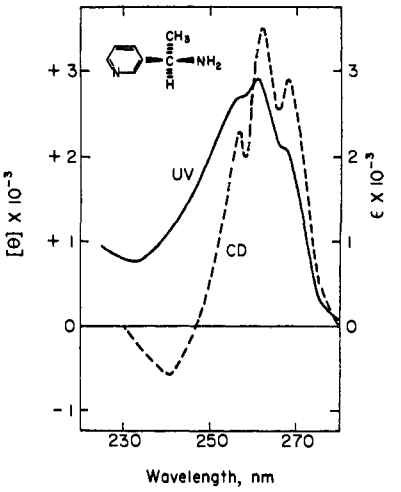


Figure 2. Uv and CD spectra of (*R*)-(+)-1-(3-pyridyl)ethylamine [(*R*)-**2a**] in 0.1 *M* methanolic potassium hydroxide.

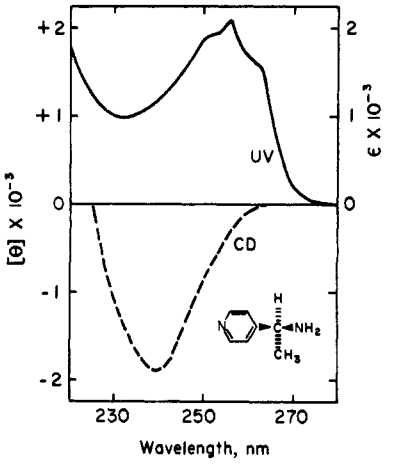


Figure 3. Uv and CD spectra of (*S*)-(−)-1-(4-pyridyl)ethylamine [(*S*)-**3a**] in 0.1 *M* methanolic potassium hydroxide.

hexane. The optical instability of (*S*)-**1c**, as compared with (*S*)-**3c** and (*S*)-**4b**, is due to the enhanced acidity of the proton at the chiral center in (*S*)-**1c**.[17]

As seen in Table I, the uv and CD spectra of (*S*)-**3c** and (*S*)-**4b** are very similar. The spectra of (*S*)-**4b** have been discussed in detail.[8] The rotatory perturbation of the salicylidinimino chromophore by a 4-pyridyl group is essentially the same as that by a phenyl group, both groups belonging to the C_{2v} point group. For (*S*)-**1c**, the CD maxima are positive as predicted by the sector rule for the salicylidinimino chromophore,[5] but the molecular ellipticity for each maximum is much larger than for the corresponding maxima in the CD spectra of (*S*)-**3c** and (*S*)-**4b**. This is probably associated with the C_s point group for the 2-pyridyl moiety in (*S*)-**1c**.

Description of the CD Spectra of the Amines and Amine Dihydrochlorides. Table II summarizes both the uv and the CD spectral data for (*S*)-(−)-1-(2-, 3-, and 4-pyridyl)ethylamine [(*S*)-**1a**, (*S*)-**2a**, and (*S*)-**3a**] and (*R*)-(+)-1-(3-pyridyl)ethylamine [(*R*)-**2a**] in 0.1 *M* potassium hydroxide in methanol, prepared by dissolving the respective dihydrochloride in this solvent.[18] The complete uv and CD spectra of (*S*)-**1a**, (*R*)-**2a**, and (*S*)-**3a** are shown in Figures 1–3. In each uv spectrum an absorption maximum occurs near 260 nm flanked by shoulders near 255 and 265 nm. These extrema (maximum and shoulders) are assigned to the $\pi \rightarrow \pi^*$ (^1L_b) transition of the pyridyl chromophore,[20] the position and intensity of the respective maxima being in accord with those tabulated for the three isomeric picolines.[21] The two shoulders and maximum in each uv spectrum are associated with excitation to different vibrational states of the electronically excited state. As reported earlier for other optically active 2- and 3-substituted pyridyl compounds,[19,22,23] a CD maximum is found corresponding to each of these uv extrema in the spectra of (*S*)-**1a**, (*R*)-**2a**, and (*S*)-**2a**. No CD maximum was found in the spectrum of (*S*)-**3a** from 240 to 300 nm. In each CD spectrum, however, there is a maximum near 240 nm. For (*S*)-**1a**, (*R*)-**2a**, and (*S*)-**2a** this maximum is opposite in sign to that associated with the 260 nm transition. No corresponding absorption maximum near 240 nm was detected in any of the uv spectra.

The CD data in Table II are in accord with the qualitative observation[6] that the ORD curves of (*S*)-**1a** and (*S*)-**2a** show distinct Cotton effects in the 240–270 nm region, positive for (*S*)-**1a** and negative for (*S*)-**2a**. (*S*)-**3a** shows a negative Cotton effect displaced to a shorter wavelength.[6]

The longest wavelength n $\rightarrow$ π^* isotropic absorption maximum for pyridine in a hydrocarbon solvent, although obscured by the lowest energy $\pi \rightarrow \pi^*$ transi-

(17) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience, New York, N. Y., 1960, pp 174–177.

(18) With 100-fold excess equivalents of potassium hydroxide, it can be calculated that the amount of diprotonated or monoprotonated amine in these solutions is extremely small.[19]

(19) A. Tomita, E. Ochiai, H. Hirai, and S. Makishima, *J. Org. Chem.*, 31, 4307 (1966).

(20) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 361–375.

(21) Reference 20, p 375.

(22) G. Fodor, E. Bauerschmidt, and J. C. Craig, *Can. J. Chem.*, 47, 4393 (1969).

