When cyclohexanol (10 ml) and RaNi-200° (9 g) were heated in refluxing benzene (40 ml) during 48 hr, gas chromatography of the product mixture showed the presence of cyclohexanone and cyclohexanol in a 35:65 ratio. The former ketone was characterized as its 2,4-dinitrophenylhydrazone, mp 160–161°, (lit.[31] mp 162°).

(31) N. R. Campbell, *Analyst*, **61**, 393 (1936).

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# The Effect of Hydrogen Chloride on the Optical Rotation of Nicotine

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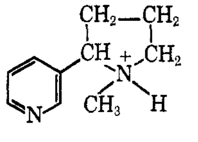
The optical rotatory dispersion curve of (−)-nicotine has been investigated by several workers,[1–3] and (−)-nicotine has been assigned the (*S*) configuration.[3] In a previous paper,[4] the effects of various Lewis acids on the optical rotation of nicotine have been shown, using dimethylformamide as a solvent. However, owing to the strong absorption band of dimethylformamide, the rotatory dispersion in ultraviolet region could not be studied. The study in this region was thought advisable, because it would clarify the mechanism of the optical rotational change of nicotine in detail. The present work was undertaken to determine the effect of hydrogen chloride (the simplest model compound of Lewis acid) on the optical rotatory dispersion and circular dichroism curves of (*S*)-nicotine. The protonated nicotine is easily soluble in transparent solvents (such as alcohol and water). Since the first and the second ionization constants of nicotine are sufficiently different, all species, *i.e.*, nicotine, nicotine monohydrochloride (1), and nicotine dihydrochloride (2), can be obtained separately in solution. Therefore, the difference between the effect of the protonation on the pyrrolidine nitrogen of nicotine and that of the protonation on the pyridine nitrogen would clearly be demonstrated. The fraction of species present at various hydrogen chloride concentrations can be calculated using the following $pK_a$ values which were obtained from the pH titration at 15°: 6.28 and 2.37 in 95% alcohol, and 8.03 and 3.44 in water.[5] When equimolar amount of hydrogen chloride is added to nicotine, 97.6% of the nicotine is in the monoprotonated form 1 in 95% alcohol (pH 4.52), and 99.7% in water (pH 6.20). When hydrogen chloride is added in excess (HCl/nicotine = 5.0), 65.0% is as the diprotonated form 2 in 95% alcohol (pH 2.10), and 94.5% in water (pH 2.20).



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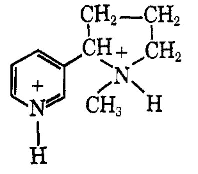

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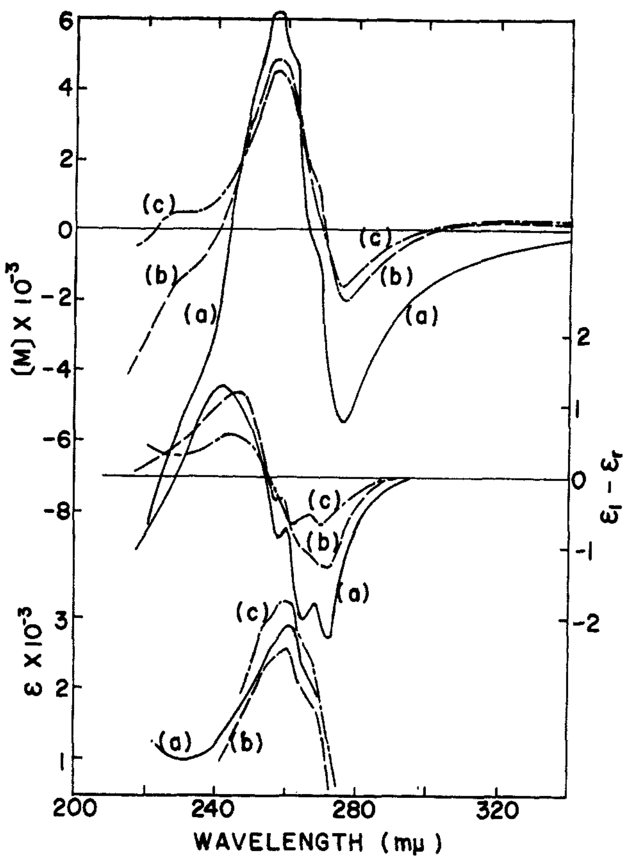

Figure 1.—Rotatory dispersion, circular dichroism, and absorption curves for nicotine–hydrogen chloride in 95% alcohol. Mole ratios of HCl/nicotine are (a) 0.0, (b) 1.0, (c) 5.0.

