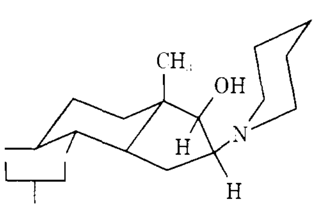
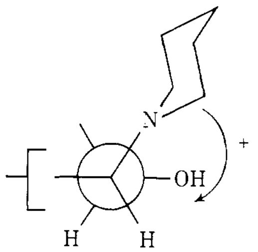
Table II. CD Data for Cyclic 1,2-Amino Alcohol–Pr(DPM)$_3$ Mixtures in Carbon Tetrachloride[a]

No.	Entry[b]	Chirality	10^3M	10^3[Pr(DPM)$_3$], M	$[\theta] \times 10^{-4}$ (nm)[c]
10	3β-Hydroxy-16β-piperidinoandrost-5-en-17-one	(+)	1.1	1.0	+2.1 (312)
			0.9		+0.34 (312)[d]
11	3β,17β-Dihydroxy-16β-piperidinoandrost-5-ene	(+)	1.4	1.4	+2.4 (304)
12	3β,5α-Dihydroxy-6β-piperidinoandrostan-17-one	Diaxial	1.3	1.2	+1.1 (303)
			0.31		+1.1 (305)
13	3β,5β-Dihydroxy-6α-piperidinoandrostan-17-one	(+)	0.74	0.89	+1.24 (303)
			0.74		+0.87 (305)
14	3β,5α,17β-Trihydroxy-6β-piperidinoandrostane	Diaxial	1.4	1.9	−0.0093 (320)
15	3β,5β,17β-Trihydroxy-6α-piperidinoandrostane	(+)	1.35	1.5	+0.44 (309)

[a] See footnote *a* to Table I. [b] Compounds **10–13** were prepared as described by C. L. Hewett and D. S. Savage, *J. Chem. Soc. C*, 484 (1966); 582 (1967). Compounds **14** and **15** were prepared by NaBH$_4$ reduction of compounds **12** and **13**. [c] Only the high wavelength CE is given. [d] This is not the λ_{max} of the CD of **10**. The λ_{max} is ≅290 nm, $[\theta] = 0.56 \times 10^4$.



11



though, in itself, only four examples might normally be insufficient for the formulation of a definitive rule for predicting a CD sign, the similarity of the 1,2-amino hydroxy steroids in curve shape, and magnitude, to the α-glycol steroids leads us to believe that the effect is general. Entry **12** exhibits a [θ] of the same magnitude for the diaxial 5α-hydroxy-6β-amine with or without Pr(DPM)$_3$, indicating that the diaxial compound is incapable of the necessary bidentate contact with the metal.[10] Diaxial α-glycols, including cholestane-3β,5α,6β-triol, were also found to show no CE in the presence of Pr(DPM)$_3$.[2] Reduction of **12** to **14** enabled us to again examine the diaxial system in the absence of the interfering CD of the 17-ketone. This compound showed only a very weak CE, attributable to a simple amine in the presence of Pr(DPM)$_3$. Entries **13** and **15** illustrate that the diequatorial isomers corresponding to **12** and **14** do show the expected CD effect. Entry **10** is of particular interest in that it indicates that an α-amino ketone can act as a bidentate for complexing with Pr(DPM)$_3$ and suggests that the sign of the first CE of α-amino ketones follows the same chirality rules as the α-glycols and 1,2-amino alcohols. In the case of the α-amino ketones, the normal Pr(DPM)$_3$ complex CE was superimposed on a broad CE at 380–400 nm, which was attributed to the carbonyl itself.

In summary, we have found that the method for establishing the chirality of cyclic α-glycols[2] with Pr(DPM)$_3$ can be extended to cyclic 1,2-amino alcohols (and possibly for α-amino ketones) and that Pr(DPM)$_3$ can be used in a micromethod for determining the configuration of simple amines. However, application of these methods to a compound of unknown structure should be approached cautiously since it might be possible to mistake a strong amine CE for a weak 1,2-amino alcohol CE (compare entries **9** and **15**).

The investigation of the extension of this method to acylic 1,2-amino alcohols will be reported in a separate communication.

Acknowledgement. We thank Dr. M. E. Wall of this laboratory for his kind encouragement and support of this work and Dr. S. G. Levine, North Carolina State University at Raleigh, for helpful discussions involving this work. We would also like to thank Abraham Philip for the synthesis of compound **9**.

