261. Optical Rotatory Dispersion and Circular Dichroism Part LXXV: Circular Dichroism of Some Aryl-amino acids [1]

by **W. Klyne, P. M. Scopes,** and **R. N. Thomas**
Westfield College, Hampstead, London, N.W. 3
and **H. Dahn**
Institute of Organic Chemistry, University of Lausanne

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Summary. CD. curves have been recorded for α-aryl-α-amino acids, esters and amides related to α-phenylglycine, α-phenyl-alanine and their N-dimethyl derivatives, and for the corresponding α-cyclohexyl-α-amino acids and esters. Compounds with the (*S*)-configuration at the single asymmetric carbon atom give strong positive *Cotton* effects near 220 nm. The conformations of the acids are discussed and compared with those of other α-amino acids.

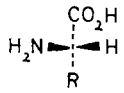
The chiroptical properties of carboxylic acids bearing either an amino group [2] [3] [4] or an aryl substituent [3] [5–7] at the α-carbon atom have been investigated in considerable detail. Surveys of the ORD. [2] and CD. [3] of the protein amino-acids and of the CD. of less common amino-acids [4] have shown that all compounds with the (L*S*)-configuration at C-2 (I) (which is usually but not always (*S*) according to the Sequence Rule) give positive *Cotton* effects, provided that there is no unusual conformational constraint, and that no other chromophore absorbs in the same region of the spectrum. Naturally occurring β-aryl-α-amino acids and related model compounds have been studied by several groups [3] [5] [6], and comparisons have been made between these acids and the corresponding α-aryl-α-amino acids [3] [6] (II, X = NH_2), in which the aromatic chromophore is directly attached to the asymmetric centre. In all cases a weak *Cotton* effect, with considerable fine structure, is observed at 260–280 nm, and a second strong *Cotton* effect near 220 nm. The first of these two bands can be assigned to the weak ^1L_b transition of the aromatic chromophore, but the proximity of the $n \rightarrow \pi^*$ transition of the carboxyl group and the ^1L_a transition of the aromatic ring, both occurring at about 215 nm, make the assignment of the transition at short wavelength difficult.

Recently, *Craig et al.* [7] have studied a series of α-alkyl-phenylacetic acids (II, X = alkyl) and have detected two *Cotton* effects between 210 and 230 nm (in addition to the weak ^1L_b *Cotton* effect at ~ 260 nm). These two *Cotton* effects are of the same sign, but their precise positions and relative intensities vary according to the nature of the alkyl substituent at the α-carbon atom. The authors suggest that the band at shortest wavelength (*ca.* 213 nm) is due to the ^1L_a transition of the aryl chromophore and that the band at slightly longer wavelength (*ca.* 223 nm) is due to a mixed transition resulting from non-bonded interaction of the π-orbital of the benzene ring with the 2 ϱ_y and π^* orbitals of the carbonyl group.

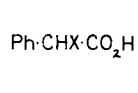
Analogous α-hydroxy-α-aryl-carboxylic acids (II, X = OH) have been studied both by ORD. [8] and more recently by CD. [9] [10]. In particular, *Djerassi et al.* [10]

have studied the CD. of mandelic acid and several closely related compounds, and have also reported two *Cotton* effects, one near 220 nm and a subsidiary band of lower intensity near 240 nm. These authors suggest that the main *Cotton* effect at 220 nm is primarily associated with an enhanced $n \rightarrow \pi^*$ transition of the carboxyl group and only secondarily, if at all, with the ^1L_a transition of the aryl ring. The longer wavelength band near 240 nm is also attributed to the $n \rightarrow \pi^*$ transition of the carboxyl group in an alternative conformation.

We have now investigated the CD. of a series of compounds related to (*S*)-α-phenylglycine and (*S*)-α-phenyl-alanine, which contain an α-aryl substituent, and an α-amino or substituted α-amino group adjacent to a carboxyl group, and which are analogous to the series of α-alkylaryl acids and α-hydroxylaryl acids studied by *Craig* [7] and by *Djerassi* [10], respectively.