(23) G. Gottarelli and B. Samori, *Tetrahedron Lett.*, 2055 (1970).

Table II. Spectral Data for the Optically Active 1-(2-, 3-, and 4-Pyridyl)ethylamines in 0.1 *M* Methanolic Potassium Hydroxide[a]

Compound	Extrema	Wavelength, nm (ϵ^b or $[\theta]^c$)						
(*S*)-**1a**	Uv max	267 (2900)[d]		261 (4000)		256 (3600)[d]		
	CD max	267 (+3200)		261 (+4100)		257 (+2600)[d]	242 (−1900)	230 (−1500)[e]
	CD min		265 (+3000)					
(*R*)-**2a**	Uv max	267 (2100)[d]		261 (2900)		257 (2700)[d]		
	CD max	268 (+2900)		262 (+3500)		257 (+2300)	241 (−580)	230 (±0)[e]
	CD min		266 (+2500)		258 (+2000)			
(*S*)-**2a**	CD max	268 (−3200)		262 (−3700)		257 (−2100)	240 (+520)	230 (±0)[e]
	CD min		266 (−2300)		259 (−1900)			
(*S*)-**3a**	Uv max	262 (1600)[d]		256 (2100)		252 (1900)[d]		
	CD max						240 (−1900)	225 (±0)[e]

[a] Prepared by dissolving the dihydrochloride in the solvent. [b] Molar absorptivity at *c* 1.12 × 10^{-4} to 3.07 × 10^{-4} mol/l. [c] Molecular ellipticity at a temperature of 25–28° with *c* 7.70 × 10^{-3} to 9.82 × 10^{-3} g/100 ml (3.95 × 10^{-4} to 5.03 × 10^{-4} mol/ml). [d] Shoulder. [e] Cut-off.

tion absorption band, has been determined to be at 270 nm (ϵ 450)[21,24] with its band origin (0–0 transition) in the gas phase at 288 nm.[24,25] Each of the three isomeric picolines in the gas phase[26] or in isooctane[24] shows this same n → π^* absorption band with band origin and absorption maximum at about the same wavelength.[27] As with all n → π^* transitions,[28] on changing the solvent from isooctane to 95% ethanol, the absorption band at 270 nm is shifted to shorter wavelength and is even more overlapped by the π → π^* transition.[24] Nevertheless, the band maximum for the lowest energy n → π^* transition of pyridine and the picolines in ethanol is expected to be at a longer wavelength than the lowest energy π → π^* transition maximum at about 260 nm.[27] Since **1a–3a** can be considered to be substituted picolines, the CD maximum at 240 nm for (*S*)-**1a**, (*R*)-**2a**, (*S*)-**2a**, and (*S*)-**3a** in methanol is due to a transition distinct from the lowest energy n → π^* and π → π^* transitions of the pyridyl chromophore.

It has been shown[29] that oppositely signed Cotton effects in close proximity to one another can affect the position and magnitude of their respective CD maxima. Since no CD maximum associated with the π → π^* transition was detected in the spectrum of (*S*)-**3a** in methanol, the CD maximum at 240 nm fixes the position of its isotropic absorption band maximum. This indicates that the maximum near 240 nm in the CD spectra of (*S*)-**1a**, (*R*)-**2a**, and (*S*)-**2a** is also associated with a uv band also centered near 240 nm. It is to be noted, however, that no CD maximum associated with the lowest energy n → π^* transition at about 270 nm was detected in any of the spectra.

There has been some speculation[24] that for pyridine in the spectral region 210–260 nm there is, in addition to the strong π → π^* transition, a weaker n → π^* transition. Since even in the gas phase the π → π^* band is very diffuse, this higher energy n → π^* transition has never been identified and is not mentioned in the recent critical review of the azabenzene spectra by Innes, Byrne, and Ross.[30] The analysis below suggests that the maximum near 240 nm in the CD spectra of (*S*)-**1a**, (*R*)-2a, (*S*)-**2a**, and (*S*)-**3a** may be associated with an n → π^* transition of the pyridyl chromophore with isotropic absorption maximum at about the same wavelength.

The data in Table III bear on this point. In Table III are shown the uv maxima for (*S*)-(−)-1-(2- and 4-pyridyl)ethylamine dihydrochloride [(*S*)-**1b** and (*S*)-**3b**] and (*R*)-(−)-1-(3-pyridyl)ethylamine dihydrochloride [(*R*)-**2b**] in 0.1 *M* methanolic hydrogen chloride. This solvent was used to ensure that protonation of the pyridyl nitrogen is complete. As with pyridine in concentrated sulfuric acid,[20,31] the vibrational fine structure of the π → π^* absorption band disappears, and the intensity of the absorption maximum is increased without appreciable shift in wavelength. More importantly, (*S*)-**1b**, (*R*)-**2b**, (*S*)-**2b**, and (*S*)-**3b** in 0.1 *M* methanolic hydrogen chloride show no dichroic absorption from 230 to 300 nm.[32] As expected the CD maximum near 240 nm disappears, and in the spectrum of (*S*)-**1b** and (*R*)-**2b** a CD maximum associated with the π → π^* transition could no longer be detected at the maximum allowable concentration for CD measurements in this spectral region.