G. N. Mitchell, F. I. Carroll*
Chemistry and Life Sciences Division, Research Triangle Institute
Research Triangle Park, North Carolina 27709

Received July 23, 1973

---

(10) Compound 12 would be expected to show an effect similar to the simple amines shown in Table I. However, this effect is probably obscured by the CE of the 17-ketone function.

A Study of Optically Active Diastereomeric Charge-Transfer Complexes

Sir:

Charge-transfer complex formation may play an important part in understanding the structure and function of natural products.[1–5] Moser[6] and Briegleb[7] attempted a quantitative study of ORD and CD spectra[8] of optically active charge-transfer complexes. This paper reports the circular dichroism spectra of the charge-transfer (CT) absorption bands of two diastereomeric CT complexes. Of interest to us was the question whether diastereomeric CT complexes show measurably different chiroptical properties.

As the donor molecule we used (+)- and (−)-hexahelicene.[9,10] Its optical purity[9] and absolute configuration[11] have been established. As optically active acceptor (+)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid (TAPA) was used (see Chart I). The resolution of *dl*-hexahelicene (II) using (+)-TAPA (I)[12] is usually interpreted[12] as follows. Diastereomeric charge-transfer complexes are formed and the helicene

---

(1) E. J. Gabbey, *J. Amer. Chem. Soc.*, **90**, 6574 (1968); E. J. Gabbey and A. de Paolis, *ibid.*, **93**, 562 (1971); J. A. Secrist III and N. J. Leonard, *ibid.*, **94**, 1702 (1972).

(2) J. Verhoeven and P. Schwijzer, *Helv. Chim. Acta*, **55**, 2572 (1972).

(3) M. A. Slifkin and R. H. Walmsley, *Spectrochim. Acta, Part A*, **26**, 1237 (1970).

(4) M. Gouterman and P. E. Stevenson, *J. Chem. Phys.*, **37**, 2266 (1962).

(5) R. H. Sarma, P. Dannies, and N. O. Kaplan, *Biochemistry*, **7**, 4359 (1968).

(6) P. Moser, *Helv. Chim. Acta*, **51**, 1831 (1968).

(7) G. Briegleb, H. G. Kuball, and K. Henschel, *Z. Phys. Chem. (Frankfurt am Main)*, **46**, 229 (1965).

(8) The CD spectra were recorded on a Dichrograph Roussel-Jouan Model CD 185 with a 1-mm cell. The uv spectra were recorded on a Carl Zeiss M4 Q III with a PMQ III recorder. Spectrograde chloroform was used as solvent.

(9) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4765 (1956).

(10) R. H. Martin, M. J. Marchant, and M. Baes, *Helv. Chim. Acta*, **54**, 358 (1971).

(11) J. Tribout, R. H. Martin, M. Doyle, and H. Wynberg, *Tetrahedron Lett.*, 2839 (1972).

(12) M. S. Newman, W. B. Lutz, and D. Lednicer, *J. Amer. Chem. Soc.*, 77, 3420 (1955).

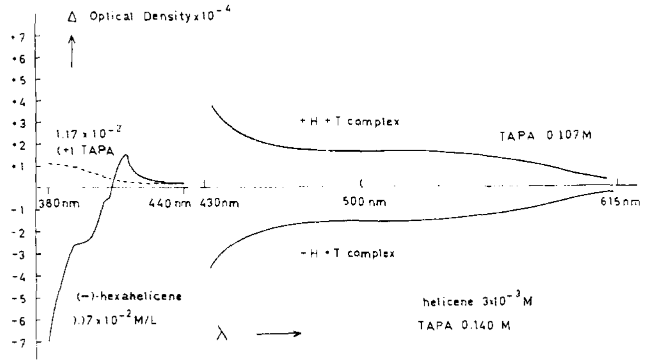
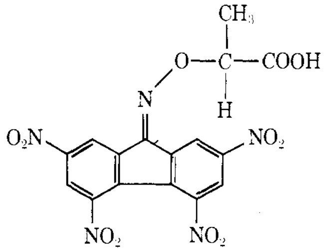


Figure 1.

Chart I

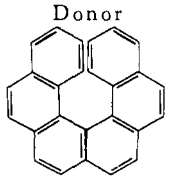
Acceptor



I

(+)-TAPA

Donor



II

Complex

$$A_+ + D_+ \overset{K_-}{\rightleftharpoons} A_+D_+$$

$$A_+ + D_- \overset{K_-}{\rightleftharpoons} A_+D_-$$

(+)-hexahelicene ——→ $K_+ = 4.6$

(−)-hexahelicene ——→ $K_- = 5.5$

enantiomer which complexes poorest with (+)-TAPA crystallizes from solution. Although no spectral data of these complexes have been recorded, it has been noted[12] that solutions become deeply colored. Naturally the successful resolution itself is strong supportive evidence for the hypothesis that indeed the diastereomeric CT complexes have different equilibrium constants.

