

Chart 2.

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The Solvent Effects on the Optical Rotatory Dispersion of Dithiocarbamates of Amines

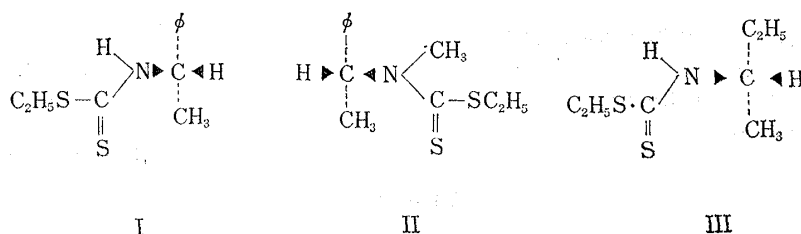
Various types of solvent effects on the optical rotatory dispersion (ORD) and the circular dichroism (CD) of several compounds have been reported¹⁻⁸⁾ and they had also been reviewed by Djerassi, *et al.*⁹⁾

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The present authors have recently reported on the solvent effects in the ORD curves of dithiocarbamate¹⁰⁾ and N-thioacyl¹¹⁾ derivatives of α -amino acids, and the sign of Cotton effect was found to be reversed by the solvent used.

Few studies¹²⁻¹⁴⁾ on the ORD curves of dithiocarbamates of amines, for the suggestion of absolute configuration, have been reported, therefore the solvent effects of the dithiocarbamates of amines were subsequently investigated in our laboratory. It is the purpose of the present paper to report these different findings from the cases of α -amino acids.

(S)-(-)-N-Dithiocarbethoxy- α -methylbenzylamine (I) was considered to be an attractive model compound in order to compare its ORD and CD curves with those of L-alanine dithiocarbamate previously reported.^{10,11)} The ORD curves of I were determined in such the various solvents used as in previous papers.^{10,11)} When each of methanol, acetic acid, ethyl acetate, acetone and pyridine was used as a solvent, the compound (I) exhibited a similar positive Cotton effect in every case (Fig. 1). However, when



dichloromethane, dioxane, benzene, chloroform, carbon tetrachloride or *n*-heptane was used as a solvent, a Cotton effect of I was found evidently to be reversed from positive to negative as being mentioned above (Figs. 2 and 3), and the shape and the amplitude were of solvent dependence. The increase in amplitude followed to the order of the solvents from dichloromethane to *n*-heptane.

In order to confirm these phenomena, CD measurements which are generally able to resolve two overlapping Cotton effects better than the method by ORD measurements were carried out in some of the solvents above-mentioned (Fig. 4). In methanol, only a positive CD maximum was observed, whereas in dichloromethane, dioxane benzene or chloroform, I actually gave rise to two CD maxima of opposite sign whose magnitudes are solvent dependent. The CD band at the longer wave length is positive, however the one at the shorter wave length negative. The former band decreases gradually whilst the latter increases in the order of the solvents from dichloromethane to chloroform except dioxane (Fig. 4). Only a simple large CD negative maximum was observed in *n*-heptane (Fig. 4), furthermore in the case of carbon tetrachloride, a positive CD maximum was hardly recognized, and just a large negative CD maximum was observed. However the outset of the CD maximum at the longer wave length was located at the shorter wave length than the one in *n*-heptane. Therefore it is presumably supposed that a small positive CD maximum of I in carbon tetrachloride might be hidden in the large CD negative maximum (Fig. 4).

These results show that when the solvent is varied from methanol to *n*-heptane in the aforementioned order, a negative CD band of I grows larger gradually at the

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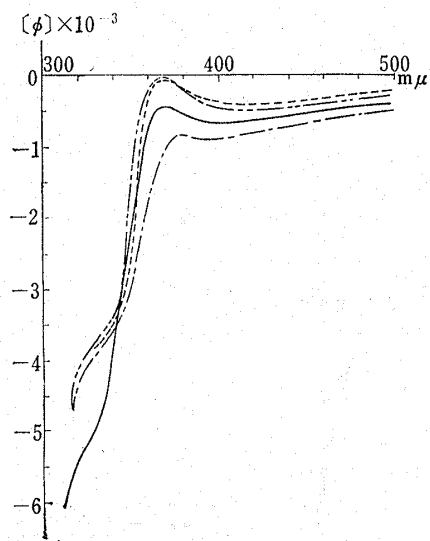


Fig. 1. Optical Rotatory Dispersion Curves of I

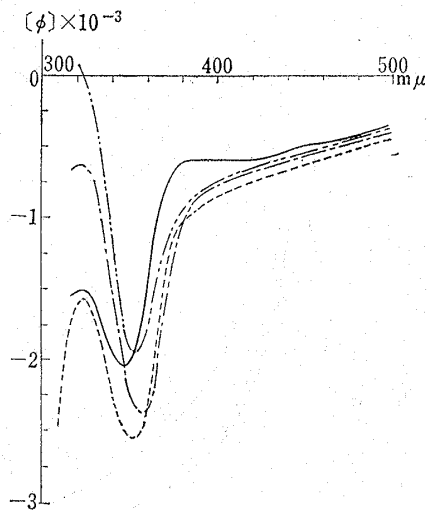
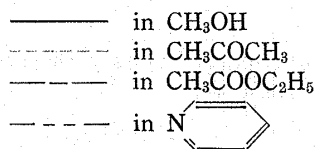