Table III. Uv Maxima for Optically Active 1-(2-, 3-, and 4-Pyridyl)ethylamine Dihydrochloride in 0.1 *M* Methanolic Hydrogen Chloride

Compd	Wavelength, nm (ϵ^a)
(*S*)-**1b**	261 (7600)
(*R*)-**2b**	260 (6400)
(*S*)-**3b**	257 (5100)

[a] Molar absorptivity at 4.66 × 10^{-5} to 1.33 × 10^{-4} mol/l.

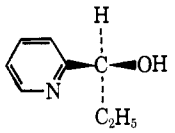
Earlier uv and CD measurements[19,22,23] with chiral 2- and 3-substituted pyridines show spectra similar to those of (*S*)-**1a** and (*S*)-**2a**. Table IV summarizes the reported spectra for (*S*)-(−)-1-(2-pyridyl)propanol[22,33] [(*S*)-**6**], (*S*)-(−)-1-(3-pyridyl)ethanol[23,34] [(*S*)-**7a**], (*S*)-(−)-5-hydroxy-5,6,7,8-tetrahydroquinoline[23,34] [(*S*)-**8a**], and (*S*)-(−)-nicotine[19,33] [(*S*)-**9a**]. As seen in Table IV, these four compounds show at least three CD maxima corresponding to different vibrational transitions of the lowest energy π → π^* transition of the pyridyl chromophore. Each compound also shows another CD maximum near 240 nm.

(24) H. P. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).
(25) S. F. Mason, *J. Chem. Soc.*, 1240 (1959).
(26) J. H. Rush and H. Sponer, *J. Chem. Phys.*, 20, 1847 (1952).
(27) L. Goodman and R. W. Harrell, *ibid.*, **30**, 1131 (1959).
(28) G. J. Brealey and M. Kasha, *J. Amer. Chem. Soc.*, 77, 4462 (1955).
(29) K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *ibid.*, **87**, 66 (1965).
(30) K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectrosc.*, **22**, 125 (1967).
(31) "UV Atlas of Organic Compounds," Vol. III, Plenum Press, New York, N. Y., 1967, G5/1 and G5/7.
(32) *c* 8.70 × 10^{-4} to 4.00 × 10^{-3} g/100 ml (4.46 × 10^{-5} to 2.05 × 10^{-4} mol/l.).
(33) Rotatory power in 95% ethanol or ethanol.
(34) Rotatory power in methanol.

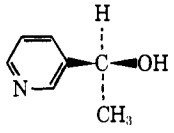
Table IV. Spectral Data for Some Optically Active 2- and 3-Substituted Pyridines

Compd	Extrema	Wavelength, nm (ϵ^a or $[\theta]^b$)			
(*S*)-**6**[c]	Uv max[d]	269 (1700)	262 (2100)	257 (2000)	
	CD max[e]	272 (−230)	264 (−530)	258 (−530)	238 (−3000)[f]
(*S*)-**7a**[g]	Uv max[h]	266 (~2000)[i]	260 (~3000)	257 (~2500)[i,j]	
	CD max[h]	267 (−3300)	263 (−3300)	256 (−2000)[i]	241 (+990)[k]
(*S*)-**8a**[g]	Uv max[h]	270 (~4000)[i]	266 (~5000)	261 (~4000)[i]	
	CD max[h]	270 (−4300)[l]	265 (−3000)[i]	263 (−2300)[i]	240 (+1300)[m]
(*S*)-**9a**[n]	Uv max[e]	267 (2200)[i]	261 (2800)	255 (2600)	
	CD max[e]	272 (−7600)	264 (−6600)	258 (−3000)	243 (+4000)

[a] Molar absorptivity. [b] Molecular ellipticity. [c] From ref 22. [d] Ethanol as the solvent. [e] 95% ethanol as the solvent. [f] Shoulder also at 220 nm ([θ] − 1060). [g] From figure in ref 23. [h] Methanol as the solvent. [i] Shoulder. [j] Shoulder also at 253 nm (ε ~2000). [k] Maximum also at 213 nm ([θ] +2000). [l] Maximum also at 273 nm ([θ] −4000). [m] Maximum also at 213 nm ([θ] +9900). [n] From figure in ref 19.

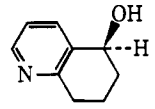


(*S*)-**6**

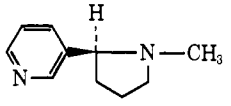


(*S*)-**7a**
(*S*)-**7b**, hydrochloride

Measurements of the CD spectra of the respective hydrochloride salts confirm the view that this latter CD maximum is associated with the higher energy $n \rightarrow \pi^*$ transition of the pyridyl chromophore.



(*S*)-**8a**
(*S*)-**8b**, hydrochloride



(*S*)-**9a**
(*S*)-**9b**, pyrrolidine hydrochloride
(*S*)-**9c**, dihydrochloride

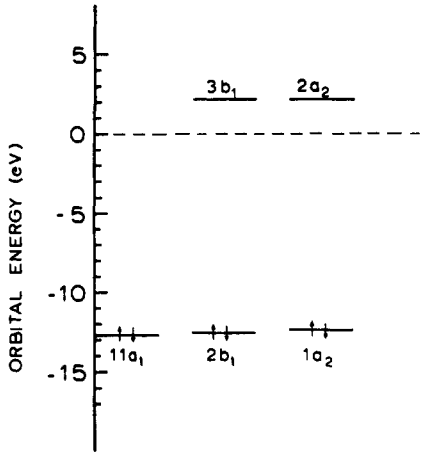


Figure 4. The highest filled and lowest empty orbitals of pyridine as adapted from ref 35.