I



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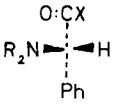

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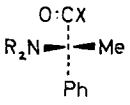
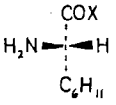
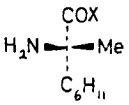


IV

III, IV	R	X
a	H	OH
b	H	OMe
c	H	NH_2
d	Me	OH
e	Me	OMe
f	Me	NH_2
g	Me	OEt

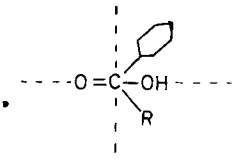


V



VI

V, VI	X
a	OH
b	OEt



VII

Results. – Table 1 presents the CD. data recorded in water and in hydrochloric acid solution for (*S*)-α-phenylglycine (III, R = H, X = OH), (*S*)-α-phenyl-alanine (IV, R = H, X = OH), N-dimethyl-(*S*)-α-phenylglycine (III, R = CH_3, X = OH) and N-dimethyl-(*S*)-α-phenyl-alanine (IV, R = CH_3, X = OH) and their methyl esters and amides. For comparison, the corresponding saturated acids (*S*)-α-cyclohexyl-glycine (V, X = OH) and (*S*)-α-cyclohexyl-alanine (VI, X = OH) and their ethyl esters have also been examined and the CD. data included in Table 1 (p. 2427). The configurations of all these compounds are known ([11] and literature cited therein).

Each of the aromatic compounds (IIIa–f, IVa–g) shows a weak negative *Cotton* effect with characteristic vibrational fine structure centred at 260 nm and larger positive *Cotton* effects at shorter wavelengths. In some cases the experimental curves show a maximum and a distinct shoulder suggesting the superposition of more than one *Cotton* effect; in other cases only one clear maximum is detected. (*S*)-Phenylglycine for example, has a strong positive *Cotton* effect with a maximum at 204 nm in water and a pronounced shoulder at 214 nm; whereas in acid solution, the maximum occurs at 217 nm and the shoulder at 202 nm. In contrast, the corresponding ester and amide show only one pronounced maximum at 217–218 nm and 220 nm, respectively. A similar pattern occurs for (*S*)-α-phenyl-alanine and its derivatives. For the N-dimethylated series (III and IV, R = CH_3) the CD. curves of the methyl esters and of the amides as well as those of the parent acids show evidence of overlapping *Cotton* effects in the 200–230 nm region.

In order to analyse these results and to try and identify the transitions involved, a *Dupont* curve resolver has been used to separate the experimental curves into their component Gaussian bands. The results of this analysis are given in Table 2 (p. 2429), where the experimental results are compared with the Gaussian components of the best fitting sum-curve. Curve fitting was carried out from 200–250 nm only and did not include the very weak negative *Cotton* effect centred at 260 nm.

The simplest aryl acid examined, (*S*)-phenylglycine (IIIa) has a positive maximum at 204 nm in water with a shoulder at 214 nm, but in acid the maximum shifts to 217 nm with a shoulder at 202 nm. Curve resolution suggests that both of these curves arise from superposition of Gaussian bands with maxima at 216–217 nm and at 200–201 nm. For aqueous solution the two maxima are about equal in magnitude, but in acid solution the band at longer wavelength becomes much larger than that at 200 nm. The absolute values of $\Delta\varepsilon$ (+6 to +10) are of the order of magnitude usually associated with inherently dissymmetric chromophores. The methyl ester of (*S*)-phenylglycine (IIIb) was available only as the hydrochloride; this compound in water and in acid gave essentially similar curves, showing that the presence of excess hydrochloric acid in solution has virtually no effect on the CD. curve. Resolution of this curve suggests the presence of two overlapping Gaussian bands with maxima at 217 nm and 202 nm, very similar in magnitude and position to those of the parent acid. The CD. curve of the corresponding amide (IIIc) in water can also be resolved into two Gaussian components, but both are shifted to longer wavelength by about 8 nm as compared with the corresponding acid. In acid solution the single maximum appears to be Gaussian in form.

(*S*)-α-Phenyl-alanine and its ester and amide (IV, R = H, X = OH or OMe or NH_2) differ from the phenylglycine series in that hydrogen at C-2 is replaced by a methyl group. The CD. curves for these compounds (IVa–c) are similar to those of the phenylglycine analogues (IIIa–c), except that the methyl ester hydrochloride as well as the amide give CD. curves which are essentially Gaussian in shape. It is significant that the $\Delta\varepsilon$ values are all smaller in the phenylalanine than in the phenylglycine series.

Table 1 (b) gives CD. data for (*S*)-2-dimethylamino-2-phenyl-acetic acid (IIId) and (*S*)-2-dimethylamino-2-phenyl-propionic acid (IVd), compounds related to (*S*)-phenylglycine and (*S*)-α-phenyl-alanine in which the amino group at C-2 is

replaced by a dimethylamino group. The acid and methyl ester (IIId, e) are very similar to the simpler amino-acids IIIa, b. The $\Delta\varepsilon$ values are smaller than in the phenylglycine series. The same general pattern is followed by the dimethylamino analogues of α-phenyl-alanine, except that the main maximum of the parent acid in water has an exceptionally large $\Delta\varepsilon$ value, +18.80 at 205 nm.

