STUDIES OF INTER- AND INTRA-MOLECULAR DONOR-ACCEPTOR INTERACTIONS-III^{1,2}

OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM OF AN OPTICALLY ACTIVE INTRA-MOLECULAR CHARGE-TRANSFER TRANSITION

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Abstract—The absorption spectrum of N-[1-(p-anisyl)-2-propyl]-4-cyanopyridinium chloride (IV) shows a long wavelength absorption band, which is attributed to an intramolecular charge transfer transition. This transition is shown to be optically active and displays a clear Cotton effect which is positive for th: (S)-enantiomer.

INTRODUCTION

OPTICAL rotatory dispersion (ORD) and circular dichroism (CD) arise from electronic transitions occurring in chiral molecules. The condition for an optically active electronic transition is a non-zero rotational strength R, i.e. non-zero electrical and magnetic transition dipole moments μ_e and μ_m

$$R = \overline{\mu_e} \cdot \overline{\mu_m}$$

While for inherently dissymmetric chromophores^{3,4} R can reach a value of $\sim 10^{-38}$ cgs, this will be several orders of magnitude smaller for such chromophores as the carbonyl group for which the optical activity must be induced by a dissymmetric environment.

Apart from optical activity associated with transitions in isolated chromophoric systems, an important class of optically active systems is formed by molecules showing homoconjugation, 5-7 i.e. a way of coupling "through space" between two or more chromophoric groups.

The model of homoconjugation bears some analogy to the system described in this paper, where charge transfer (CT) interaction occurs between a π -electron-donor and acceptor incorporated within one dissymmetric molecule at positions excluding direct mesomerism.

Related studies in this field are limited to the CT within copper chelates^{8,9} and to *inter*-molecular CT-complexes of tetracyanoethylene and some optically active electron donors.¹⁰

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RESULTS AND DISCUSSION

In previous studies¹ we have shown that an intramolecular CT-transition can be observed in a system containing the electron-donating *p*-anisyl group connected by a chain of two methylene groups to a 4-cyanopyridinium group as an electron acceptor.



SCHEME 1. Reaction scheme for the synthesis of (+)-[S]-N-[1-(p-anisyl)-2-propyl]-4-cyanopyridinium chloride (IV)

A compound (IV) with the same donor and acceptor linked by an aliphatic chain containing an asymmetric centre was prepared according to Scheme 1. (+)-[S]-p-methoxy-hydratropic acid (I) is reduced to the corresponding alcohol, which is converted into the [S]-p-toluenesulphonate (II).

Fusion of II with 4-cyanopyridine gives a mixture of the isomeric pyridinium salts IV and V in a ratio 4:1. Since the reaction takes place through the intermediate phenonium ion $III^{2, 11}$ products IV and V have the steric configurations as depicted in Scheme 1. The main product IV can be purified by crystallization and is used as the model compound in the present investigation.

The assumption that the formation of IV and V is not accompanied by racemization is substantiated by the fact that the similar reaction of 4-cyanopyridine with the *erythro*-compound VI gives exclusively the *erythro*-pyridinium salt.² The UV,

ORD and CD spectra of IV measured in 96% ethanol are collected in Fig. 1. This clearly shows that the CT absorption band in the UV absorption spectrum, coincidences with the spectral region where ORD and CD show their characteristic extremes.

	Intramolecular CT- transition of IV	Intermolecular CT-transition ¹⁰ for the complex TCNE/(+)camphor	Units
ν̃ _{max}	29,540	27,300	cm ⁻¹
£max	692	774	$L.mol^{-1}.cm^{-1}$
(∆ ṽ),	7760	5200	cm ⁻¹
(v _{CD}) _{mex}	28,750	27,200	cm ⁻¹
Δε _{mex}	+0.60	-0.40	$L . mol^{-1} . cm^{-1}$
$(\Delta \tilde{v}_{CD})_{+}$	6450	3500	cm ⁻¹
R	3.11.10-40	$-1.2.10^{-40}$	cm^5 . g. sec^{-2}
D	1.77.10 ⁻³⁶	1·23 . 10 ⁻³⁶	cm^5 .g.sec ⁻²
g	0·70.10 ⁻³	$-0.37.10^{-3}$	•
ſ	0-026	_	
μ	1.33	1-1	Debye
$\mu_{m}\cos\theta$	2.33.10-22	$-1.2.10^{-22}$	$cm^{\frac{1}{2}}$, $g^{\frac{1}{2}}$, sec^{-1}
a	2100	1580	degrees
Ь	~80	61	nm
(vord)mex	26,100	29,500	cm ⁻¹
(VORD)min	32,800	25.000	cm ⁻¹

TABLE 1. SPECTROSCOPIC PROPERTIES FOR THE INTRAMOLECULAR CT TRANSITION OF IV.
For comparison, results for an intermolecular CT transition ¹⁰ are included

In Table 1 several parameters calculated from the spectra are collected. The following formulae were used:

dipole strength:	$D = 91.8 \cdot 10^{-40} \int \frac{\varepsilon}{\tilde{v}} d\tilde{v} = \mu_e^2$
oscillator strength:	$f = 0.476 . 10^{30} \tilde{v}_{\max} D$
rotational strength:	$R = 22.9 \cdot 10^{-40} \int \frac{\Delta \varepsilon}{\tilde{v}} \mathrm{d}\tilde{v}$
dissymmetry factor:	$g=4.\frac{R}{D}$

where ε is the molar extinction coefficient, \tilde{v} is the wave-number in cm⁻¹ and \tilde{v}_{max} is the absorption maximum.