For (*S*)-(−)-nicotine [(*S*)-**9a**] in 95% ethanol with 1 equiv of hydrogen chloride added, 97.6% of the nicotine is in the form of its monoprotonated salt [(*S*)-**9b**].[19] Since the nitrogen atom of the pyridyl chromophore is unprotonated, the CD spectrum still shows CD maxima at 246 nm ([θ] +4000) and 271 nm ([θ] −4300). In 95% ethanol with 5 equiv of hydrogen chloride added there is *ca.* 35% of (*S*)-**9b** and 65% of the diprotonated salt (*S*)-**9c** present.[19] The CD spectrum shows similar maxima as before but with reduced intensity. If (*S*)-**9c** is assumed to show no dichroic absorption from 230 to 300 nm, the intensities of the CD maxima roughly correlate with the amount of (*S*)-**9b** present in the solution. Similarly, in both methanol and 10% hydrochloric acid, (*S*)-**7b** shows only one CD maximum near 225 nm.[23] (*S*)-**8a** in 10% hydrochloric acid [(*S*)-**8b**] shows CD maxima at 228 and 270 nm, but one near 240 nm is no longer present.[23]

Interpretation of the CD Spectra. The availability of Innes, Byrne, and Ross's review of the pyridine spectrum[30] and of thorough SCF calculations on the pyridine ground state by Clementi[35] makes the substituted pyridines an especially fortunate case for study. But even with these aids, we shall not be able to interpret all features of the CD spectra unambiguously.

In these substituted pyridines, the optical activity is almost certainly due to transitions within the pyridine ring, with the substituent serving only as a perturbation which destroys the ring symmetry. Since the activity is of this type, rather than being caused by a coupling of ring and substituent transitions, the theoretical methods to be used are those described by Schellman.[36]

The orbital energies of pyridine are shown in Figure 4. Although the difference in orbital energies alone does not determine the energy of excitation, it is usually the major factor, and it will probably be sufficient to consider only states arising from transitions between the three highest filled and the two lowest empty orbitals. The filled orbitals $2b_1$ and $1a_2$ correspond to the highest filled degenerate e_{1g} pair in benzene, and $3b_1$ and $2a_2$ correspond to the lowest empty e_{2u} benzene levels. Note that these degeneracies are barely split in pyridine. Excitation of one electron in benzene from e_{1g} to e_{2u} gives rise to three singlet states: B_{2u} (256 nm), B_{1u} (200 nm), and a degenerate E_{1u} (180 nm). Electric dipole transitions are allowed only to the E_{1u} state. The corresponding pyridine singlet states have all been observed: B_2 at 261 nm, A_1 at 201 nm, and a broad absorption due to a second pair of B_2 and A_1 states at 182 nm. Although all four transitions are allowed in the pyridine C_{2v} symmetry, in fact the wave functions are not vastly different from those of benzene, and the 182-nm absorption corresponding to the benzene E_{1u} state is by far the strongest.[30] The $11a_1$ orbital in pyridine is mainly the nitrogen lone pair.[35] The allowed transition from it to $3b_1$ gives a B_1 singlet whose absorption is observed weakly at 288 nm. Transition from $11a_1$ to $2a_1$ is symmetry forbidden and has not been observed.[30] These states are summarized in Table V.

(35) E. Clementi, *J. Chem. Phys.*, **46**, 4731 (1967).

(36) J. A. Schellman, *ibid.*, **44**, 55 (1966).

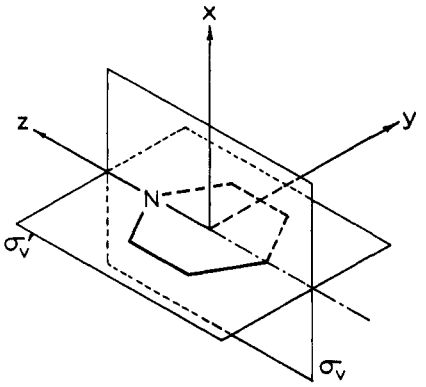


Figure 5. Coordinate axes and symmetry planes of the pyridines.

Table V. Singlet States of Pyridine

State	Wavelength of transition from ground state (nm)[a]	Oscillator strength[a]	Description
$1A_1$			Ground state
$1B_1$	287.6	0.003	Allowed n → π* excitation of orbital $11a_1$ to $3b_1$
$1B_2$	260.8	0.04	Lowest π → π* excitation
$2A_1$	201.0	0.10	π → π*
$2B_2$, $3A_1$	182	1.3	Strong absorption corresponding to first allowed π → π* transition in benzene
$1A_2$	Not observed		Forbidden n → π* transition

[a] From ref 30.

The substituted pyridines (*S*)-**7a** and (*S*)-**8a** studied by Gottarelli and Samori[23] have CD spectra whose dominant features are similar to ours. Both show a strong dichroic absorption at 260 nm with a weaker band of opposite sign around 240 nm. These authors considered the possible explanation of their spectra in terms of mixing of the $1B_1$ (n → π*) and $1B_2$ (π → π*) states by the substituent perturbation. They found that they could not explain their results since their first-order perturbation treatment predicted equal and opposite rotational strengths for the two bands. Note at this point that in their work they took the σ_v symmetry plane to be the plane of the aromatic ring. We shall use the conventions of Innes, Byrne, and Ross[30] with a right-handed coordinate system whose positive z axis goes through the ring nitrogen and whose y axis is in the ring plane as shown in Figure 5. Our σ_v plane is perpendicular to the ring, and our σ_v' plane is the ring plane. It follows that we label states B_1 or B_2, respectively, where Gottarelli and Samori use B_2 or B_1.