Few of the aromatic acids could be examined below 198 nm, but in at least one case, (*S*)-α-phenyl-alanine (IVa), there was evidence for a further *Cotton* effect with a maximum near 190 nm, presumably associated with the $^1B_{ab}$ transition of the aromatic chromophore, expected in that region.

Table 1 (c) gives the CD. data for (*S*)-(+)-2-amino-2-cyclohexyl-acetic acid (Va)[1]), (*S*)-(+)-2-amino-2-cyclohexyl-propionic acid (VIa) and for their ethyl esters. The *Cotton* effects are much smaller in magnitude than those for the corresponding aromatic acids and the curves are essentially Gaussian in form. It is significant that the $\Delta\varepsilon$ value is greater for (*S*)-(+)-2-amino-2-cyclohexyl-acetic acid than for (*S*)-(+)-2-amino-2-cyclohexyl-propionic acid (+1.56 and +0.52, respectively). This parallels the situation for the aryl acids for which (*S*)-phenylglycine has a much larger *Cotton* effect at 217 nm than (*S*)-α-phenyl-alanine ($\Delta\varepsilon$ = +9.87 and +5.20, respectively).

Discussion. – The results described above may now be compared with those obtained previously for related compounds [7] [10]. The closest analogies for the α-amino-α-aryl acids are the α-hydroxy-α-aryl acids studied by *Djerassi et al.* [10], for which the *Cotton* effects are very similar both in sign and magnitude.

		$\Delta\varepsilon$	λ (nm)
	(*S*)-Phenylglycine [(*S*)-2-amino-2-phenyl-acetic acid (in acid)]	−0.23	260
		+9.87	217
cf.	(*S*)-Mandelic acid [(*S*)-2-hydroxy-2-phenyl-acetic acid] [10]	−0.08	260
		+12.4	222
	(*S*)-α-Phenyl-alanine [(*S*)-2-amino-2-phenyl-propionic acid (in acid)]	−0.15	261
		+5.20	218
cf.	(*S*)-Atrolactic acid [(*S*)-2-hydroxy-2-phenyl-propionic acid] [10]	−0.32	260
		+5.42	220

In the two series the same relationship holds between the sign of the *Cotton* effect and the absolute configuration at the single asymmetric centre, and the results are sufficiently close to suggest that the same transitions are responsible for the observed *Cotton* effects. In addition to the main CD. bands mentioned above, *Djerassi et al.* noted the presence in some compounds (including atrolactic acid) of an additional band near 240 nm, which they ascribed to the same electronic transition as the 220 nm band, but which can be considered as arising from other solvated species or from different rotational conformers around the $C\alpha$–CO_2H bond. These small, long wavelength *Cotton* effects have previously been noted in lactic acid [12], in amino-acids [13] and in mercaptopropionic acids [14], but, with the possible exception of

[1]) In the course of this work, one sample of (*S*)-(+)-2-amino-2-cyclohexyl-acetic acid was examined which proved to be contaminated with the parent aromatic compound (*S*)-phenylglycine. The CD. curve gave a clear and roughly quantitative indication of the presence of impurity (a) by the appearance of the ^1L_b band near 260 nm and (b) by the appreciable enhancement of the *Cotton* effect near 215 nm.

(*S*)-2-dimethylamino-2-phenyl-propionic acid, were not detected for any of the compounds listed in Table 1. Whereas for the hydroxy and amino aryl acids (II, X = OH and NH_2) the signs of the 260 nm and 220 nm *Cotton* effects are opposite, (negative at 260 nm and positive at 220 nm for the (*S*) isomer), *Craig* [7] has reported two *Cotton* effects of the *same* sign for α-alkylaryl acids (II, X = alkyl).

All authors agree in associating the long wavelength, low intensity *Cotton* effect at 260 nm with the ^1L_b transition of the aromatic ring, but there have been several different views on the number and origin of the bands near 220 nm. *Djerassi* [10] noted one *Cotton* effect at or near 220 nm whereas *Craig et al.* [7] observed either two distinct maxima or a single maximum with a pronounced shoulder. As shown in Table 1, the aryl amino acids also have *Cotton* effects with pronounced shoulders indicating clearly the presence of more than one component in the observed curve. Furthermore the magnitude and wavelength of the *Cotton* effect implies that some interaction is taking place between the aryl and carboxyl chromophores.

