

The Circular Dichroism of S(+)-Lactic Acid

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WE have measured the circular dichroism of S(+)-lactic acid (which gives a single spot paper chromatogram) in various solvents with a Roussel-Jouan Dichrographe (200—600 $m\mu$ theoretical range) using 1—1.5% solutions with an optical path length of 0.1—20 mm. We observed a negative circular dichroic band with a maximum at 240—250 $m\mu$ and a strong positive band the exact position of which could not be ascertained (below *ca.* 210 $m\mu$).

These results are to be compared with those of Dirkx and Sixma¹ who found a positive Cotton effect at 222.5 $m\mu$ in the optical rotatory dispersion and also with those of Craig and Roy² and Urry and Eyring³ who extended the optical rotatory dispersion measurements to shorter wavelengths. Our results show that the band nearest the visible is negative rather than positive. This illustrates the superiority of circular dichroism measurements since our results are not inconsistent with those of the previous authors but merely of a more precise

nature in this context. The precision leads, however, to the drawing of conclusions which are the opposite to those drawn from the optical rotatory dispersion curves by Urry and Eyring.³ These authors considered that "the extremum at the long wavelength side of 220 $m\mu$ is due to the $n-\pi^*$ transition of the acyl moiety". If we accept

TABLE

Circular dichroism of S(+)-lactic acid at 25°

Solvent	λ_{\max}	$\Delta\epsilon$ negative (1st extremum)
Water	241 $m\mu$	47×10^{-4}
Methanol	243	48
Ethanol	244.5	56
n-Propanol	244.5	56
Isopropanol	244.5	56
n-Butanol	245	60
Chloroform	246	71
Diethyl ether	250	91
1 N-HCl soln.	242	42

their assignment of the band nearest the visible region as an $n-\pi^*$ transition then this must be the band at *ca.* 240 $m\mu$. Thus the $n-\pi^*$ transition in *S*(+)-lactic acid has a sign opposite to that previously supposed.

It is noteworthy that *S*(+)-lactic acid shows no negative Cotton effect in alkaline solution which is consistent with the absence of $n-\pi^*$ transitions in

the salts. The positive circular dichroism maximum below 210 $m\mu$ will then be ascribable to the other transitions of the molecule including $\pi-\pi^*$.

In view of the importance of the $n-\pi^*$ transition in the assignment of configuration, a re-examination of the spectra of the configurationally related amino-acids^{4,5} is being completed.

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¹ I. P. Dirkx and F. L. J. Sixma, *Rec. Trav. chim.*, 1964, **83**, 531.

² J. C. Craig and S. K. Roy, *Tetrahedron*, 1965, **21**, 1847.

³ D. W. Urry and H. Eyring, *J. Amer. Chem. Soc.*, 1964, **86**, 4578.

⁴ B. Sjöberg, A. Fredga, and C. Djerassi, *J. Amer. Chem. Soc.*, 1959, **81**, 5002.

⁵ J. A. Mills and W. Klyne, *Progr. Stereochem.*, 1954, **1**, 206.