Of the observed transitions in Table V, only those to the $1B_1$ and $1B_2$ states are accessible with our CD instrument. These two states lie closest together and would be expected to show most mixing under the substituent perturbation. Nevertheless, as we shall show below, the high oscillator strength of the $2B_2$ transition may cause this more distant state to make a significant contribution to the $1B_1$ (n → π*) rotational strength. We wish also to consider the possibility that the CD band at 240 nm may be that of the $1A_2$ state. The fact that electric dipole transition to this state is forbidden does not imply that it will have no rotational strength. On the contrary, the CD spectrum is potentially a powerful tool for locating electric dipole forbidden transitions. Goodman[37] has estimated the transition to this A_2 state should lie at about 256 nm. This would be in the range of our observations. Let us therefore consider the $1B_1$, $1B_2$, and $1A_2$ states of pyridine and allow them to mix under the influence of the substituent perturbation with all excited states listed in Table V. To first order, the perturbed states are then as shown in (1)

$$\begin{aligned}
|1B_1\rangle &= |1B_1) + C(1B_1,1A_2)\,|1A_2) + \\
&\quad C(1B_1,1B_2)\,|1B_2) + C(1B_1,2A_2)\,|2A_1) + \\
&\quad C(1B_1,2B_2)\,|2B_2) + C(1B_1,3A_1)\,|3A_1) \\
|1B_2\rangle &= |1B_2) + C(1B_2,1A_2)\,|1A_2) - \\
&\quad C(1B_1,1B_2)\,|1B_1) + C(1B_2,2A_1)\,|2A_1) + \\
&\quad C(1B_2,2B_2)\,|2B_2) + C(1B_2,3A_1)\,|3A_1) \\
|1A_2\rangle &= |1A_2) - C(1B_1,1A_2)\,|1B_1) - \\
&\quad C(1B_2,1A_2)\,|1B_2) + C(1A_2,2A_1)\,|2A_1) + \\
&\quad C(1A_2,2B_2)\,|2E_2) + C(1A_2,3A_1)\,|3A_1)
\end{aligned} \tag{1}$$

where

$$C(1B_1,1A_2) = (1A_2|V|1B_1)/(E_{1B_1} - E_{1A_2}) \tag{2}$$

and similarly for the other coefficients. The angular brackets in (1) refer to first-order states and the round brackets to zero-order states. V in (2) is the potential of the substituent. The rotational strength of the $1B_1 \leftarrow 1A_1$ transition is then to first-order

$$\begin{aligned}
&R(1B_1\leftarrow 1A_1) = \langle 1A_1|\mathfrak{y}|1B_1\rangle\cdot\langle 1B_1|\mathbf{m}|1A_1\rangle = \\
&C(1B_1,1B_2)[\mu_x m_x + \mu_y m_y] + C(1B_1,2B_2)[\mu_x m_x' + \mu_y' m_y]
\end{aligned} \tag{3}$$

and similarly for the other two states

$$R(1B_2\leftarrow 1A_1) = -C(1B_1,1B_2)[\mu_x m_x + \mu_y m_y] \tag{4}$$

$$R(1A_2\leftarrow 1A_1) = C(1A_2,2A_1)\mu_z m_z + C(1A_2,3A_1)\mu_z' m_z \tag{5}$$

where $\mathfrak{y}$ and $\mathbf{m}$ are the electric and magnetic dipole operators. The contributing components of these operators in (3)–(5) are given in (6). If the second

$$\begin{aligned}
&\mu_x = (1A_1|\mathfrak{y}|1B_1) \quad \mu_y = (1A_1|\mathfrak{y}|1B_2) \\
&m_y = (1B_1|\mathbf{m}|1A_1) \quad m_x' = (2B_2|\mathbf{m}|1A_1) \\
&\mu_z = (1A_1|\mathfrak{y}|2A_1) \quad \mu_z' = (1A_1|\mathfrak{y}|3A_1) \\
&\qquad\qquad m_x = (1B_2|\mathbf{m}|1A_1) \\
&\qquad\qquad \mu_y' = (1A_1|\mathfrak{y}|2B_2) \\
&\qquad\qquad m_z = (1A_2|\mathbf{m}|1A_1)
\end{aligned} \tag{6}$$

term in (3) were negligible, then the rotational strengths of the $1B_2$ and $1B_1$ transitions would be equal and opposite as predicted by Gottarelli and Samori,[23] but not as found experimentally. We cannot calculate the relative size of the entire first and second terms in (3) because we do not know the magnitude of the magnetic transition moments, but we can compare the second parts of each term using the wavelengths and oscillator strengths in Table V using eq 7, where ν is the

(37) L. Goodman, *J. Mol. Spectrosc.*, **6**, 109 (1961).

$$\frac{C(1B_1,2B_2)\mu_y' m_y}{C(1B_1,1B_2)\mu_y m_y} = \frac{(2B_2|V|1B_1)\nu(1B_2\leftarrow 1B_1)}{(1B_2|V|1B_1)\nu(2B_2\leftarrow 1B_1)} \times \left[\frac{f(2B_2\leftarrow 1A_1)\nu(1B_2\leftarrow 1A_1)}{f(1B_2\leftarrow 1A_1)\nu(2B_2\leftarrow 1A_1)}\right]^{1/2} = 0.8(2B_2|V|1B_1)/(1B_2|V|1B_1) \quad (7)$$

frequency and f is the oscillator strength. Thus we see that the greater oscillator strength of the more distant $2B_2$ state has almost entirely overcome its larger energy denominator in the perturbation coefficient. It is therefore not unreasonable to suppose that the second term of (3) is comparable to the first. Hence even in first order the rotational strengths of $1B_1$ and $1B_2$ are not predicted to be equal.