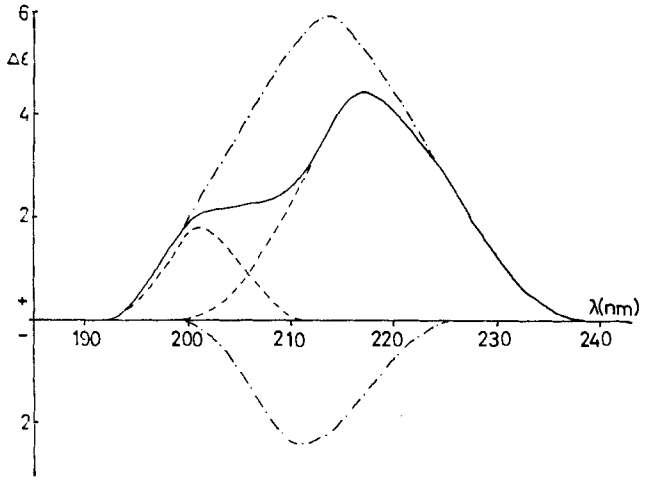
If the CD. curve of (*S*)-2-amino-2-cyclohexyl-propionic acid (VIa), $\Delta\varepsilon$ +0.52 at 206 nm is compared with that of the aromatic analogue (*S*)-2-amino-2-phenyl-propionic acid (IVa), $\Delta\varepsilon$ +5.20 at 218 nm, it is obvious that there is a very great increase in magnitude of the *Cotton* effect and an appreciable red-shift in wavelength of the maximum on changing from the saturated to the aromatic compound. This change is so marked that it must be attributed to some form of interaction and, in fact, a marked enhancement of the *Cotton* effect and red-shift of the wavelength of the maximum would be expected by comparison with other cases of homoconjugation [15].

In their recent paper [10] *Djerassi et al.* discuss the characteristics of homoconjugated molecules, taking as their example the classic case of β,γ-unsaturated ketones having a suitable geometry for the interaction of the two chromophores through space. The CD. curve is characterised by equal and opposite rotational strengths for the absorptions of the two chromophores (both rotational strengths being enhanced) and by a red shift in the position of the carbonyl maximum. If this were directly applicable to aryl acids the authors [10] would have expected to observe an intense negative *Cotton* effect in the 200–215 nm region, due to the aromatic chromophore, equivalent in intensity but opposite in sign to that actually observed near 220 nm. The failure to observe a negative *Cotton* effect might be due to the very unfavourable anisotropy ratio for the ^1L_a band, but the authors conclude by suggesting that the observed *Cotton* effect at 220 nm be 'primarily associated with the enhanced $n \rightarrow \pi^*$ transition of the carboxyl group – and only secondarily if at all to a transition of the phenyl group'.

As noted above and shown in Table 2, the CD. curves of many of the amino-aryl-carboxylic acids, their esters and amides can each be resolved into sets of two overlapping bands, one near 218 nm and one near 200 nm, and it appears that these two components may correspond to enhanced carboxyl and ^1L_a transitions respectively[2]). However, in accordance with *Craig*'s observations [7] with α-alkyl-aryl acids, the signs of the two *Cotton* effects are the *same*, and *not* opposite as anticipated by *Djerassi* [10].

[2]) In an extensive paper on the aromatic chromophore in tyrosine, *Hooker & Schellman* [16] ascribe the CD. band at about 220 nm essentially to the ^1L_a aromatic transition.

Careful inspection of the CD. results reveals that in some cases, although not in all, an alternative analysis of the experimental curves is possible. For example, (*S*)-2-dimethylamino-2-phenylpropionic acid methyl ester (IVe) has an experimental CD. curve with a maximum ($\Delta\varepsilon$ +4.41) at 217 nm and a pronounced shoulder ($\Delta\varepsilon$ +2.20 *sh*) at 204 nm. This can be resolved (see Fig.) into two overlapping positive bands $\Delta\varepsilon$ +4.41 (217 nm) and +1.8 (201 nm), or alternatively into bands of *opposite* sign $\Delta\varepsilon$ +5.9 (214 nm) and −2.4 (211 nm). This latter resolution is into two components of opposite sign as expected by *Djerassi* for a homoconjugated system, but the wavelengths of the maxima are very close to those expected for the isolated carboxyl and aromatic chromophores and do not show any wavelength change as anticipated for interacting systems. We consider that the analysis showing two superimposed positive curves is more likely to be the correct one, but the existence of two plausible solutions to this problem underlines the ambiguities inherent in attempted resolution of curves for which the underlying electronic transitions are not known.



