The Vacuum Ultraviolet–Circular Dichroism Spectrum of an Isolated Pyridine Chromophore

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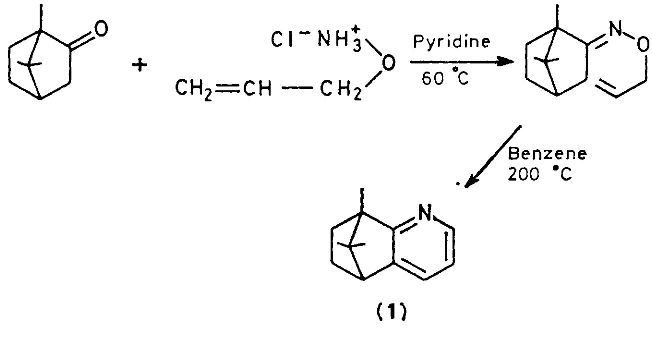
The circular dichroism spectrum of (+)-5,6,7,8-tetrahydro-8,9,9-trimethyl-5,8-methanoquinoline, a molecule containing a pyridine chromophore perturbed by an alkyl moiety has been carried out down to 170 nm through the region of the allowed $\pi \rightarrow \pi^*$ transitions.

The circular dichroism (c.d.) spectra of the pyridine chromophore have been studied extensively[1–7] down to 230 nm, but there are no reports in the literature concerning the high energy side of the c.d. spectrum below 200 nm, where the transition to the 'E_{1u}' benzene-like states should be observable.[8]



Scheme 1

We present here the u.v. and c.d. spectra of (+)-5,6,7,8-tetrahydro-8,9,9-trimethyl-5,8-methanoquinoline (**1**) down to 170 nm. In this molecule a pyridine chromophore is chirally perturbed by a 'rigid' alkyl moiety and hence an average of the molecular optical activity over several conformers, leading generally to a low dissymmetry factor ($g = \Delta\epsilon/\epsilon$), can be excluded. This aspect is particularly important here, where the c.d. associated with electrically allowed transitions is studied.

A simple method has recently been devised[9] for the synthesis of 5,6,7,8-tetrahydroquinoline starting from cyclohexanone. This suggested the possibility of obtaining the chiral pyridine chromophore (**1**), starting from (+)-camphor, as shown in Scheme 1.†

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† After bulb to bulb distillation, (**1**) gave: b.p. 130 °C (11 Torr); $[\alpha]_D^{17}$ + 30.95° (*c* 2.1, cyclohexane); the mass spectrum showed the molecular ion *m/z* 187 (M^+); ^1H n.m.r. (60 MHz, CCl_4), δ: 8—6.6 (m, 3H, aromatic), 2.8—2.7 (d, 2H), 2.4—1.7 (m, 3H), 1.3 (s, 3H), 1.0 (s, 3H), and 0.5 (s, 3H).

The overall chemical yield of (**1**) is dependent on the yield of the second step, which is very low ($\leqslant 10\%$). Accordingly, large amounts of black tar were recovered. As no differences in optical rotatory power have been observed for samples of (**1**) from different preparations and as the mechanism proposed[9] for the cyclization step does not involve the asymmetric carbon atoms, it can reasonably be assumed that no relevant racemization occurs and hence the optical purity of (**1**) is substantially that of the starting (+)-camphor (*ca.* 95%).

The u.v. spectrum‡ in n-heptane shows three main regions of absorption between 300 and 170 nm, with maxima at 277, 215, and 185 nm (Figure 1). According to the accepted literature assignment,[8] these bands can be attributed to the $1^1A_1 \rightarrow 1^1B_2(^1L_b)$, $1^1A_1 \rightarrow 2^1A_1(^1L_a)$, and $1^1A_1 \rightarrow 2^1B_2$, $1^1A_1 \rightarrow 3^1A_1(`E_{1u}')$ transitions of the pyridine chromophore.

In the c.d. spectrum at least five bands are well defined in the same spectral range (Figure 1). Following the previous analysis of the c.d. spectrum of (−)-2(1,2,2-trimethylpropyl)pyridine,[10] the dichroic absorptions down to 230 nm can be interpreted in terms of at least two transitions: a $\pi \rightarrow \pi^*$ positive c.d. absorption at about 280 nm ($^1A_1 \rightarrow 1^1B_2$) and a negative c.d. band at 250 nm, whose $n \rightarrow \pi^*$ character is indicated by the strong blue-shift on changing from heptane to methanol as solvent.