The fact that all CD bands disappear in strong acid is easily explainable since all terms in the rotational strengths (3)–(5) contain a factor μ_x, m_y, or m_z depending upon a transition from the ring-nitrogen unshared pair. This is tied up by protonation, making all such terms vanish. It remains to explain why the strong CD band of (*S*)-**1a** and (*R*)-**2a** at 260 nm does not appear in the 4-pyridyl compound (*S*)-**3a** (Figures 1–3), and to identify the state giving rise to each CD band. In all three compounds the uv absorption around 260 nm must almost certainly be due to the $1B_2 \leftarrow 1A_1$ ($\pi \rightarrow \pi^*$) transition. It is barely shifted from the location of this transition in unsubstituted pyridine which in turn is shifted only 5 nm from the analogous $B_{2u} \leftarrow A_{1g}$ transition in benzene. The correspondence to within 1 nm of each peak and shoulder of the 260-nm CD bands to a peak or shoulder of this uv absorption suggests very strongly that these CD bands are due to the $1B_2 \leftarrow 1A_1$ transition. One might then assign the 240-nm rotational band to the $1B_1 \leftarrow 1A_1$ ($n \rightarrow \pi^*$) transition. However, this would require that the substituent perturbation shift this transition 45 nm to the blue from its position in pyridine while leaving the $\pi \rightarrow \pi^*$ transition unmoved. Three things argue against this. First, the shift seems much too large.[27] Second, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands should be shifted in opposite and roughly equal directions by an inductive substituent.[27] Third, the amine inductive effect is one of electron attraction[38] and hence should shift the $n \rightarrow \pi^*$ transition to the *red*.[27] We therefore suggest the alternative possibility that the $1B_1 \leftarrow 1A_1$ dichroic absorption is too weak to be observed and that the 240-nm dichroic absorption is due instead to the $1A_2 \leftarrow 1A_1$ ($n \rightarrow \pi^*$) forbidden transition. We have shown above that the $1B_1 \leftarrow 1A_1$ and $1B_2 \leftarrow 1A_1$ transitions are not expected to have equal but opposite rotational strengths. The contributions of the $2B_2$ and $1B_2$ states may be in opposite directions and hence cause the dichroic absorption of $1B_1 \leftarrow 1A_1$ nearly to vanish. The 240-nm band does lie roughly where predicted by Goodman.[37,39]

The vanishing of the 260-nm dichroic absorption in the CD spectrum of (*S*)-**3a** also follows easily from our model. Every term in the rotational strengths (3)–(5) contains a perturbation coefficient that will vanish unless V has an A_2 component in the C_{2v} group. This potential may be expressed in terms of a multipole expansion centered at any point on a line through the substituted ring carbon atom and through the ring atom para to it. Any monopole term will have complete symmetry and will make no contribution to the rotational strength, leaving the dipole terms to dominate.[36] For the 2-pyridyl and 3-pyridyl compounds (*S*)-**1a** and (*R*)-**2a**, the out-of-plane component of the dipole moment will contain an A_2 part and hence will make a contribution to the rotational strength. But for the 4-pyridyl compound (*S*)-**3a** none of the dipole terms can contain an A_2 component. The rotational strength of the 260-nm band for this compound must then depend upon quadrupole and higher terms in the multipole expansion and is therefore expected to be much weaker. However, these arguments apply equally to the 240-nm band. It is not easy to see why this band remains in (*S*)-**3a**, and in fact is strongest there. It may be that dipole and quadrupole contributions to this band are both significant but of opposite sign. The vanishing of the dipole terms in the 4-pyridyl compound would then cause enhanced dichroic absorption, but a confirmation of this would require detailed computation. Similarly, a prediction of the magnitudes, or even the signs, of each CD band would also require detailed and accurate wave mechanical calculations as well as knowledge of the conformational equilibrium for each compound.

Experimental Section

Boiling points are not corrected. Melting points were taken in open capillary tubes, unless noted otherwise, and are corrected. Optical rotations at the sodium D-line were measured using a visual polarimeter and a 1-dm sample tube. Isotropic absorption (uv) spectra were obtained with a Cary Model 14 spectrophotometer using matched 1-cm cells and the normal variable slit. Circular dichroism (CD) curves were measured using a Cary Model 60 spectropolarimeter equipped with a CD Model 6001 accessory. The slit was programmed for a spectral band width of 1.5 nm, and a 1-cm cell was used. Cut-off was indicated when the dynode voltage reached 400 V. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of Pyridylamine Dihydrochlorides. Dry hydrogen chloride was added to 0.60–3.10 g (4.9–25.4 mmol) of amine in 50 ml of ether. Except for (*S*)-**2b** which was not recrystallized, the resulting precipitate was recrystallized once or twice from methanol–ether. The amine salt was obtained in 34–99% yield.