Alternative resolutions of the CD. curve of (S)-(−)-*Dimethylamino-2-phenyl-propionic acid methyl ester* (*IVe*)

Experimental curve (————). Resolution into two Gaussian curves of the same sign (– – – – –). Resolution into two Gaussian curves of opposite sign (–·–·–·–·–)

Conformation. – We have previously shown that the observed signs of the carboxyl *Cotton* effects of several types of acids [17] may be rationalised according to the carboxyl sector rule [18] if the molecule is assumed to adopt a conformation in which the carboxyl group eclipses one of the adjacent C_α–C_β bonds. However, in amino-acids and in hydroxy-acids *X*-ray studies indicate [19] that the preferred conformation is that in which the carboxyl group is coplanar with the amino or hydroxy substituent.

Jorgenson [20] has recently noted that if the carboxyl sector rule [18] is applied to α-amino acids in this preferred conformation, the sign of the observed *Cotton* effect is as predicted, *i.e.* positive for compounds with the (*S*)-configuration.

Additional evidence for this conformation (VII) can be obtained by consideration of pairs of cyclohexyl- and aryl-amino acids derived from acetic acid and propionic acid respectively. When the molecule of (*S*)-2-amino-2-cyclohexyl-acetic acid (Va) is viewed along the bisectrix of the OCO angle, the amino group is eclipsed by the carboxyl group, the cyclohexyl substituent lies in a region of positive contribution and the hydrogen atom in a region of negative contribution (VII, R = H). A positive *Cotton* effect would therefore be expected. For (*S*)-2-amino-2-cyclohexyl-propionic acid (VIa) the hydrogen in the back lower right sector is replaced by a methyl group (*i.e.* projection VII, R = Me). Since this group falls in a region of negative contribution, the magnitude of the *Cotton* effects would be expected to be *less* for the α-substituted propionic acid than for the acetic acid analogues, in accordance with experimental fact. The same relationship holds for the corresponding α-aryl acids, their methyl esters and amides (IIIa and IVa, IIIb and IVb, IIIc and IVc); in each case the compound derived from acetic acid has a larger positive *Cotton* effect than that derived from propionic acid.

We therefore conclude that the α-amino-α-cyclohexyl-carboxylic acids and α-amino-α-aryl-carboxylic acids may reasonably be considered to adopt this preferred conformation.

Experimental. – The compounds used in this work were prepared in Lausanne by Dr. *D. Aubort* and Dr. *K. Wentrup*. Microanalyses were performed by Dr. *K. Eder*, Ecole de Chimie, University of Geneva.

(R)-(−)-*2-Amino-2-phenyl-acetic acid methyl ester hydrochloride* (*ent.-IIIb*). 0.96 g (6.3 mmoles) of (*R*)-(−)-2-amino-2-phenyl-acetic acid was esterified at 0° with methanol-HCl. The solvent was evaporated, the ester recrystallized from methanol-ether: 0.41 g (32%) of m.p. 222–223° (lit. [27] for racemic methyl ester-HCl: m.p. 224°); $[\alpha]_D^{24} = -119°$ ($c = 1.09$ in H_2O). IR. (KBr): 2850, 2700, 2630 cm^{-1} (NH_3^+); 1741 cm^{-1} (C=O).

(R)-(−)-*2-Dimethylamino-2-phenyl-acetamide* (*ent.-IIIf*). 0.51 g (3.4 mmoles) of (*R*)-(−)-2-amino-phenyl-acetamide [22] and 0.8 ml formaline (38%) in 10 ml methanol were hydrogenated in the presence of 0.52 g Pd–C catalyst (5%). H_2 uptake: 165 ml (23°, 713 Torr) = 94%. The catalyst was removed by filtration, the solvent by evaporation in vacuo and the residue recrystallized from ethyl acetate: 0.39 g (64%) of m.p. 172–173°; $[\alpha]_D^{24} = -89°$ ($c = 1.10$ in EtOH). IR. (KBr): 3330, 3150 cm^{-1} (NH), 1645 cm^{-1} (CO). NMR. ($CDCl_3$): $\delta = 2.25$ ppm (*s*, 6H); 3.75 ppm (*s*, 1 H); 7.37 ppm (*s*, 5 H).

