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CD-SPECTRA OF N,N'-DIBENZOYLAMINO ACIDS AND RELATED COMPOUNDS: EVIDENCE FOR THE CONFORMATION OF ACYCLIC DIAMINO COMPOUNDS.**

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In our recent publication on di-DNP*** chirality rule$^{1)}$, the CD-spectra of N,N'-di-DNP-amino acids were interpreted from the chirality rule and conformational analysis. Evidence for the validity of the conformational analysis there used is presented in this paper.

The well established dibenzoate chirality rule$^{2)}$ is based on the fact that the transition dipole responsible for the 230 nm band is nearly parallel to the alcoholic C-O bond. Calculation of the transition moment for benzamide proved that it is also nearly parallel to the trans N-H bond****. So, the chirality rule seemed extendable to the benzamide system, and it was confirmed by preparing the dibenzoyl derivative (I) of trans-1,2-cyclohexanediamine (Fig.1).

Compounds (II) is the acyclic analog of (I), and considered to exist as a mixture of three staggered conformers (A, B and C) as shown in Fig.2. The conformer (A) is predicted to contribute negative to the longer wavelength band and positive to the shorter wavelength band by comparison of the chirality between the C-NHBz bonds with that in compound (I), the conformer (D) in Fig.2. In the conformer (C) the chirality is reversed, so just oppositely signed contribution to the CD-spectrum is predicted. The conformer (B) would give no appreciable contribution because of the symmetric arrangement of the benzoyl groups in it. From the observed CD-spectrum for II, it can be concluded that the conformer (A) must be more populated than (C). This provides the experimental

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**This paper constitute Part IX of "Optical Rotatory Dispersion of Nitrobenzene Derivatives". ***DNP=2,4-dinitrophenyl.

****The authors are grateful to Dr. T. Kobayashi for the calculation.

support to the validity of the conformational analysis for the di-DNP-derivatives in the previous paper$^{1)}$.

The same pattern of CD-spectra (Fig.1) were observed for the N,N'-dibenzoylamino acids (III_a-III_d). The fact also indicates the validity of the assumption that elongation of the methylene chain (the conformer (E) in Fig.2) would not alter the statistical average direction of the C-N_ω bond.

The difference in magnitude of ellipticity between the spectra of II and III_a can be attributed to the partial cancelling effect due to the carboxylic function, since N-benzoyl-L-alanine shows antipodal CD-spectrum of low intensity to those of the compounds III_a-III_d.

Compounds IV and V are the oxygen analogs of I and II, respectively, and show spectra of the same pattern (Table 1), indicating that such an analysis can be applied to the mixed system.

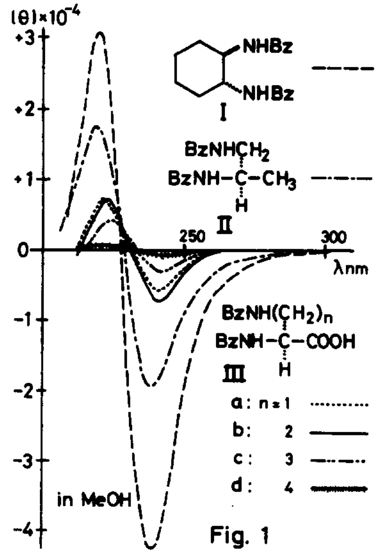

Fig. 1

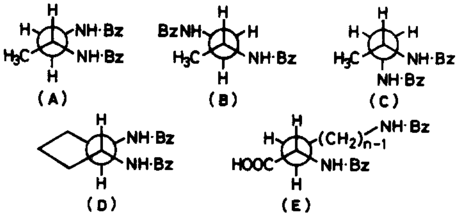

Fig. 2

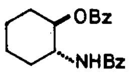 IV	BzOCH₂ BzNH···C···CH₃ H V
$[\theta]_{222}$ +31800	$[\theta]_{221}$ -10000
$[\theta]_{228}$ 0	$[\theta]_{227}$ 0
$[\theta]_{238}$ -55700	$[\theta]_{236}$ +18300

Table 1

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References

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2. N. Harada and K. Nakanishi: J. Amer. Chem. Soc., 91, 3989-3991 (1969)