When (+)-hexahelicene ($[\alpha]^{20}_{578}$ +2717°; $CHCl_3$) and (+)-TAPA ($[\alpha]^{20}_{578} = +80°$; $CHCl_3$) were mixed in chloroform and the circular dichroism of the resulting solution was recorded, the spectrum shown in Figure 1 was obtained. A broad positive CD band with a maximum at 510 nm is observed.

Neither (+)- nor (−)-hexahelicene nor (+)-TAPA separately exhibit circular dichroism between 430 and 600 nm (see Figure 1 for the CD spectra of the individual components). A comparison with the CD spectrum (Figure 1) obtained from the diastereomeric complex, namely the complex from (−)-hexahelicene ($[\alpha]^{20}_{578}$ −3016°; $CHCl_3$) and (+)-TAPA ($[\alpha]^{20}_{578}$ +80°; $CHCl_3$) is instructive. Again a broad absorption band is observed at 510 nm. It is clear that the two diastereomeric complexes have charge-transfer bands at the same wavelength and that their rotational strengths are slightly different in magnitude and opposite in sign. The observation that these diastereomeric complexes furnish CD spectra in the CT region which are nearly mirror images of one another suggests strongly that the donor component (in this case (+)- and (−)-hexahelicene) dominates the sign of the ellipticity.

Both CD spectra show a second absorption band up to 430 nm, having the same sign of rotational strength as the band at 510 nm. This second absorption at the end of the spectrum could not be detected entirely. This band might be attributed to a second charge-transfer absorption. The equilibrium constant of each complex was determined with circular dichroism using the equation

$$O/[D]_0[A]_0 = K[O_m - (O/[D]_0)]$$

for $[A]_0 \gg$ [complex]. When $D + A \rightleftarrows DA$, K_+ is the equilibrium constant for the (+)-hexahelicene–(+)-TAPA and K_- for the (−)-hexahelicene–(+)-TAPA complex. O is the area under the charge-transfer absorption band. O_m is the maximum area for $s = 1$, where $s = [\text{complex}]/[D]_0$. Instead of the area under the band the difference in optical density at various wavelengths can also be used. $\pm[D]_0$ and $+[A]_0$ are the original donor and acceptor concentrations. The following data were found: $K_+ = 4.6$ with $s = 0.45$ and $K_- = 5.5$ with $s = 0.51$. The accuracy of these data was secured by determining the sum of the equilibrium constants of the two complexes using ultraviolet spectroscopy.[8] A modified Scatchard equation was used, with the necessary condition that the racemic component must be in excess. With $K_{\text{tot}} = \Sigma_i K_i$ and $\epsilon_{\text{eff}} = \Sigma_i K_i \epsilon_i / \Sigma_i K_i$ this gives $E/0.5[D]_0[A]_0 = K_{\text{tot}}[\epsilon_{\text{eff}} - (E/[A]_0)]$; $[D]_0$ is in excess. E is the absorbance of the complexes and ϵ_{eff} is the effective extinction coefficient. The following data were obtained: $K_{\text{tot}} = 10.0$ and $\epsilon_{\text{eff}} = 830$ with $s = 0.63$. This means that the K_+ and K_- are in good agreement with the determined K_{tot}, although these values were obtained with different techniques and under different conditions.

It appears safe to conclude that—at least for the case at hand—diastereomeric charge-transfer complexes have significantly different physical properties and that a careful study of the CD spectra of CT bands of chiral acceptors (donors) and chiral natural products might provide useful information.

Acknowledgment. We thank Dr. Jan Verhoeven of the University of Amsterdam for helpful discussions.

Hans Wynberg,* Koop Lammertsma
Department of Organic Chemistry, The University
Groningen, The Netherlands

Received June 18, 1973

Photochemical Rearrangements of Neutral and Protonated 4-Pyrones

Sir:

The photochemistry of 4-pyrones has been shown to be remarkably dependent on the number of substituents present in the pyrone ring. Thus although the dimerization of 2,6-disubstituted-4-pyrones is a well-documented photochemical reaction,[1,2] Ishibi has

---

(1) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, 80, 6150 (1958).

(2) N. Sugiyama, Y. Sato, and C. Kashirma, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).