For comparison the data for the (+)-camphor/tetracyanoethylene complex measured by Briegleb *et al.*¹⁰ are included in Table 1. This demonstrates that the results for the intramolecular and intermolecular CT transition are fully comparable.

In a CT transition an electron is excited from the highest occupied molecular orbital of the donor to the lowest vacant orbital of the acceptor, resulting in a characteristically broad absorption band.¹²

The CT band of IV has a maximum at 29,540 cm⁻¹ in ethanol with a bandwidth of 7760 cm⁻¹. The bandwidth of the CD band is of the same order, $(\Delta \tilde{v}_{CD})_{\frac{1}{2}} = 6450$ cm⁻¹. These broad bands contrast clearly with the bandwidth of normal absorption bands. Thus the difference in bandshape observed in absorption is also reflected in the ORD and CD curves (cf. Fig. 1).



FIG. 1 UV spectrum, ORD and CD curves of IV in ethanol (96%) at 25°. (Corrected for optical impurity).

From other studies^{1, 2} we know that the relative orientation of the donor- and acceptor-system has a marked influence on the intensity of the CT absorption band, i.e. on μ_e . Whether such an influence also exists for μ_m and particularly for the vector product $R = \overline{\mu_e} \cdot \overline{\mu_m}$ might be concluded from the temperature dependence of the ORD and CD spectra and by studying systems where the donor and acceptor are fixed relative to each other.

The present study shows that intramolecular CT transitions can be used for the measurement of ORD and CD, their relative long-wavelength position being of great advantage. More work is required to study the relation between absolute configuration and the nature of the Cotton effect for these systems.

EXPERIMENTAL PART

Spectra. UV absorption spectra were measured on a Cary model 14 recording spectrophotometer.

For the ORD-measurements a spectropolarimeter Spectropol-1 could be used by the courtesy of Mr. M. de Belilovsky of Fica. The circular dichroism was measured on a Roussel-Jouan Dichrographe in the Laboratory of Prof. Oosterhoff at Leiden University and we acknowledge the assistance of Dr. H. J. C.

Jacobs and Dr. C. A. Emeis who carried out the measurements. The ORD measurements were reproduced in our own laboratory on a Fica Spectropol-1 by Dr. E. R. de Waard.

Syntheses

(+)-[S]-p-Methoxyhydratropic acid (I). p-anisyldiethylmalonate (b.p. 136–137°/07 mm) was obtained from p-methoxyphenyl-acetic acid ethyl ester.¹³ Alkylation¹⁴ was achieved with methyliodide under the influence of one equivalent of NaOEt, yielding p-anisyl, methyl-diethylmalonate, which after saponification and decarboxylation gave the racemic p-methoxyhydratropic acid m.p. 54–55° (from ligroine).

Resolution. The strychnine salt from 23.7 g of the racemic acid was crystallized four times from a 3.1 water-EtOH; 3.15 g of partly resolved acid (I) was recovered, m.p. 77-78°, $[\phi]_D^{22} = 111.8^\circ$ in EtOH, after addition of base $[\phi]_D^{22} = -11^\circ$.

The (+)-[S]-configuration was assigned to I because it is known,¹⁵ that (+)-hydratropic acids, substituted in the phenyl group, all have the [S]-configuration.

Furthermore there is a large decrease in rotation when a [S]-hydratropic acid is converted into its anion, a phenomenon also observed for I.

In order to determine the optical purity of I, the corresponding acid chloride was made to react with (+) [S]-amphetamine, yielding the amide VII.



In the NMR spectrum the Me protons (a) and (b) in VII have different chemical shifts for the S:S and the R:S diastereoisomers:

S:S isomer: a-CH₃: 152-0 Hz; b-CH₃: 112-7 Hz R:S isomer: a-CH₃: 153-5 Hz; b-CH₃: 109-5 Hz (NMR measured at 100 MHz in CDCl₃ relative to TMS)

From integration of the NMR signals I was found to contain 83.8% of the (+)-acid.

The optical purity of I was also assessed by gaschromatographic separation of its (+)-menthyl esters (obtained from (+)-menthol and the acid chloride of I).

The separation of diastereoisomeric menthyl esters was achieved on a 4 m $\times \frac{1}{8}$ in, 10% Apiezon L on chromosorb AW column at 160°, using a Varian Aerograph 1520 instrument. For I the amount of (+)-acid was found to be:

$$85.6\%$$
 (+)-acid by GLC.

The optical purity of I is thus calculated from the average of both results, as being about 70%. Based on the observed molecular rotation of $[\phi]_{D}^{2^2} + 111 \cdot 8^\circ$ the rotation of pure $(+) \cdot [S]$ -*p*-methoxyhydratropic acid is calculated as $[\phi]_{D}^{2^2} + 160^\circ$.

(+)-[S]-N-[1-(p-anisyl)-2-propyl]-4-cyanopyridinium chloride (IV). I was reduced with LAH in ether to [S]-2-(p-anisyl)propanol, which was converted into the [S]-p-toluenesulphonate II, m.p. 57-57.5 (cf. Ref. 2 and 11).

The product IV was obtained by reaction with 4-cyanopyridine according to our method described earlier; 2 m.p. 203-208°, $[\phi]_{b^2}^{b^2} + 163^{\circ}$ in ethanol.

In the NMR spectrum both the chemical shifts of the methyl-protons and of the α -pyridinium-ring protons differ for the isomers IV and V.² By integration of the NMR signals it was found that the product IV—used in the spectroscopic measurements—still contained about 3% of V.

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