$C_{10}H_{14}N_2O$ (178.2) Calc. C 67.38 H 7.92 N 15.72% Found C 67.33 H 7.98 N 15.85%

(R)-(−)-*2-Amino-2-cyclohexyl-acetic acid ethyl ester hydrochloride* (*ent.-Vb*) [28]. 0.15 g (0.97 mmole) of (*R*)-(−)-2-amino-2-cyclohexyl-acetic acid [25] was esterified in EtOH—HCl at 0°. The solvent was evaporated, the ester recrystallized from EtOH—Et_2O: 0.095 g (44%) of m.p. 158–159°. IR. (KBr): 3000–2860 cm^{-1} (NH_3^+); 1735 cm^{-1} (C=O).

$C_{10}H_{20}ClNO_2$ (221.7) Calc. C 54.17 H 9.09 N 6.32% Found C 54.03 H 9.09 N 6.30%

(S)-(+)-*2-Amino-2-phenyl-propionic acid methyl ester hydrochloride* (*IVb*) [29]. 0.27 g (1.6 mmoles) of (*S*)-(+)-2-amino-2-phenyl-propionic acid [23] was esterified in MeOH—HCl at 0°. The solvent was evaporated, the ester-hydrochloride decomposed by neutralization with NH_3 and extracted with benzene. After evaporation the ester-HCl was precipitated from ether solution by HCl gas: 0.25 g (71%) of m.p. 128°; $[\alpha]_D^{24} = +63.0°$ ($c = 1.20$ in H_2O). IR. (KBr): 2830 cm^{-1} (NH_3^+); 1755 cm^{-1} (C=O).

$C_{10}H_{14}ClNO_2$ (215.7) Calc. C 55.69 H 6.54 N 6.50% Found C 55.78 H 6.48 N 6.60%

CD. curves were measured at *Westfield College* on a *Roussell-Jouan* Dichrograph-185. Aqueous and dilute acid solutions were employed with a concentration of about 1 mg/ml. Curve resolutions

Table 1. *Circular dichroism and absorption spectra of Phenylglycine and related compounds*
(all results are expressed for the (*S*)-configuration)

No.	Name and Formula	UV. (H_2O) ε	UV. (H_2O) λ (nm)	CD. (H_2O) $\Delta\varepsilon$	CD. (H_2O) λ (nm)	CD. (HCl) $\Delta\varepsilon$	CD. (HCl) λ (nm)
a)	*Phenylglycine and α-Phenyl-alanine, acids, esters and amides*						
IIIa[a])	(*S*)-(+)-2-Amino-2-phenyl-acetic acid (Phenylglycine) [21]			−0.16 *sh*	267	−0.19 *sh*	267
				−0.20 *m*	260	−0.23 *m*	260
				−0.14 *sh*	255	−0.16 *sh*	254
				−0.08 *sh*	249	−0.07 *sh*	249
				+6.31 *sh*	214	+9.87 *m*	217
				+8.77 *m*	204	+3.29 *sh*	202
IIIb[a])	(*S*)-(+)-2-Amino-2-phenyl-acetic acid methyl ester hydrochloride (Phenylglycine methyl ester hydrochloride)		268	−0.26 *sh*	266	−0.26 *sh*	266
		196	262	−0.32 *m*	260	−0.32 *m*	260
			257	−0.18 *sh*	254	−0.23 *sh*	254
			252	−0.09 *sh*	248	−0.09 *sh*	249
		1010	221	+12.30 *m*	217	+11.80 *m*	217
IIIc[a])	(*S*)-(+)-2-Amino-2-phenyl-acetamide (Phenylglycine amide) [22]		264	−0.06 *sh*	268	−0.27 *sh*	267
		200	258	−0.08 *m*	261	−0.32 *m*	261
			252	−0.05 *sh*	254	−0.22 *sh*	254
						−0.09 *sh*	250
		1970	220	+3.95 *m*	222	+6.99 *m*	220
IVa	(*S*)-(+)-2-Amino-2-phenyl-propionic acid (α-Phenyl-alanine) [23]		267	−0.10 *sh*	267	−0.13 *sh*	267
		216	261	−0.13 *m*	261	−0.15 *m*	261
			256	−0.09 *sh*	255	−0.11 *sh*	255
			251	−0.04 *sh*	249	−0.04 *sh*	250
				+3.90 *sh*	209	+5.20 *m*	218
		1867	217	+6.48 *m*	204	+1.51 *sh*	200
				−10.40!	192	−6.48!	196
IVb	(*S*)-(+)-2-Amino-2-phenyl-propionic acid methyl ester hydrochloride (α-Phenyl-alanine methyl ester hydrochloride)		267	−0.16 *sh*	267	−0.15 *sh*	267
		220	261	−0.18 *m*	260	−0.20 *m*	261
			257	−0.12 *sh*	254	−0.11 *sh*	254
			251	−0.06 *sh*	248	−0.06 *sh*	248
		2020	216	+6.42 *m*	218	+5.43 *m*	218
IVc	(*S*)-(+)-2-Amino-2-phenyl-propionamide (α-Phenyl-alanine amide) [19]		264	−0.05 *sh*	267	−0.02 *sh*	266
		195	257	−0.07 *m*	260	−0.24 *m*	260
			251	−0.06 *sh*	254	−0.19 *sh*	254
				−0.06 *sh*	244	−0.08 *sh*	249
		1855	219	+1.65 *m*	219	+4.12 *m*	221
b)	*N-Dimethyl-α-phenylglycine and N-Dimethyl-α-phenyl-alanine, acids, esters and amides*						
IIId[a])	(*S*)-(+)-2-Dimethylamino-2-phenyl-acetic acid [20]		267	−0.22 *sh*	267	−0.23 *sh*	267
		267	261	−0.26 *m*	261	−0.28 *m*	261
			256	−0.18 *sh*	255	−0.19 *sh*	255
			250	−0.09 *sh*	249	−0.08 *sh*	250
				+4.82 *sh*	215	+7.63 *m*	217
		2320	220	+8.84 *m*	204	+5.02 *sh*	204
IIIe[a])	(*S*)-(+)-2-Dimethylamino-2-phenyl-acetic acid methyl ester [20]			−0.05 *sh*	268	−0.13 *sh*	267
				−0.07 *m*	261	−0.18 *m*	261
				−0.06 *sh*	255	−0.11 *sh*	256
				−0.04 *sh*	249	−0.05 *sh*	250
				+4.28 *m*	213	+6.42 *m*	219
				+2.94 *sh*	203	+3.21 *sh*	202

