Tetrahedron Letters No.24, pp. 2055-2058, 1970. Pergamon Press. Printed in Great Britain.

THE OPTICAL ACTIVITY OF THE PYRIDINE CHROMOPHORE (*)

G. Gottarelli and B. Samori

Istituto di Chimica degli Intermedi, Universita di Bologna, Italy.

(Received in UK 16 April 1970; accepted for publication 23 April 1970)

Although some attention has recently been paid to the optical activity of nicotine and analogous asymmetrically perturbed pyridines, (1), (2), attempts to interpret the long wavelength CD bands of nicotine (1) seem to be unsuccessful. It was suggested that the two bands at 245 and 268 nm of opposite sign were due to the $2_{pz} \rightarrow 3_s$ pyrolidine nitrogen transition and the $\pi \rightarrow \pi^*$ transition of the pyridine ring respectively, or possibly to $\pi \rightarrow \pi^*$ transitions in different conformers. To clarify this problem, a more simple system is needed in order to rule out major conformational effects and also the mixing of the shorter wavelength extra-chromophoric transitions.

To this end we have synthesised optically active S(-)-5-hydroxy 5,6,7,8 - tetrahydroquinoline (I) and S(-)-pyridyl methyl carbinol (II), and we have examined their CD spectra in several solvents at different temperatures (fig.1). In both cases two bands analogous to those previously described for nicotine are present and have opposite signs. A change of solvent from methanol to dioxane causes an increase in the rotational strength of both bands and a slight red shift. Cooling from +21 to -70°C causes practically no change in the CD spectrum of (I) but slightly increases the amplitudes of both bands in (II). The effect of added hydrochloric acid is to produce a major change in the CD spectra. The long wavelength absorption of pyridine around 270 nm is known to be caused by both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition, which are almost completely overlapped (3); the former transition is described in group theoretical terms as ${}^1B_2 \leftarrow {}^1A_1$ and has an electric transition moment polarised perpendicular to the molecular plane (y direction) and a magnetic moment in the plane (4). The latter, assigned as ${}^1B_1 \leftarrow {}^1A_1$, has an electric and a magnetic transition moment in the plane and perpendicular to it, respectively (4), (5).

(*) Work supported by C.N.R.

The rotational strength of an optically active transition between ground state 0 and excited state e is given as

$$R_{e0} = \mathrm{Im}\langle 0|\hat{\mu}|e\rangle \cdot \langle e|\hat{m}|0\rangle$$

where $\hat{\mu}$ and $\hat{m}$ are the electric and magnetic dipole operators, respectively (6). Pyridine itself is optically inactive, having mutually perpendicular electric and magnetic transition moments. The asymmetric substituent provides a perturbation which mixes states of different symmetry and causes the transition to become optically active (7). Restricting the treatment to first order perturbation theory, and neglecting all other transitions lying at shorter wavelength, the corrected states are

$$|B_1\rangle = |B_1) + C_1\,|B_2) \qquad C_1 = -C_2 = \frac{(B_1\,|\,V\,|\,B_2)}{E_{B_2} - E_{B_1}}$$
$$|B_2\rangle = |B_2) + C_2\,|B_1)$$

where V is the perturbing potential, the ground state in this simple approach being uncorrected. The rotational strength of the transition ${}^1B_2 \leftarrow {}^1A_1$ is therefore

$$\langle {}^1A_1|\hat{\mu}|{}^1B_2\rangle\langle {}^1B_2|\hat{m}|{}^1A_1\rangle = \left\{({}^1A_1|\hat{\mu}|{}^1B_2) + C_2\,({}^1A_1|\hat{\mu}|{}^1B_1)\right\}\cdot\left\{({}^1B_2|\hat{m}|{}^1A_1) + C_2\,({}^1B_1|\hat{m}|{}^1A_1)\right\} = (\underline{\mu}_y + C_2\underline{\mu}_x)\cdot(\underline{m}_x + C_2\underline{m}_y) = C_2\,(\mu_y m_y + \mu_x m_x)$$

analogously for ${}^1B_1 \leftarrow {}^1A_1$

$$R_{B_1\leftarrow A_1} = C_1\,(\mu_y m_y + \mu_x m_x) = -\,R_{B_2\leftarrow A_1}$$