Fig. 2. Optical Rotatory Dispersion Curves of I

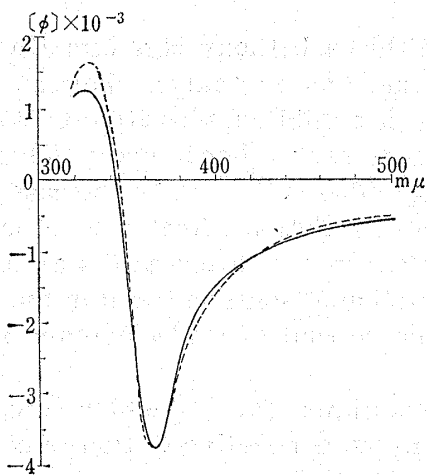
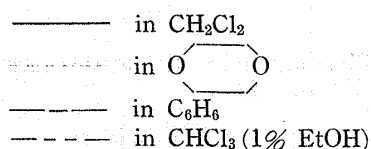


Fig. 3. Optical Rotatory Dispersion Curves of I

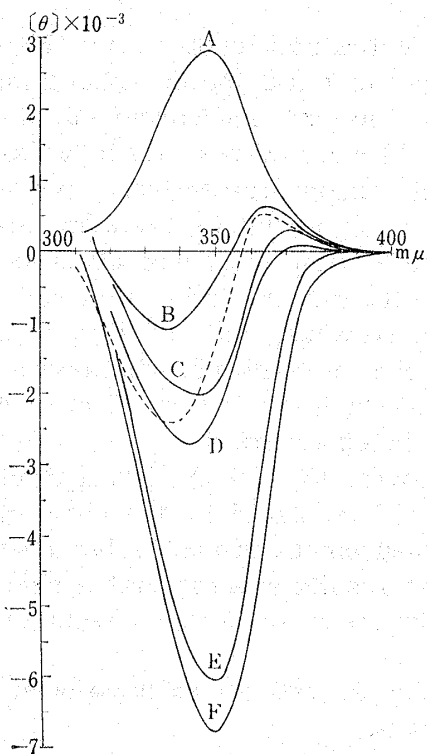
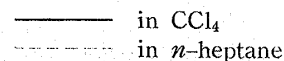
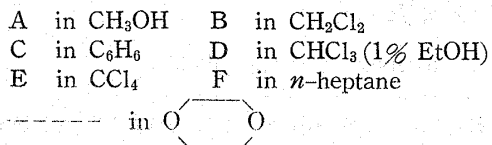


Fig. 4. Circular Dichroism Curves of I



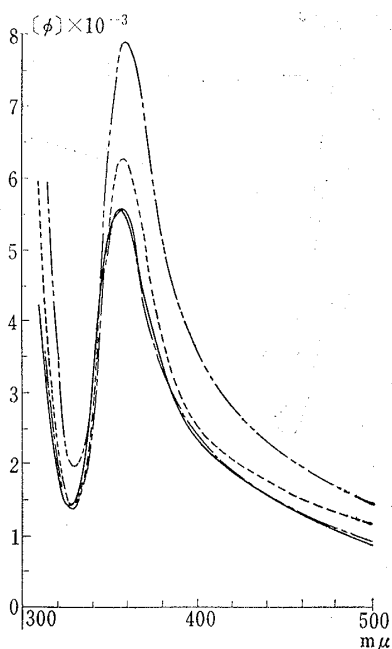


Fig. 5. Optical Rotatory Dispersion Curves of II

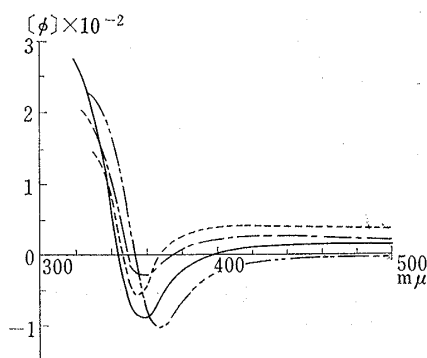
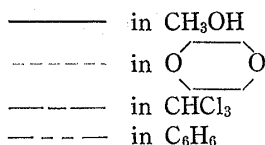
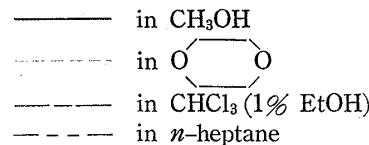


Fig. 6. Optical Rotatory Dispersion Curves of III



expense of the positive one, and this phenomena are inconsistent with the tendency in the case of L-alanine dithiocarbamate.¹⁰⁾

Next, the ORD measurements of (*R*)-(+) -N-dithiocarbethoxy-N, α -dimethylbenzylamine¹⁵⁾ (II) were carried out in various solvents such as methanol, dioxane, chloroform and benzene respectively, and unexpectedly, II exhibited a positive Cotton effect which is very similar in the shape and the amplitude each other in every solvent, and no inverse Cotton effect was observed among these solvents (Fig. 5). In the case of N-dithiocarbethoxy-N-methyl-L-alanine¹⁰⁾ no inversion of a Cotton effect was observed in the same solvents, but the sign of the Cotton effect in the latter case was in accord with the sign of N-dithiocarbethoxy-L-alanine in methanol solution, and in the present case, the sign of the Cotton effect of II was as same as that of I in *n*-heptane solution, the case being reversed.

Moreover, (*S*)-(+) -N-dithiocarbethoxy-2-aminobutane (III) in which the phenyl group of I is replaced by the ethyl group, gave rise to a negative Cotton effect in the ORD measurement in each solvent described above (Fig. 6).

These results suggest that a phenyl group as well as a carboxylic group participates in the inversion of Cotton effects of N-dithiocarbamate derivatives by the solvents used.

Further investigations have been continued on the various types of amines and amino acids.

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