Table 1 (contd.)

No.	Name and Formula	UV. (H_2O) ε	UV. (H_2O) λ (nm)	CD. (H_2O) $\Delta\varepsilon$	CD. (H_2O) λ (nm)	CD. (HCl) $\Delta\varepsilon$	CD. (HCl) λ (nm)
IIIf[a]	(*S*)-(+)-2-Dimethylamino-2-phenyl-acetamide		269	−0.12 *sh*	268	−0.28 *sh*	268
			264	−0.14 *m*	262	−0.32 *m*	262
		280	259	−0.07 *sh*	255	−0.19 *sh*	255
			253			−0.06 *sh*	252
		4240	221	+4.53 *sh*	212	+5.40 *m*	221
		13300	198	+7.45 *m*	198	+5.26!	202
IVd[a]	(*S*)-(+)-2-Dimethylamino-2-phenyl-propionic acid[b] [24]		269	−0.43 *sh*	268	−0.48 *sh*	268
		270	263	−0.54 *m*	262	−0.57 *m*	262
			259	−0.36 *sh*	256	−0.41 *sh*	256
			252	−0.18 *sh*	250	−0.16 *sh*	250
				+0.11 ?*m*	239		
		2110	221	−0.68 ?*m*	229		
				+18.80 *m*	205	+7.05 *m*	219
IVe	(*S*)-(−)-2-Dimethylamino-2-phenyl-propionic acid methylester [24]			−0.13 *sh*	269	−0.18 *sh*	268
				−0.20 *m*	261	−0.20 *m*	261
				−0.17 *sh*	255	−0.15 *sh*	255
				−0.18 *sh*	243	−0.09 *sh*	249
				+4.41 *m*	217	+4.75 *m*	220
				+2.20 *sh*	204	+2.94 *sh*	205
IVg	(*S*)-(+)-2-Dimethylamino-2-phenyl-propionic acid ethyl ester [19]			−0.19 *sh*	267	−0.30 *sh*	268
				−0.30 *sh*	261	−0.34 *m*	261
				−0.34 *m*	254	−0.24 *sh*	255
				+2.71 *m*	214	−0.12 *sh*	249
				+5.41!	197	+6.49 *m*	220
						+4.60!	199
IVe-metho-iodide	Methoiodide of (*S*)-(+)-2-dimethylamino-2-phenyl-propionic acid methyl ester [19]		271	−0.32 *sh*	269	−0.33 *sh*	269
		340	264	−0.41 *m*	263	−0.40 *m*	262
			257	−0.30 *sh*	256	−0.30 *sh*	256
				−0.13 *sh*	251	−0.16 *sh*	253
		8990	231	+5.91 *m*	221	+5.45 *m*	223
IVf	(*S*)-(−)-2-Dimethylamino-2-phenylpropionamide [19]		270	−0.21 *sh*	267	−0.27 *sh*	269
		310	264	−0.33 *sh*	262	−0.32 *m*	263
			259			−0.23 *sh*	256
						−0.10 *sh*	251
				−1.02 *m*	237	+3.78 *m*	223
		2160	221	+2.00 *sh*	213	+1.78 *sh*	202
				+4.89!	198	+2.67!	200
c)	*α-Cyclohexyl-glycine and α-Cyclohexyl-alanine and their esters*						
Va[a]	(*S*)-(+)-2-Amino-2-cyclohexyl-acetic acid [25]			+0.91 *m*	198	+1.56 *m*	209
Vb[a]	(*S*)-(+)-2-Amino-2-cyclohexyl-acetic acid ethyl ester hydrochloride					+1.40 *m*	208
VIa	(*S*)-(+)-2-Amino-2-cyclohexyl-propionic acid [19]			+0.67 *m*	198	+0.52 *m*	206
VIb	(*S*)-(+)-2-Amino-2-cyclohexyl-propionic acid ethyl ester [26]			+0.26 *m*	210	+0.23 *m*	205