Two bands of equal and opposite sign are therefore expected. In order that the coefficients C_1 and C_2 are non-vanishing the perturbing potential V must belong to the pseudo scalar representation A_2 in group C_{2v}, and a quadrant symmetry rule is expected (7). In going from aprotic to protic solvents a decrease in intensity of both bands is expected, owing to the hydrogen bond formation which reduces both μ_y and m_x. The large energy difference between the two CD maxima is caused by overlapping and mutual cancellation of the two oppositely signed bands. The difference between theory and experiment concerning the areas of the two bands is due to the approximations of the treatment, which neglects the perturbations arising from the higher energy transitions. The band around 213 nm, not previously reported, does not show a corresponding maximum in the U.V. absorption and is likely to be related to the p band of pyridine, shifted to longer wavelength by overlapping and mutual cancellation with an adjacent band of opposite-sign. The effect of hydrochloric acid is difficult to understand as the $n \rightarrow \pi^*$ transition disappears, and the potential due to the proton strongly perturbs the aromatic system; however, theoretical calculations do not give results agreeing with experiment (8), (9). Nevertheless the disappearance of the coupled CD band system provides further evidence for the correctness of the suggested mechanism.

Experimental

(I) was synthesised following the method described by Zymalkowski et al. (10). It was resolved into optical antipodes by fractional crystallisation of the dibenzoyl(+)-tartrate, from absolute ethanol, to constant optical rotation: free base $[\alpha]_D^{20}$ = - 44,2 (C = 0,8 MeOH).

(II) was obtained from 3-acetylpyridine (11) by sodium borohydride reduction. It was resolved by crystallisation of the (+) tartrate from MeOH to constant optical rotation: free base $[\alpha]_D^{20}$ = - 40,2 (C = 0,87 MeOH).

The absolute configuration was found to be (S) for both (I) and (II) by means of Horeau's method (12). The similarity of the CD spectra with that of S (-) nicotine, and the absence of major conformational changes supports this assignment.

CD spectra were measured using a Jouan II Dichrograph.

Acknowledgements We thank Professor S.F. Mason for useful discussion and comments and Mr. A.F. Drake for assistance in recording low temperature CD spectra.

REFERENCES

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

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

(3) G. Coppens, C. Gillet, J. Nasielski and E. VanderDonckt, Spectrochim.Acta, **18**, 1441 (1962).

(4) H.H. Jaffe and M. Orchin, Theory and Application of U.V. Spectroscopy, Wiley (1962).

(5) J.N. Murrell, The Theory of Electronic Spectra of Organic Molecules, Methuen (1963).

(6) L. Rosenfeld, Z.Physik, **52**, 161 (1928).

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

(8) S. Mataga and N. Mataga, Bull.Chem.Soc.Japan, **32**, 521 (1959).

(9) R.D. Brown and M.L. Heffernan, Aust.J.Chem., **12**, 554 (1959).

(10) F. Zymalkowski and H. Rimek, Arch.Pharm., **294**, 759 (1961).

(11) A.R. Katritzky, J.Chem.Soc., 2586 (1955).

(12) A. Horeau, Tetrahedron Letters, 506 (1961); 965 (1962).

