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CD-SPECTRA OF N-2,4-DINITROPHENYL(DNP) DERIVATIVES OF AROMATIC AMINO ACIDS A SIMPLE METHOD FOR DETERMINING THEIR ABSOLUTE CONFIGURATION**

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In the course of systematic study of the chiroptical properties of DNP-α-amino acids, we noted that CD-spectra of DNP-aromatic amino acids show characteristic pattern, which is somewhat different from those of N_α,N_ω-di-DNP-amino acids[1),2)]. They have lower intensity and their shorter wavelength band (ca.335 nm) lies shorter than that(ca.360 nm) of the di-DNP-amino acids.

The CD-spectra of common DNP-aromatic amino acids are reproduced in Fig. 1

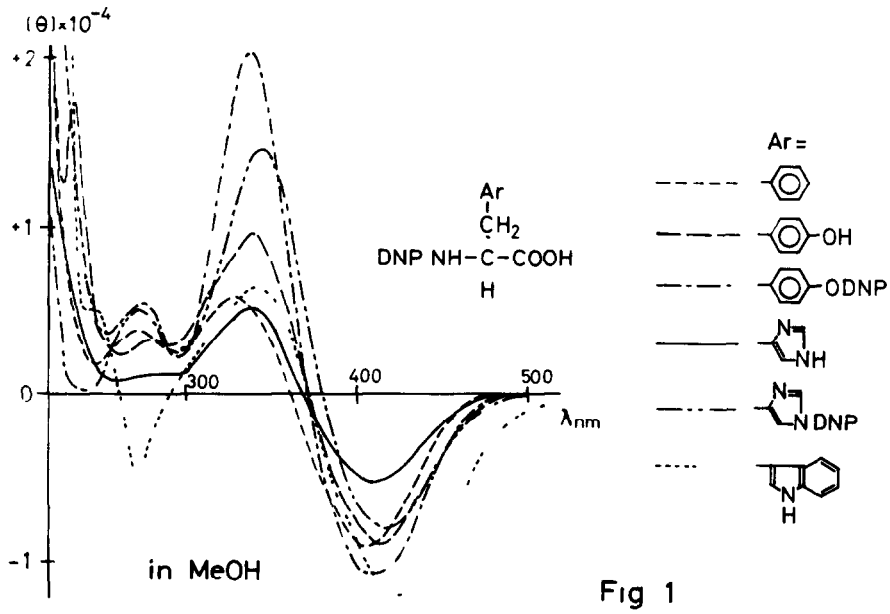

Fig 1

** This paper constitutes Part VIII of "Optical Rotatory Dispersion of Nitrobenzene Derivatives"

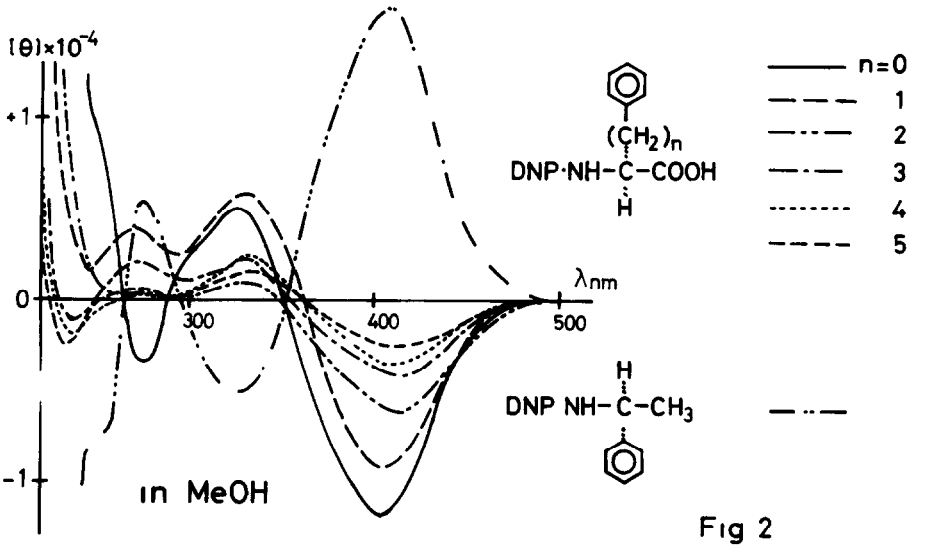

Fig 2

All show similar pattern above 300 nm and the sign of the Cotton effect is negative for the longer wavelength band. The DNP-derivatives of L-phenylalanine homologs also show very similar pattern of CD-spectra (Fig. 2).

Hence, the CD-pattern seems the general characteristic of aromatic α-amino acids and should be useful for determining the absolute configuration of new aromatic amino acids in micromoles quantity, which occur sometimes in biologically interesting peptides[3].

These characteristic CD-pattern, especially the longer wavelength negative band, can be explained by exciton coupling of the transition moments (μ_1 and μ_2)*** of DNP-chromophore with that of the aromatic one ($\mu_{//}$) based on the following assumptions. (i) the conformer (a) would be more stable than (c), (ii) contribution from the conformer (b) is negligible because of the symmetric arrangement of the two chromophores, (iii) the effect of the perpendicular aromatic transition $\mu_\perp$ is much less than that of μ_2 in magnitude due to free rotation about the CH_2-arom. bond, and (iv) presence of the longer methylene chain in the phenylalanine homologs would not alter the statistical mean direction of μ_2 in rough approximation from that of phenylalanine (Fig. 3 and 4).

*** μ_1 and μ_2 correspond to the longer and the shorter wavelength band, respectively, and μ_1 is nearly parallel to the C-N bond[1].

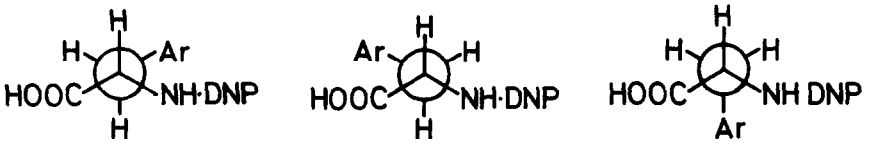

Fig 3

Calculation of the rotatory strength for the conformer (a) according to the equation by Schellman[4] gave the sign agreed with that of the observed

Di-DNP derivatives are present for histidine and tyrosine and they also show similar CD-pattern. So, the usefulness of the above empirical rule is kept for these amino acids though the origin may be di-DNP interaction.

In the case of phenylglycine (Fig 2, n=0), inspection of the molecular model for the expected favoured conformer proves the same chirality between the two interacting moments as for the others (Fig. 5). Since, DNP-S-α-phenylethyl-amine showed CD-spectrum antipodal with that of DNP-S-phenylglycine (Fig. 2) the relation seems widely applicable, e.g to pharmacodynamic amines. Its extension to the related compounds is in progress.

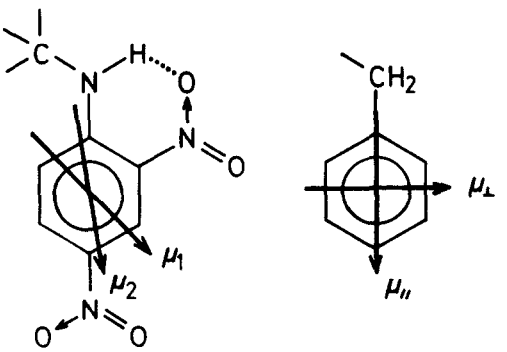

Fig 4

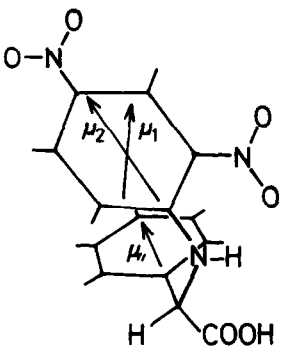

Fig 5

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