[a] Measured in the enantiomeric *R*-series.

[b] Sample 44% optical purity: $\Delta\varepsilon$ value corrected to 100% purity.

m = maximum, *sh* = shoulder, ! = lowest wavelength measured.

Table 2. *Curve Resolution of CD. data*

	Results in H_2O				Results in acid			
	'Best' Resolution		Experimental Result		'Best' Resolution		Experimental Result	
	$\Delta\varepsilon$	λ (nm)	$\Delta\varepsilon$	λ (nm)	$\Delta\varepsilon$	λ (nm)	$\Delta\varepsilon$	λ (nm)
IIIa	+5.92	216	+6.31 *sh*	214	+9.87	217	+9.87 *m*	217
	+7.50	201	+8.77 *m*	204	+1.60	200	+3.29 *sh*	202
IIIb					+11.80	217	+11.80 *m*	217
					+3.00	202		
IIIc	+3.95	224	+3.95 *m*	222	G	G	+6.99 *m*	220
	+1.56	210						
IVa	+1.30	218	+3.90 *sh*	209	+5.20	218	+5.20 *m*	218
	+8.50	201	+6.48 *m*	204	+1.04	198	+1.51 *m*	200
	−18.80	189	−10.40!	192	−10.40	193	−6.48!	196
IVb					G	G	+5.43 *m*	218
IVc	G	G	+1.65 *m*	219	G	G	+4.12 *m*	221
IIId	+0.88	227						
	+3.54	217	+4.82 *sh*	215	+7.63	218	+7.63 *m*	217
	+8.84	204	+8.84 *m*	204	+2.75	202	+5.02 *sh*	204
IIIe	+4.28	215	+4.28 *m*	213	+6.42	219	+6.42 *m*	219
	+1.53	202	+2.94 *sh*	203	+2.05	202	+3.21 *sh*	202
IIIf	+4.38	216	+4.53 *sh*	212	+5.26	223	+5.40 *m*	221
	+6.45	197	+7.45 *m*	198	+5.26	202	+5.26!	202
IVd	−0.08	228	−0.08 *m*	229				
	+3.60	216	+18.80 *m*	205	G	G	+7.05 *m*	219
	+18.80	205						
IVe	+4.41	217	+4.41 *m*	217	+4.75	220	+4.75 *m*	220
	+1.80	201	+2.20 *sh*	204	+2.40	203	+2.94 *sh*	205
IVg			−1.45 *m*	235				
	G	G	+2.71 *m*	214	G	G	+6.49 *m*	220
			+5.41!	197			+4.60!	199
IVe-metho-iodide	+1.20	232			+1.00	232		
	+5.91	221	+5.91 *m*	221	+5.45	221	+5.45 *m*	223
IVf			−1.02 *m*	237	G	G	+3.78 *m*	223
	G	G	+2.00 *m*	213			+1.78 *sh*	202
			+4.89!	198			+2.67!	200

Results marked G are those for which the experimental curve was already essentially Gaussian. *m* = maximum, *sh* = shoulder, ! = lowest wavelength measured.

were performed at *Westfield College* on a *Dupont* 310 Curve Resolver, with 6 channels available for analysis.

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