Polarization of the Main Absorption Bands of the 1-Ethylquinolinium Ion by Dichroism Analysis

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It has been determined, from fluorescence measurements, that the main part of the first absorption band of the quinolinium ion (perchlorate) is polarized along the long axis of the ring and may be assigned to the ^1L_b transition, while the ^1L_a transition polarized along the short axis is hidden on the longer-wavelength side of the first band.[1] In order to obtain some information about the polarization directions of the first and second bands of the quinolinium ion, we carried out a dichroism analysis using the stretched PVA sheet.[2] If the first absorption involves the transitions to the ^1L_a and ^1L_b states corresponding to those of naphthalene, the intense second band may plausibly be identified as the transition to ^1B_b. For that reason, on the assumption that the ^1B_b transition is along the long axis, we will be able to determine the direction of the transition of the first band by comparing it with that of the second, used as a standard.

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[1] H. Zimmermann and N. Joop, *Z. Electrochem.*, **65**, 61 (1961).

[2] Y. Tanizaki, This Bulletin, **38**, 1798 (1965); **32**, 75 (1959).

Experimental

The compounds employed were 1-ethylquinolinium iodide, 1-ethyl-2-methylquinolinium iodide, and 1-ethyl-4-methylquinolinium iodide. 1-Ethylquinolinium iodide was synthesized from commercial quinoline and ethyl iodide, and then purified by repeated recrystallizations from methanol solutions (mp 157°C; 158°C in the literature). The others were supplied as pure samples by the Fuji Photo Film Research Laboratory.

The sample sheets were prepared in a way described elsewhere.[3] The solution for the dyeing bath was prepared using a mixed solvent of water and ethanol, about 1 : 10 in volume. The dichroism measurements for the first and second band regions were carried out separately, using sample sheets with different concentrations, because of the large difference in absorption intensities between the two bands. The data for the first band region were taken from the sample sheet containing a quantity about two times that of the second.

Results and Discussion

Figure 1 shows the dichroic spectra and the $R_d(=D_{\parallel}/D_{\perp})$ curve of the 1-ethylquinolinium ion.

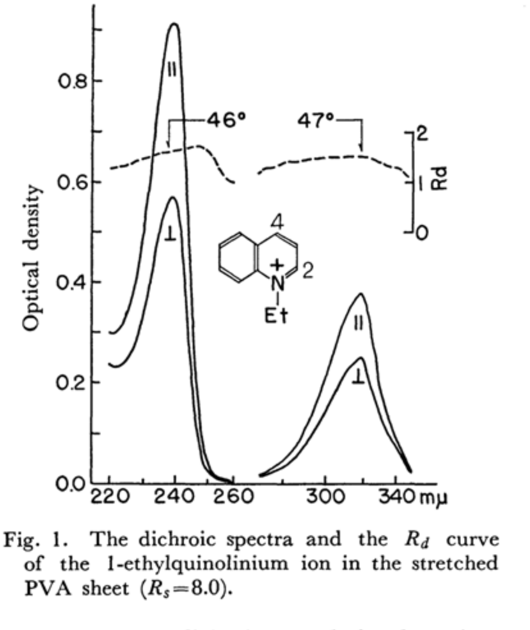

Fig. 1. The dichroic spectra and the R_d curve of the 1-ethylquinolinium ion in the stretched PVA sheet (R_s=8.0).

According to the dichroism analysis, the orientation angles at the maximum points of the first band (318 mμ) and the second band (238 mμ) are, respectively, 47° and 46°. The angle between two transition vectors can be estimated by either the numerical difference between or a summation of the orientation angles. In this case the angle between the transitions becomes 1° (diff.) or 93° (summ.). Under the experimental conditions used here, unfortunately, the angle could not be determined within an accuracy of 2—3°. Accordingly, from only the above results, we cannot decide whether the two transition vectors are parallel or orthogonal to each other.

We attempted to utilize the substitution effect, by which we can expect some change merely in the direction of the orientation axis of the molecule. The absorption spectra of the 2-methyl and 4-methyl derivatives of the 1-ethylquinolinium ion closely resemble that of the mother ion, and the maximum points of the corresponding bands are almost identical. This implies that the methyl group provides no essential change in the transition property of the 1-ethylquinolinium ion.

