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A METHOD FOR DETERMINING THE CHIRALITY OF DIAMINO COMPOUNDS: DI-DNP CHIRALITY RULE

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Previously, it was found that doubly 2,4-dinitrophenylated (DNP) amino acids I - IV show a characteristic pattern of ORD-spectrum around 360nm, which indicates the interaction of the two DNP chromophores.[1)] The fact that all these compounds show very similar pattern of CD-spectra (Fig. 1), seems to reflect their common feature of stereochemistry:(L)-configuration and can be explained on the basis of conformational analyses and di-DNP chirality rule, a relation between the sign of the Cotton effects and the chirality of the two DNP-groups, which is proposed here.

The CD-spectra have three maxima, two negative and one positive. The

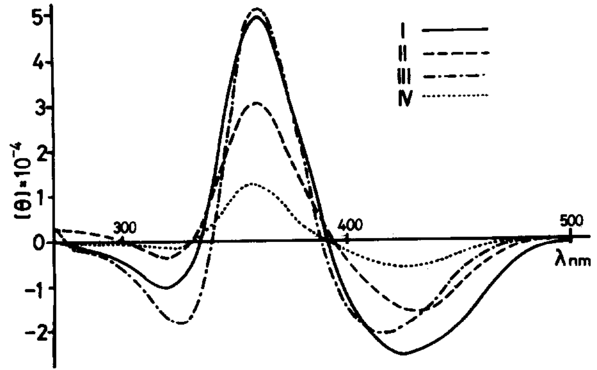
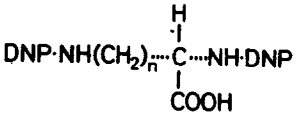


Fig. 1

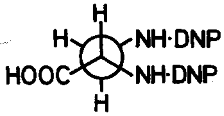


$$\mathrm{DNP{\cdot}NH(CH_2)_n\cdots\overset{H}{\underset{COOH}{C}}\cdots NH{\cdot}DNP}$$

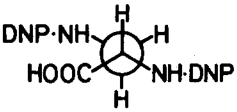
I n=1
II n=2
III n=3
IV n=4

absorption spectra of DNP-derivatives have two bands in the wavelength region, main peak near 350nm and a shoulder near 400nm when measured in MeOH. It is well known that interaction of two transition moments with the same energy causes splitting of the energy level and results in broadening of absorption spectra and a pair of Cotton effects with opposite sign. The CD-spectra shown in Fig. 1 seem to be composed of two pairs of Cotton effects, which are partially overlapped, corresponding to the two bands in absorption spectra. However, the discussion in the present communication is confined to the longer wavelength part of the CD-spectra.

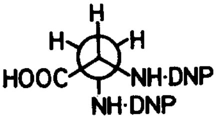
Among the three staggered conformations (A), (B) and (C) of the compound (I), only (A) is considered to contribute to the CD-spectrum considerably, because (B) has no chirality concerning the two DNP-chromophores and (C) would be far less populated than the others on account of steric crowdedness. Hence, the negative chirality as in (A) should correspond to the signs of the paired Cotton effects: first (longer wavelength), negative and second (shorter wavelength), positive. In compounds II - IV, a few methylene groups exist between β-carbon and the ω-DNPNH-group. However, presence of the methylene chain seems not to alter the situation significantly, because the conformer (D) would still be the main source of the Cotton effects and the angle between the two C-N bonds would not vary so much to affect the sign. Thus, the observed CD-spectra of compounds II - IV also can be explained rationally.



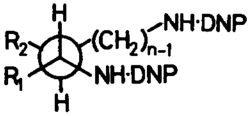
(A)



(B)



(C)



(D) R_1=COOH, R_2=H, n=2~4
(E) R_1, R_2=$-(CH_2)_4-$, n=1
(F) R_1=CH_3, R_2=H, n=1

The di-DNP-derivative(V) of (-)-trans-cyclohexanediamine(VI) which has nearly fixed conformation and known absolute configuration (E)[2] showed CD-spectrum very similar to those of I - IV but of much higher amplitude (Fig. 2) reflecting the fixed conformation.

