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ASYMMETRIC REACTIONS. XXXIX.*

CIRCULAR DICHROISM OF SOME ALKYLPHENYLACETIC ACIDS

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The results of chemical correlation¹⁻⁴ and ORD measurements⁵ indicate that all (-)- α -alkylphenylacetic acids are configurationally related and have the absolute *S* configuration.** The *N*-methylthioamide derivatives of the positively rotating acids of this series all show a positive Cotton effect⁵. In order to confirm the absolute configuration of these acids we determined their circular dichroism (CD) (Table I). *S*-(+)-Hydratropic acid (*Ia*) exhibits, e.g. in ethanol, a band with fine structure at about 260 nm with a very small positive Cotton effect ($\Delta\epsilon_{\text{max}} = 0.04$), a strongly positive CD-band at 223 nm (+4.4), and another negative at 205 nm (-1.0). The band at longest wavelength showing characteristic fine structure was clearly the ¹*L*_b-band of the benzene chromophore. The other two bands must be the aromatic ¹*L*_a-band and the carboxylic *n*- π^* -band. According to Legrand and Viennet⁶ we attribute the most intense CD-band at 223 nm to carboxylic absorption and that at 205 nm to the benzene ring. This correlation

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** After the manuscript had been completed, a similar CD study by Barth G., Voelter W., Mosher H. S., Bunnenberg E., Djerassi C. on α -substituted phenylacetic acids appeared in J. Am. Chem. Soc. 92, 875 (1970).

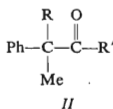
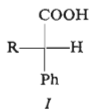
TABLE I
Optical Purity and Circular Dichroism of Alkylphenylacetic Acids

Acid	$[\alpha]_D$ (methanol)	Optical purity (ref.)	λ_{\max}^a
<i>S-Ia</i>	+91.5 ^b	100 (5)	267 (+0.03), 260 (+0.04) 223 (+4.4), 205 (-1.0)
<i>R-Ib</i>	-70.7	90.1 (5)	220 (-2.18)
<i>S-Ic</i>	+3.2	5.13 (8)	226 (+0.14)
<i>S-Id</i>	+5.0	8.04 (8)	222 (+0.20)
<i>S-Ie</i>	+3.3	5.48 (8)	224 (+0.15)
<i>R-If</i>	-4.0	6.82 (5)	214 (-0.21)

^a In ethanol, not corrected for optical purity. ^b Measured in substance.

follows from comparison with the CD of α -phenylethylamine and α -phenyl-*n*-propylamine⁷, without a carboxylic group, the $\Delta\epsilon_{\max}$ -values of which are in the range of 0.02–0.2 and 0.03–1.2 for the ¹*L*_b and ¹*L*_a-band, resp. The 223 nm CD-band of *Ia* is, however, much more intense, and this can easily be explained, for it is assumed that it is caused by carboxylic absorption. The apparent hypsochromic shift of the ¹*L*_a band (in comparison with the amines) is caused by overlap of two bands of opposite sign. Due to lower optical purity only the main band of the other acids could be measured with the dichrograph, which is, we assume, the carboxylic *n*- π^* -band. All acids with *S*-configuration exhibit a positive Cotton-effect within this band.

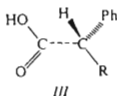
The sign may be explained by resorting to the CD of analogues of carbonyl compounds. For the latter it is known that the preferred conformation is that in which the C α -C β -bond eclipses the C=O bond. Even then there is a hydrogen atom at C α (ref.^{8–11}). Carboxylic acids possess a similar conformation in the solid state^{12,13} and we assume the same for solutions.



R = *a* Me-, *b* Et-, *c* *n*-Pr-,
d *n*-Bu-, *e* *n*-Am-, *f* *i*-Pr

Cookson and coworkers^{14,15}, have shown that the Cotton effect at axial α -phenyl substituted ketones is very large and resembles that of analogous halogen ketones. Using this argument, Moscowitz and coworkers¹⁶ have concluded that the most preferred conformation of α -phenyl substituted aliphatic ketones of type *II* is also that in which the larger alkyl group at C α eclipses the C=O bond, so that the phenyl ring has a relative geometry with respect to the carbonyl as in axial α -phenylcyclohexanones. Using many examples we have shown¹⁷ that all rules for ketones with an asymmetric first sphere can be applied to the corresponding acids (esters). The most preferred conformation of acids *Ia*–*If* with *S*-configuration would (using the above conformation-

al arguments) be *III*, and in analogy to the CD of aromatic ketones a high positive CD would be expected. A value of +4.4 is in fact very high for the CD of an open chain acid. No predictions can at present be made for the sign of the CD of aromatic bands. A similar argumentation could also be applied to the Cotton-effect of the N-methylthioamides.



positive CD

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