Figure 2 shows the dichroic spectra and the R_d curves of the 2-methyl (upper figure) and 4-methyl (below) derivatives. The location effect of the methyl group is evidently reflected in the R_d curve, *i. e.*, in the variation of the orientation axis of the molecule. The orientation angles at the maximum points of the first and second bands are 46° (320 mμ) and 44° (242 mμ) for the 2-methyl derivative, and 51° (316 mμ) and 49° (237 mμ) for the 4-methyl. The angle between the two transitions becomes, therefore, 2° (diff.) or 90° (summ.) in the case of the 2-methyl derivative, and 2° (diff.) or 100° (summ.) in the case of the 4-methyl derivative. The comparison of those numerical values indicates that the difference is better in constancy than the summation; that is to say,

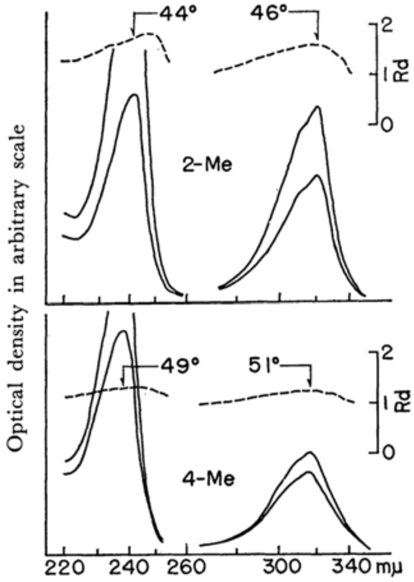

Fig. 2. The dichroic spectra and the R_d curve of the 1-ethyl-2-methylquinolinium ion (upper) and the 1-ethyl-4-methylquinolinium ion (below) in the stretched PVA sheets (R_s=8.0).

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[3] Y. Tanizaki and N. Ando, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **78**, 542 (1957).

the transition vectors of the first and second bands point in the same direction.

Let us employ such conventional notations as ^1B_b, ^1L_a and ^1L_b for the excited singlet states of the quinolinium ion, though this usage is somewhat different from the original meanings proposed by Platt.⁽4⁾ Thus, if the intense second band is attributed to the transition to the ^1B_b state, the first band may predominantly be identified as a ^1L_b transition. Such an assignment is in exact agreement with that of Zimmermann and Joop.⁽1⁾ As for the ^1L_a transition, no useful information could be obtained from our experiment. It may be seen, however, that in every case the R_d value of the first band is always smaller than that of the second; *i. e.,* the orientation angle of the first band is always larger than that of the second. This may suggest that a weak absorption, to be identified as ^1L_a with a polarization different from ^1L_b, is hidden.

The above assignment seems very plausible. Nevertheless, it must be noticed that there is a difficulty in immediately identifying the first band as the ^1L_b transition only because of the parallelism of the polarization. This difficulty arises because of the following reasons:

First, the direction of the ^1B_b transition may deviate from the original direction. The Rd behavior of the second band in Figs. 1 and 2 strongly indicates that the polarization is not uniform over the band region,⁽5⁾ though in the case of the naphthols the corresponding second band has an almost uniform polarization. This is perhaps connected with the asymmetry of the π-electron system of the quinoline skeleton.

Second, the transition directions of ^1L_a and especially ^1L_b are vibronically sensitive. Indeed, it has been clarified that the ^1L_b band in both the absorption and the fluorescence of naphthalene has a fairly large component on the short axis,⁽6⁾ the ^1L_b band of β-naphthol has its polarization completely along the short axis,⁽7⁾ and the ^1L_a band of β-naphthylamine has the same direction as that of the ^1B_b band.⁽8⁾

At any rate, it can safely be said that the polarizations of the second band and the main part of the first band of the 1-ethylquinolinium ion must be parallel, provided that they are either parallel or orthogonal to each other.

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4) J. R. Platt, *J. Chem. Phys.,* **17,** 481 (1949).

5) Y. Tanizaki, *J. Mol. Spectry.,* to be published.

6) D. S. McClure, *J. Chem. Phys.,* **22,** 1668 (1954).

7) Y. Tanizaki and S. Kubodera, *J. Mol. Spectry.,* to be published.

8) Y. Tanizaki and S. Kubodera, unpublished data.