Di-DNP-(-)-propanediamine(VII) derived from the dexrorotatory dihydrochloride(VIII) shows the same sign of Cotton effects (Fig. 2). The absolute

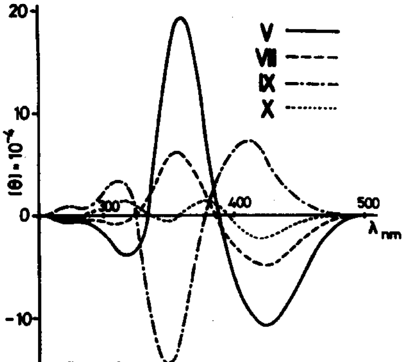
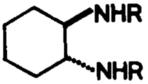
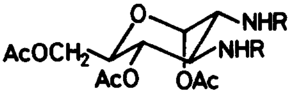


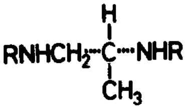
Fig. 2



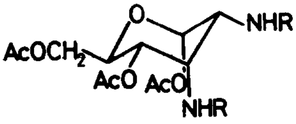
V R=DNP
VI R=H



IX R=DNP



VII R=DNP
VIII R=H

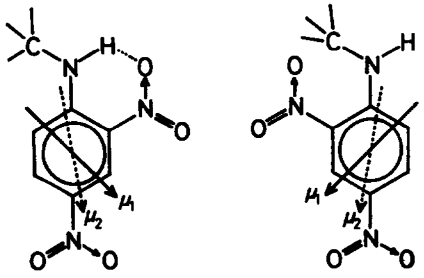


X R=DNP

configuration of VII is known[3] and can be expressed as (F). In the previous paper,[1] VII was given the wrong name (d) according to the description by Tschugaeff[4] that (-)-propanediamine gave (-)-dihydrochloride. But, re-examination showed that (-)-propanediamine gives (+)-dihydrochloride.

Di-DNP-derivatives of diaminosugars, 1,4,6-tri-O-acetoxyl-2,3-dideoxy-2,3-di-(2',4'-dinitrophenylamino)-α-D-glucopyronose(IX) and -α-D-allopyronose(X),* have negative and positive chirality, respectively. Their CD-spectra show the first negative Cotton effect for (IX) and positive for (X) as shown in Fig. 2. All these results can be summarized as a rule: Di-DNP derivatives of diamino compounds having negative (positive) C-N chirality show negative (positive) Cotton effect for the longest wavelength band.

Theoretically, the direction of the electric transition moment responsible for the absorption should be considered. For 2,4-dinitroaniline the transition moments (μ_1 and μ_2) corresponding to the longest wavelength electronic absorption band (shoulder) and the main band, respectively, were calculated to be oriented as shown in Fig. 3 by the variable integrals method II,[5] a



(G) (H)

Fig. 3

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modified Pariser-Parr-Pople type SCF-MO-CI method for π-systems.

Of the two possible planar conformers, (G) is considered to be more favoured than (H) on account of internal hydrogen bonding and steric hindrance. The transition moment (μ_1) is approximately parallel to C-N bond in the conformer (G). Thus, in most of the probable conformers due to rotation about the C-N bond of the compound(V), calculated sign** of the paired Cotton effects due to the interaction of the two transition moments (μ_1) agrees with that expected from the rule. The situation is similar for the conformer of other compounds having the same C-N chirality. Weighted means of the elliptic contributions from various probable conformers would result in permitting validity of the rule.

N. Harada and K. Nakanishi pointed out that their dibenzoate chirality rule can be extended generally to other aromatic systems if the directions of the two interacting transition moments are known.[6,7] The di-DNP chirality rule here proposed is a special case of their general statement in the result. The rule seems to be very useful for elucidating the stereochemistry of diamino compounds, e.g. diaminosugars, peptides and so on.

** Calculation was made with the equation of Schellmann.[8]

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