The rotatory dispersion, the circular dichroism, and the absorption curves of nicotine and its protonated species are shown as a function of the mole ratio (HCl/nicotine) in Figure 1. The established assignment of pyridine[6] and pyrrolidine[7] absorption spectra is applied in the following discussion. In view of the circular dichroism curves, the dispersion curves may be reasonably resolved into one plain curve and two anomalous dispersions, one of which shows a positive Cotton effect, centered at about 245 mμ, and the other, a negative Cotton effect at about 268 mμ. This negative Cotton effect may be assumed to arise from an optically active $\pi$–$\pi^*$ transition of the pyridine ring.[8] Since the magnitude of this negative Cotton effect is decreased by addition of equimolar amount of hydrogen chloride, it would appear that the transition in pyridine ring is influenced by protonation on the pyrrolidine nitrogen. The Cotton effect centered at 245 mμ is due to either the 2p$_z$–3s transition in pyrrolidine nitrogen[7] or the $\pi$–$\pi^*$ transition in pyridine ring. In the latter case, Cotton effects at 245 and 268 mμ are at-

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(1) T. S. Patterson and J. D. Fulton, *J. Chem. Soc.*, **127**, 2435 (1925).

(2) T. M. Lowry and W. V. Lloyd, *ibid.*, 1771 (1929).

(3) J. C. Craig and S. K. Roy, *Tetrahedron*, **21**, 401 (1965).

(4) A. Tomita, E. Ochiai, H. Hirai, and S. Makishima, *J. Inorg. Nucl. Chem.*, in press.

(5) Values of $pK_a$ = 7.92 and 3.32 in water (at 25°) have been reported by R. T. Fowler, *J. Appl. Chem.*, **4**, 449 (1954).

(6) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 14.

(7) L. W. Pickett, M. E. Corning, G. M. Wieder, D. A. Semenov, and J. M. Buckley, *J. Am. Chem. Soc.*, **75**, 1618 (1953).

(8) Electronic transition within aromatic rings attached to asymmetric centers have been found to be optically active by other workers; see L. Verbit, *ibid.*, **87**, 1617 (1965); G. G. Lyle, *J. Org. Chem.*, **25**, 1779 (1960).

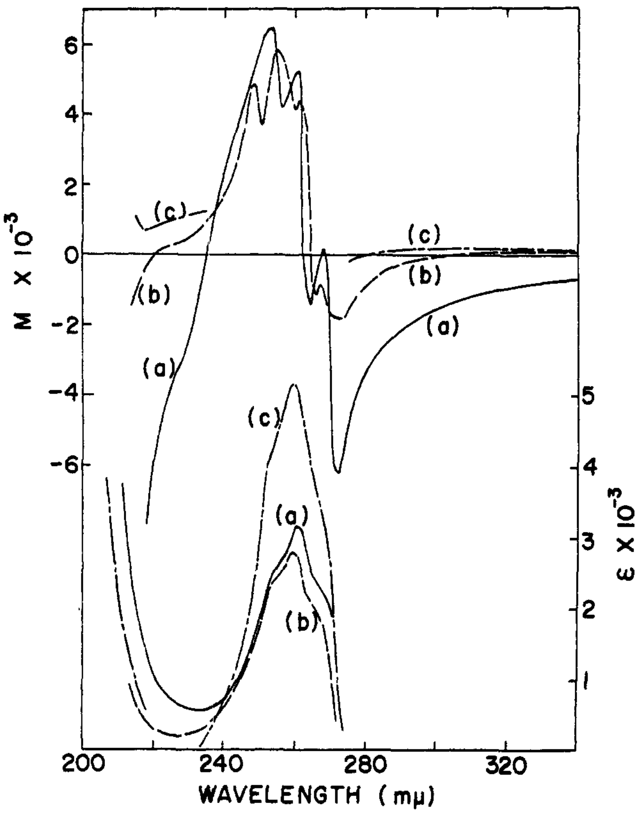

Figure 2.—Rotatory dispersion and absorption curves for nicotine–hydrogen chloride in water. Mole ratios of HCl/nicotine are (a) 0.0, (b) 1.0, (c) 5.0.

tributable to two conformers.[9] The magnitude of this Cotton effect decreased only when hydrogen chloride was added in excess. The steep descent of the dispersion curve of nicotine below 230 mμ may be partly attributed to a rotation associated with the excitation of the nonbonding electrons of pyrrolidine nitrogen to the unoccupied, antibonding $\sigma^*$ orbital. This transition, in fact, is known to occur at about 195 mμ, and shows a hypochromic effect in acidic solution.[7] The above assignment may be supported by the fact that the magnitudes of both absorption and rotation in this location are decreased by the addition of hydrogen chloride.