(*S*)-(−)-**1-(2-Pyridyl)ethylamine** [(*S*)-**1a**]. To 10.2 g (0.0835 mol) of (±)-1-(2-pyridyl)ethylamine,[9] bp 97–98° (36 mm), in 150 ml of boiling 95% ethanol was added 15.1 g (0.100 mol) of (+)-tartaric acid in 150 ml of boiling 95% ethanol. On cooling to room temperature, there was deposited 18.3 g (161%) of fine, white needles, $[\alpha]^{25}D$ +14° (*c* 4.00, H_2O). Five recrystallizations of this material from 95% ethanol gave 3.49 g (30%) of the (+)-acid tartrate salt of (*S*)-**1a**: fine, white needles, mp 157–160°, $[\alpha]^{25}D$ +5.4° (*c* 3.96, H_2O) [lit.[6] mp 163–164°, $[\alpha]^{20}D$ +5.10° (*c* 4.02, H_2O)]. Decomposition of 8.50 g (0.0312 mol) of the salt in aqueous sodium hydroxide, collection of the amine in ether, drying of this solution (NaOH), evaporation of the solvent, and distillation of the residue gave 2.39 g (63%) of (*S*)-**1a**: colorless oil, bp 96–97° (24 mm), $\alpha^{25}D$ −27.8° (neat), $[\alpha]^{25}D$ −31.4° (*c* 5.32, absolute C_2H_5OH) [lit.[6] bp 83° (14 mm), $[\alpha]^{25}D$ −28.5° (*c* 5.71, C_2H_5OH)].

(±)-**1-(2-Pyridyl)ethylamine dihydrochloride** [(±)-**1b**] was obtained as extremely hygroscopic, fine, white prisms, mp 214–217° dec.

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.25.

(*S*)-(−)-**1-(2-Pyridyl)ethylamine dihydrochloride** [(*S*)-**1b**] was obtained as extremely hygroscopic, white needles, mp 203–214° dec, $[\alpha]^{25}D$ −7.8° (*c* 4.35, H_2O).

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.13.

(*S*)-(+)-*N*-**Salicylidene-1-(2-pyridyl)ethylamine** [(*S*)-**1c**]. A solu-

(38) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 71.

(39) NOTE ADDED IN PROOF. The very recent CNDO calculations of R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, **26**, 131 (1972), give welcome support to our tentative interpretation of the CD spectra. They compute the excited singlet states of pyridine to be $n \rightarrow \pi^*$ B_1 (295 nm), $\pi \rightarrow \pi^*$ B_2 (253 nm), $n \rightarrow \pi^*$ A_2 (221 nm), $\pi \rightarrow \pi^*$ A_1 (206 nm), $\pi \rightarrow \pi^*$ A_1,B_2 (182 nm). This puts the A_2 state third above the ground state as we postulate.

tion was prepared by mixing 0.2611 g (2.137 mmol) of (*S*)-(−)-1-(2-pyridyl)ethylamine [(*S*)-**1a**)] and 0.2838 (2.323 mmol) of salicylaldehyde in methanol. This solution was then diluted to 25.00 ml. After 3 hr it had $[\alpha]^{25}D$ +140° (*c* 1.934, CH_3OH). The observed rotation of this solution remained unchanged for an additional 24 hr.

In a similar way, 0.266 g (2.18 mmol) of (*S*)-**1a** was boiled for 5 min with 0.280 g (2.29 mmol) of salicylaldehyde in methanol. Removal of the solvent and recrystallization of the residue from cyclohexane gave 0.260 g (53%) of partially racemic (*S*)-**1c**: flat, yellow prisms, mp 62–64°, $[\alpha]^{25}D$ +66.4° (*c* 4.44, absolute C_2H_5OH). Removal of the cyclohexane from the mother liquors gave 0.040 g of partially racemic (*S*)-**1c**: fine, yellow plates, mp 58–60°, $[\alpha]^{25}D$ +128° (*c* 4.20, absolute C_2H_5OH).

(*S*)-(−)- and (*R*)-(+)-1-(3-Pyridyl)ethylamine [(*S*)-2a and (*R*)-2a]. To 16.4 g (0.134 mol) of (±)-1-(3-pyridyl)ethylamine,[9] bp 119–121° (26 mm), in 250 ml of boiling ethanol was added a hot solution of 21.0 g (0.140 mol) of (+)-tartaric acid in 700 ml of 95% ethanol. On cooling to room temperature, there was deposited 34.7 g (190%) of fine, white prisms, $[\alpha]^{25}D$ +17° (*c* 4.00, H_2O). Three recrystallizations of this salt from a 3:1 mixture of isopropyl alcohol–water gave 7.60 g (42%) of the (+)-acid tartrate salt of (*S*)-**2a**: fine, white prisms, mp 188–190° dec, $[\alpha]^{25}D$ +21° (*c* 4.04, H_2O) [lit.[6] mp 193–194°, $[\alpha]^{20}D$ +20.35° (*c* 4.01, H_2O)]. Decomposition of this salt as above gave 0.60 g (18%) of (*S*)-**2a**: colorless oil, bp 118° (25 mm), $[\alpha]^{25}D$ −37.0° (*c* 4.00, absolute C_2H_5OH) [lit.[6] bp 99° (15 mm), $[\alpha]^{20}D$ −39.4° (*c* 4.60, C_2H_5OH)].