On the higher energy side of the spectrum (230—170 nm) three bands are clearly observable at about 215, 190, and 178 nm. The negative c.d. band at about 215 nm is only slightly red shifted on changing from heptane to methanol as solvent, indicating its $\pi \rightarrow \pi^*$ character. Considering its energy position, and following also a recent assignment[7] in the c.d. spectrum of 5α-cholest-2-eno[3,2-*b*]pyridine, this band can be attributed to the $1^1A_1 \rightarrow 2^1A_1(^1L_a)$ transition. A weak c.d. shoulder at about 205 nm disappears in methanol solution, indicating its $n \rightarrow \pi^*$ character. Actually an $n \rightarrow \pi^*$ transition at high energies has recently been invoked to provide a detailed interpretation of the c.d. spectrum of 5α-cholest-2-eno[3,2-*b*]pyridine,[7] and perhaps this band can be attributed to this transition. Two bands of opposite sign and similar intensity are observed corresponding to the electrically allowed $1^1A_{1g} \rightarrow {}^1E_{1u}$ benzene-like transition (200—170 nm). A possible explanation of the origin of the two bands observed below 200 nm and assigned to the 'E_{1u}' transition could be that they are due to the non degenerate components of the $1^1A_{1g} \rightarrow {}^1E_{1u}$ transition. The two components of this doubly degenerate transition are mutually perpendicularly polarized in the parent benzene chromophore,[8] and so would be expected to give c.d. bands of opposite sign, by one or more of several possible mechanisms, in a chirally perturbed derivative. For instance, static coupling calculations on the c.d. spectra of the above transitions gave a couplet in the case of 1-methylidan.[11] The c.d. couplet could also originate from the interaction of two collinear transition moments of the same chromophore, one being an electric and the other a magnetic transition dipole.[12] This mechanism requires magnetically allowed transitions of the right symmetry to give optical activity by coupling with the electric dipole of the $^1A_{1g} \rightarrow {}^1E_{1u}$ transition. A strong band has been observed[13] at 176 nm in the c.d. spectrum of 1-methylidan, and it has been attributed to magnetically allowed $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ transitions.

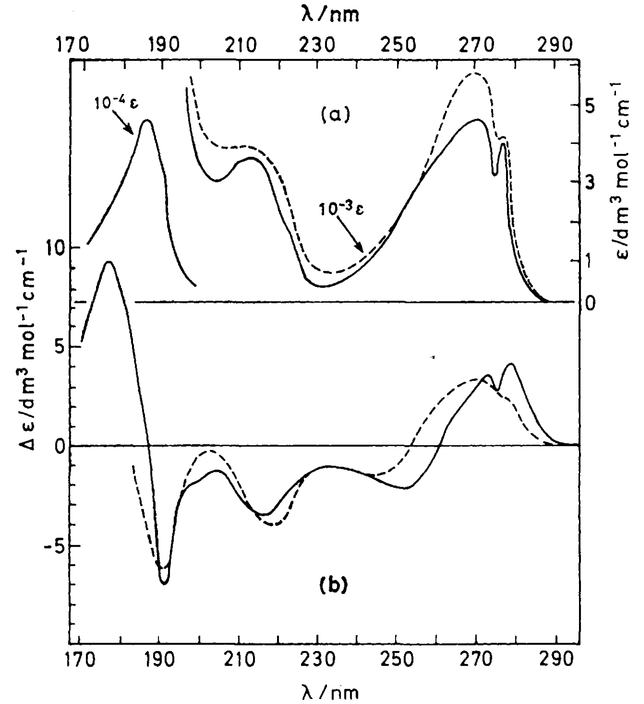

Figure 1. (a) U.v. and (b) c.d. spectra of (**1**) in hydrocarbon (———) and methanol (– – – –) solution.

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‡ U.v. and c.d. spectra of (**1**) were measured in hydrocarbon and methanol solutions (2—4 × 10^{-3} M/l) in 0.1—0.005 cm cells, using Cary 14 and Jasco J 500C spectrometers. The highest energy region (190—170 nm) was investigated by means of a vacuum u.v. spectrometer, at the Department of Biochemistry and Biophysics, Oregon State University.