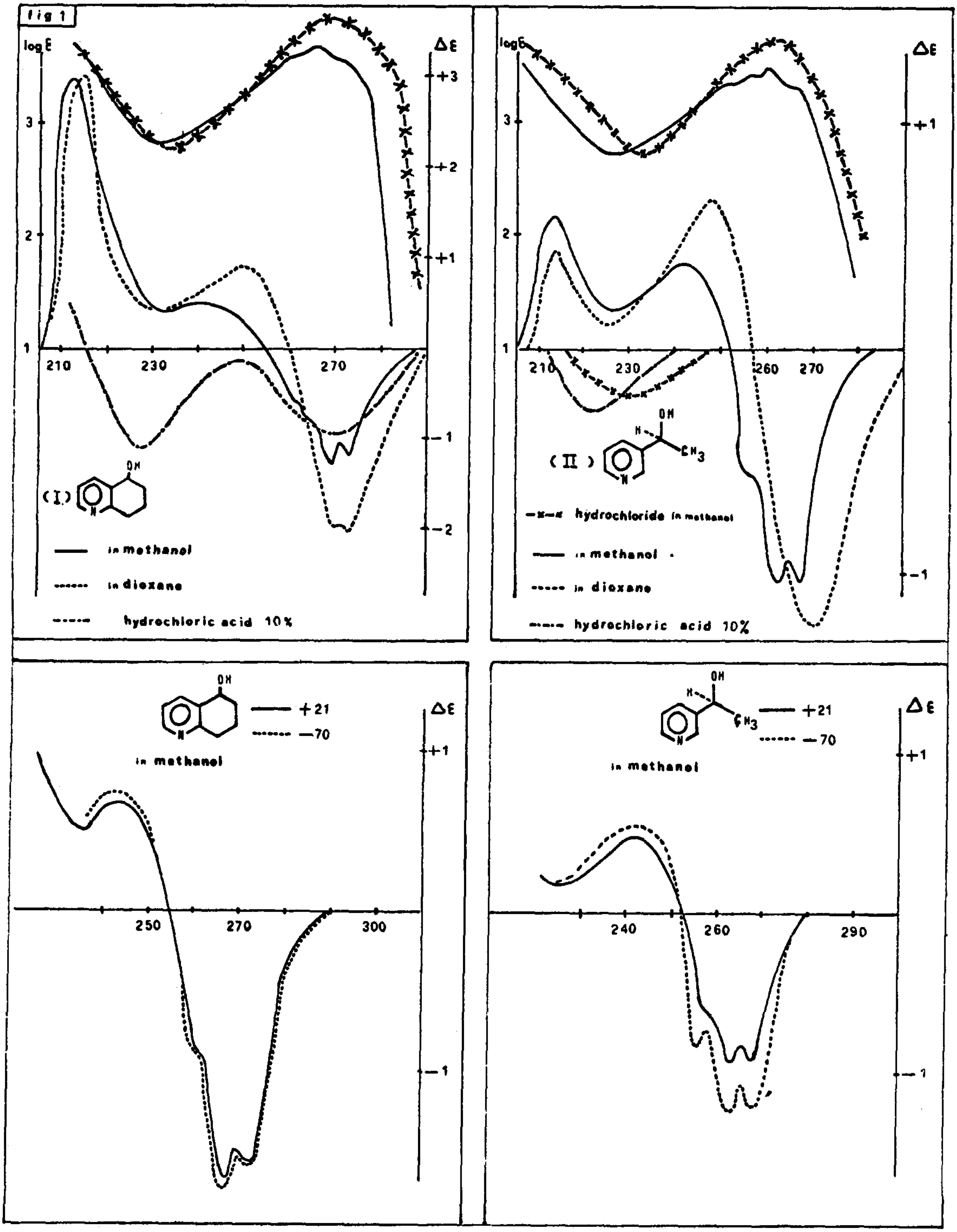
fig 1
log ε
Δε
3
2
1
+3
+2
+1
−1
−2
210
230
270
(I)
OH
N
in methanol
in dioxane
hydrochloric acid 10 %
log ε
Δε
3
2
1
+1
−1
210
230
260
270
(II)
OH
H
CH3
N
hydrochloride in methanol
in methanol
in dioxane
hydrochloric acid 10%
OH
N
+21
−70
in methanol
Δε
+1
−1
250
270
300
OH
H
CH3
N
+21
−70
in methanol
Δε
+1
−1
240
260
290