Combination of the mother liquors from the resolution above, removal of the solvent, and decomposition of the (+)-acid tartrate salt gave 6.37 g (0.0521 mol) of partially racemic (*R*)-**2a**. The latter was combined with 7.40 g (0.0614 mol) of (−)-tartaric acid in 240 ml of boiling 3:1 isopropyl alcohol–water. On cooling to room temperature, there was obtained 5.30 g (29%) of (−)-acid tartrate salt of (*R*)-**2a**: fine, white prisms, mp 183–184° dec, $[\alpha]^{25}D$ −20° (*c* 3.98, H_2O). This salt was decomposed as before, and there was obtained 0.63 g (8%) of (*R*)-**2a**: colorless oil, bp 118° (25 mm), $[\alpha]^{25}D$ +35.7° (*c* 4.87, absolute C_2H_5OH).

(±)-1-(3-Pyridyl)ethylamine dihydrochloride [(±)-2b] was obtained as hygroscopic, fine, white prisms, mp 208–213° dec.

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.10.

(*R*)-(−)-1-(3-Pyridyl)ethylamine dihydrochloride [(*R*)-2b] was obtained as extremely hygroscopic, microscopic crystals, mp 191–194°, $[\alpha]^{25}D$ −4.1° (*c* 4.09, H_2O).

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.16.

(*S*)-(+)-1-(3-Pyridyl)ethylamine dihydrochloride [(*S*)-2b] was in the form of extremely hygroscopic, fine, white prisms, mp 191–194°, $[\alpha]^{25}D$ +4.5° (*c* 5.85, H_2O).

(*S*)-(−)-1-(4-Pyridyl)ethylamine [(*S*)-3a]. To 16.7 g (0.137 mol) of (±)-1-(4-pyridyl)ethylamine,[9] bp 80–85° (1–2 mm), in 400 ml of boiling methanol was added 20.6 g (0.137 mol) of (+)-tartaric acid in 350 ml of hot methanol. After cooling to room temperature, there was obtained 29.6 g (80%) of salt, $[\alpha]^{24}D$ +22.3° (*c* 8.06, H_2O). The salt was recrystallized from methanol–water by mixing the salt with about 60 ml of boiling methanol per gram of salt and then adding water until solution was complete, usually about 20 ml of water per gram of salt. Three recrystallizations in this manner gave 10.6 g (57%) of the (+)-acid tartrate salt of (*S*)-**3a**: $[\alpha]^{25}D$ +17.7° (*c* 8.19, H_2O) [lit.[6] $[\alpha]^{20}D$ +18.15° (*c* 8.12, H_2O)]. Decomposition of 11.3 g (0.0415 mol) of salt, purified as above, in the usual way gave 3.66 g (79%) of (*S*)-**3a**: colorless oil, bp 89–91° (4 mm), $\alpha^{25}D$ −33.2° (neat), $[\alpha]^{25}D$ −28.0° (*c* 7.89, abs C_2H_5OH) [lit.[6] bp 95° (9 mm), $[\alpha]^{20}D$ −27.9° (*c* 7.44, C_2H_5OH)].

(*S*)-(−)-1-(4-Pyridyl)ethylamine dihydrochloride [(*S*)-3b] was obtained as fine, white needles, mp 151–153° dec (sealed tube), $[\alpha]^{25}D$ −4.2° (*c* 7.76, H_2O).

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.46.

(*S*)-(+)-*N*-(5-Bromosalicylidine)-1-(4-pyridyl)ethylamine [(*S*)-3c]. To a boiling solution of 0.293 g (2.40 mmol) of (*S*)-(−)-1-(4-pyridyl)-ethylamine [(*S*)-**3a**] in 5 ml of methanol was added 0.489 g (2.43 mmol) of 5-bromosalicylaldehyde in 5 ml of hot methanol. Evaporation of the solvent and crystallization of the residue from cyclohexane gave 0.407 g (56%) of (*S*)-**3c**: microscopic, yellow needles, mp 101–102°, $[\alpha]^{25}D$ +38° (*c* 1.25, absolute C_2H_5OH) [lit.[9] mp 89–90° for (±)-**3c** crystallized from ethanol–water]. After boiling this sample of (*S*)-**3c** in cyclohexane for 30 min and crystallization, its rotatory power was essentially unchanged.

Anal. Calcd for $C_{14}H_{13}BrN_2O$: C, 55.10; H, 4.29; Br, 26.19; N, 9.18. Found: C, 54.93; H, 4.25; Br, 25.99; N, 9.10.

Trimethylsilyl Migrations in the 5-Trimethylsilylbicyclo[2.1.0]pentanes[1]

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Abstract: The rates and products of the thermal isomerization of *exo*- and *endo*-5-trimethylsilylbicyclo[2.1.0]-pentane are reported. The data suggest initial formation of a diradical followed by migration of a trimethylsilyl group to give the common product, 3-trimethylsilylcyclopentene.

Possibly the simplest purely thermal hydrogen migration occurs in the isomerization of cyclopropane to propylene.[3] Thermal sigmatropic migration of silicon has been observed preferentially to that of hydrogen in 5-trimethylsilylcyclopentadiene[4] and 1-trimethylsilylindene.[5] Thus the observation that trimethylsilylcyclopropane (**1**) is thermally converted to allyl trimethylsilane (**2**) suggests (but hardly demands) preferential silicon migration here as well.[6]

This paper reports an investigation of isomerization of trimethylsilyl substituted cyclopropanes and a determination of the relative rate of migration of silicon and hydrogen. The 5-trimethylsilylbicyclo[2.1.0]pen-

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