Figure 2 shows the rotatory dispersion and the absorption curves of nicotine and its protonated species in water. In the presence of excess hydrogen chloride, the intensity of the band at 260 mμ is too large to measure the rotatory dispersion. By comparing Figure 1 with Figure 2, it would be concluded that the effects of protonation upon the rotatory dispersion of nicotine are similar both in 95% alcohol and in water.

Table I lists the $[M]_D$ values of nicotine in the presence of various amounts of hydrogen chloride. The $[M]_D$ value increases with the hydrogen chloride concentration until the mole ratio (HCl/nicotine) reaches 1.0, and decreases slightly upon a further addition of hydrogen chloride. This behavior is very similar to that of nicotine-Lewis acid system.[4] The initial increase is due to the decrease of the magnitudes of the negative circular dichroism bands at 268 and around 200 mμ. The little change of the $[M]_D$ values in the following stage can be interpreted as the result of the cancellation of two contrary effects, one of which is that mentioned just above and the other, the decrease of the magnitude of the positive circular dichroism band at 245 mμ. Accordingly, it may be concluded that the protonation on the pyridine nitrogen has a considerable effect on the optical rotation of nicotine, in spite of the nearly equal $[M]_D$ values of 1 and 2. The result obtained by the measurement at 589 mμ alone (Table I) could not lead to this conclusion.

TABLE I

$[M]_D$ VALUES OF NICOTINE IN THE PRESENCE OF HYDROGEN CHLORIDE

| HCl–nicotine | $[M]_D$ in 95% alcohol | $[M]_D$ in water |
|---|---|---|
| 0.0 | −211 | −113 |
| 0.5 | −75 | −44 |
| 1.0 | +21 | +36 |
| 2.0 | +20 | +28 |
| 5.0 | +20 | +27 |

## Experimental Section

(*S*)-Nicotine was dried over potassium hydroxide pellets, and then distilled under nitrogen atmosphere, bp 127.2° (18 mm). The rotatory dispersion and circular dichroism curves were determined using a Japan Spectroscopic Co., ORD/UV-5 spectropolarimeter. The instrument employed for the optical rotation measurement at 589 mμ was an Applied Electric Laboratory automatic polarimeter. Absorption spectra were recorded on a Hitachi EPS-2 spectrophotometer. All measurements were made at about 15°.

**(*S*)-Nicotine.**—Rotary dispersion as shown in degrees in Figure 1 ($c$ 2.53 × $10^{-3}$ mole/l., 95% alcohol) gives $[M]_{300}$ −1340, $[M]_{276}$ −5560 (trough), $[M]_{256}$ 6330 (peak), $[M]_{220}$ −8290. Rotary dispersion as shown in degrees in Figure 2 ($c$ 2.51 × $10^{-3}$ mole/l., water) gives $[M]_{300}$ −1475, $[M]_{272}$ −6380 (trough), $[M]_{263}$ 6580 (peak), $[M]_{220}$ −5780.

**(*S*)-Nicotine Monohydrochloride** (1).—Rotary dispersion as shown in degrees in Figure 1 ($c$ 2.53 × $10^{-3}$ mole/l., 95% alcohol) gives $[M]_{305}$ 0, $[M]_{277}$ −1980 (trough), $[M]_{256}$ 4850 (peak), $[M]_{220}$ −2760. Rotary dispersion as shown in degrees in Figure 2 ($c$ 2.50 × $10^{-3}$ mole/l., water) gives $[M]_{310}$ 0, $[M]_{272}$ −1880 (trough), $[M]_{256}$ 5800 (peak), $[M]_{219}$ 0.

**(*S*)-Nicotine Dihydrochloride** (2).—Rotary dispersion as shown in degrees in Figure 1 ($c$ 2.47 × $10^{-3}$ mole/l., 95% alcohol, purity 65%, see text) gives $[M]_{300}$ 0, $[M]_{276}$ −1580 (trough), $[M]_{256}$ 4450 (peak), $[M]_{222}$ 0. Rotary dispersion as shown in degrees in Figure 2 ($c$ 2.50 × $10^{-3}$ mole/l., water) gives $[M]_{300}$ 150, $[M]_{281}$ 0, $[M]_{220}$ 800.

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[9] K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 66 (1965).

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# Hydrazinolysis of Some Chlorosulfonated Pentavalent Phosphorus Esters

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The preparation and characterization of tris(*p*-chlorosulfonylphenyl) phosphate (1) and bis(*p*-chlorosulfonylphenyl) methylphosphonate (2) has been described recently.[1] This account summarizes the results obtained when these novel phosphorus compounds bearing sulfonyl chloride functions (1 and 2) are treated with hydrazine. In addition, the chlorosulfonation of several dialkyl benzylphosphonates and the subsequent

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[1] J. E. Herweh, *J. Org. Chem.*, **31**, 2422 (1966).