On the Difference between L-Forms and the Corresponding DL-Forms of Amino Acids in their Solid-State Infrared Spectra

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This paper is concerned with an interesting fact which led us to a conclusion that there are three different modes of composition of D- and L-molecules in so-called racemates of amino acids.

We have compared infrared spectra[1] of optically active forms in solid states with those of the corresponding racemates for a variety of amino acids, and have found that these results of the comparisons are grouped in three classes, A, B and C, as given below. It is remarkable that the distinction between these classes is sharp and that there is none intermediate between them.

(A) In class A, *the spectra of the L- and DL-forms are identical.*—Examples[1]: threonine, histidine hydrochloride monohydrate. Here, every band of the DL-form is observed at the same position with the same relative intensity as the corresponding band of the L-form, within the limits of experimental error.

(B) In class B, *the spectra of the L- and DL-forms are a little different from each other.*—Examples[1]: tyrosine (see Fig. 1), alanine, leucine, phenylalanine, asparagine, tryptophan. Here, as illustrated in Fig. 1, some of the bands of the DL-form are observed at different positions and/or with different relative intensities from the corresponding bands of the L-form, but all the bands of the DL-form are observed within 20 cm^{-1} from the corresponding bands of the L-form. Sometimes a band of the L-form splits into two in the DL-form, or a band of the DL-form splits into two in the L-form. But the splitting is mostly observed within a distance of 20 cm^{-1}.

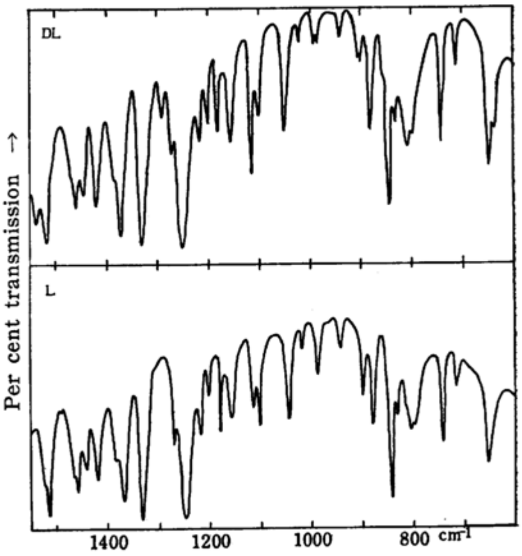

Fig. 1. Infrared spectra of DL- and L-forms of tyrosine in KBr disks.

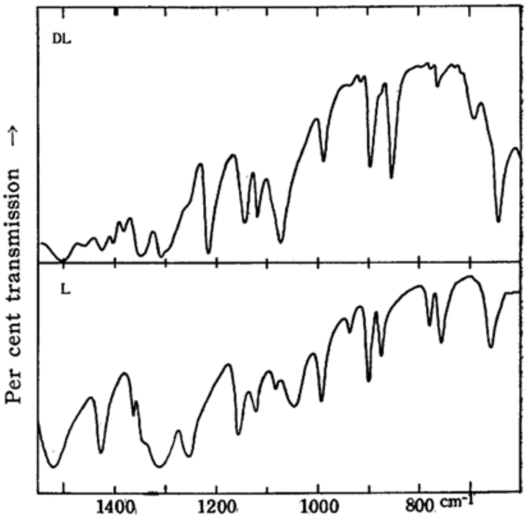

Fig. 2. Infrared spectra of DL- and L-forms of aspartic acid in KBr disks.

(C) In class C, *the spectra of the L- and DL-forms are greatly different from each other.*—Examples[1]: aspartic acid (see Fig. 2), valine, isoleucine, serine, methionine, proline, lysine hydrochloride. Here, as illustrated in Fig. 2, many of the bands of the DL-form have no corresponding bands within 20 cm^{-1} in the spectrum of the L-form; and/or many of the bands of

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[1] For the infrared spectra observed, see M. Tsuboi and T. Takenishi, *J. Japanese Chemistry* (*Kagaku-no-Ryoiki*), *Zokan*, No. 7, Nankodo Co. (1959).

the L-form have no corresponding bands within $20\,\text{cm}^{-1}$ in the spectrum of the DL-form.

The comparisons of the infrared spectra in the solid states of optically active forms with those of the corresponding racemates have also been made by several authors[2-6] for several amino acids. All of these results, so far as is known to us, are grouped, without exception, in the same way as above.

From the above, we are led to consider that the three classes correspond to three different modes in which the D- and L-forms compose the DL-forms in solid states. Thus, in class A, the DL-form is merely a racemic mixture of the D- and L-forms; in class B, the crystal of the DL-form has a lattice composed of the D- and L-molecules, but the composing molecules are essentially identical in configuration with the molecules in the crystal lattice of the active forms; and in class C, the molecules composing the DL-form take different configurations from those in the D- and L-forms.

In the case where the crystal lattice of a racemate is composed of D- and L-molecules, the crystalline force field in it must of course be different from that in the lattice of the optically active crystal which is formed solely by the D- or L-molecules. This difference in the force field must be essentially of the same degree as that between different polymorphic forms of an ionic crystal[7], and must cause just as much difference in spectra as actually observed in class B.

On the other hand, no spectral difference is expected between a mechanical mixture of the D- and L-crystals and its component crystals, because all factors influencing the molecular and lattice vibrations must be exactly identical in the D- and L-crystals, as well as in their mixtures. Then, it may be concluded that the DL-form in class A is a mechanical mixture of the D- and L-crystals. For threonine, one of the examples for class A, Shoemaker et al.[8] reached, from X-ray examinations, a conclusion consistent with the above.

Considered on the basis of the accumulated knowledge on the internal rotations around the C–C and other single bonds[9,10] many of the amino acid molecules are expected to form rotational isomers with small energy differences. For such amino acids, the different crystalline force fields between the DL- and L-forms may result in occurrence of different rotational isomers[11]. Between these rotational isomers a great difference is expected in their infrared spectra. The great spectral difference actually observed in class C may be attributed to such rotational isomerism.

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