

Differences in the IR Absorption of the Stereoisomers of Certain Dibasic Carboxylic Acids

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Eliel and Kofron¹ have examined the infrared spectra of the optical isomers of the acid phthalic ester of *p*-ethylphenylmethyl-carbinol. Their results show that the (+), (-), and racemic forms have identical spectra in chloroform solution but that those of the crystalline forms, taken as nujol mulls, exhibit significant differences. The absence of free OH stretching frequency and at the same time a shift in the main carbonyl frequency was most interesting. This effect, however, was not general for all substances of the type in question, and the authors came to the conclusion that only when the (+) and (-) forms alone cannot dimerize, changes in the main carbonylic frequencies may be expected. — In order to obtain more evidence about the infrared absorption of optically active substances and stereoisomers in general certain simple α,α' -disubstituted dicarboxylic acids and some other optically active substances have been examined.

Although it is quite obvious from the theoretical point of view that the (+) and (-) forms should give identical spectra in solution, it may be possible that the racemic compounds show some differences in concentrated solutions owing to stronger bonds of the hydrogen-bond type. Concentrated (nearly saturated) solutions of some optically active and racemic substances have thus been investigated in order to give possible support to the assumption mentioned above. The α,α' -dimethylsuccinic and α,α' -dimethylglutaric acids as well as mandelic acid were examined in chloroform solution, whilst tartaric acid, alanine and leucine were studied in aqueous solutions between 7 and 11 μ . For α,α' -dimethylsuccinic, mandelic and tartaric acid and the amino acids no differences in position or intensity of the absorption bands were found between the racemic and optically active form. In the case of α,α' -dimethylglutaric acid, however, a slight difference was observed in the broad maxima at 10.7 μ (930 cm^{-1}), commonly



Fig. 1. I: Racemic α,α' -dimethylglutaric acid in chloroform solution. II: (+)- α,α' -dimethylglutaric acid in chloroform solution.

ascribed to out of plane bendings of OH^2 . The question whether this difference (Fig. 1) is significant enough to be regarded as due to the influence of a presumable racemic compound is left open until further evidence concerning similar effects can be offered. — Using solid samples of the dicarboxylic acids on the other hand more pronounced differences between the racemic and the optically active forms could be observed, the following shifts of main frequencies being noted. The main carbonylic stretching at 5.84 μ for the active α,α' -dimethylsuccinic acid with a slight shoulder at 5.77 μ has in the racemic form given place to two distinct maxima, one at 5.77 μ and the other at 5.88 μ . The active form of α,α' -dimethylglutaric acid has its main carbonyl frequency at 5.86 μ , at which value this band remains even in the racemic form, the only difference being that a slight shoulder appears at 5.80 μ . The spectra in general show other differences as well, unexpectedly pronounced for succinic acid but, on the contrary, very slight for glutaric acid. — No differences between the (+) and (-) forms as observed by Gore and Petersen³ could be found.

As might be expected most interesting differences were observed in the spectra of the

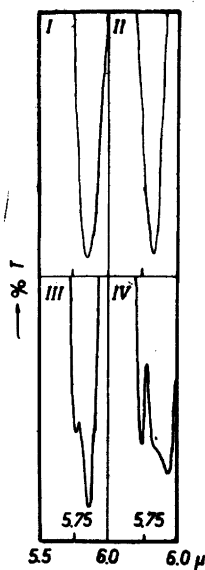


Fig. 2. I: *Meso* α,α' -dimethylsuccinic acid. II: *Meso* α,α' -dibromosuccinic acid. III: *Racemic* α,α' -dimethylsuccinic acid. IV: *Racemic* α,α' -dibromosuccinic acid.

meso and racemic forms of the same dicarboxylic acid. Both the optically inactive stereoisomers of the α,α' -dimethyl derivatives of succinic, glutaric and adipic acid were investigated, and they all showed in solid forms differences in the main frequencies. The changes were not quite similar for the different homologues, but it could be established that the effects diminished with increasing length of the carbon chain.

The racemic form of α,α' -dimethylsuccinic acid shows a double peak at 5.77μ and 5.87μ , while the *meso* form has a single peak at 5.85μ . The racemic form of α,α' -dimethylglutaric acid has the carbonyl peak at 5.86μ with a slight shoulder at 5.80μ . The *meso* form on the other hand has the corresponding peak at 5.78μ with a shoulder at 5.85μ . The shift in the absorption frequencies of the two forms of α,α' -dimethyladipic acid is too small to be determined with certainty. Both the absorption bands occurred at 5.85μ , the racemic form, however, with a slight shift to longer wavelength.

Due to the insolubility of the *meso* forms of α,α' -dimethylsuccinic and α,α' -dimethyladipic

acid in solvents suitable for infrared absorption measurements a complete investigation of the homologues in solution could not be performed. A comparison of the spectra of the two optically inactive forms of α,α' -dimethylglutaric acid in saturated chloroform solution, however, showed the carbonyl stretching frequency of the *meso* form to be at 5.79μ and that of the racemic form at 5.83μ .

From these experiments with the dicarboxylic acids the general conclusion can be reached that where a difference *does occur*, the carbonyl frequency of the racemic form is shifted to longer wavelength. More valuable and useful conclusions could be drawn by comparison of the *meso* and racemic forms of different substitution derivatives of the same acid. The behaviour of the main carbonyl absorption band seems to be characteristic for the stereoisomeric forms of acids being derived from the same dicarboxylic acid and only differing in the substituents. It should be observed that in this investigation these substituents are approximately of the same type. The carbonyl bands of α,α' -dimethylsuccinic and α,α' -dibromosuccinic acid are shown in Fig. 2. The double peaks are probably characteristic for the racemic forms of α,α' -disubstituted succinic acids, whereas the *meso* forms show single peaks. As both the isomers of α,α' -dibromosuccinic acid in dioxan solution gave well defined single peaks at 5.73μ and 5.75μ , respectively, it is obvious that the changes mentioned above were not caused by any decomposition products of the substances. It seems reasonable to the authors to explain the existence of double peaks here as due to steric effects, as such explanations have in other connections already been proposed by Duncanson⁴ for some derivatives of succinic acid.

Experimental. The solid samples of the methylsubstituted acids were examined as solid pressed potassium bromide plates according to Schiedt and Reinwein⁵. The bromo compounds were investigated as nujol mulls. The spectrophotometer used was a Perkin Elmer model 21. Detailed results and discussions will be published later in connection with further work.

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