

OPTICAL ROTATORY DISPERSION AND ABSOLUTE CONFIGURATION—XVII¹

α -ALKYLPHENYLACETIC ACIDS²

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(Received in USA 21 August 1970; Received in the UK for publication 4 September 1970)

Abstract—ORD and CD measurements on α -alkylphenylacetic acids with primary, secondary, and tertiary α -substituents agree with the evidence from gas chromatographic retention times of their diastereoisomeric amides in leading to the conclusion that all (+) acids of the series possess the same configuration.

All members of the series show two positive CD bands in the 210 to 230 nm region, and these are ascribed respectively to the benzene L_a transition, and to a mixed transition involving overlap of the π orbitals of the benzene ring with the 2p, and π^* orbitals of the carbonyl portion of the carboxyl group. Conformational effects due to the size of the α -alkyl substituent are shown to influence the intensity of the mixed transition.

THE absolute configuration of (+)-hydratropic acid (I), the parent compound of the series of α -alkylphenylacetic acids, is known^{3, 4} to be *S*, and a configurational relationship between hydratropic acid and (+)- α -ethylphenylacetic acid (II) was established using comparisons of rotations at both fixed^{5a} and variable^{5b} wavelengths.

The ORD of I was studied in the visible region⁶ and in the range of 700–275nm⁷ but only plain positive curves were observed, with high rotation at the lower wavelengths. Deficiencies in the then available instrumentation did not permit extension of these observations into the regions of the actual transitions. Because of the risks inherent in the assignment of configurational relationships from plain curves, the ORD spectra of the *N*-methylthionamide derivatives of the (+)- α -alkylphenylacetic acids I, II^{8, 9} V and VIII⁹ were examined and were found to give positive Cotton effects at 340 nm, leading to the assignment of the *S*-configuration for these acids.

However, this was at variance with the conclusions of Červinka and Hub^{10, 11} who recently ascribed the *R*-configuration to (+)-V as a result of their studies¹⁰ based on an asymmetric transformation as a means for determination of absolute configuration, and also from a reported chemical correlation¹¹ of (–)-V with *S*-(–)-2-phenyl-3-methylbutane.

In view of the element of uncertainty which is always present in the assignment of the absolute configuration of a parent series by extrapolation from the Cotton effects observed in the quite different transitions (usually at longer wavelengths) of their chromophoric derivatives, it was deemed desirable to investigate directly the Cotton effects of the parent α -alkylphenylacetic acids themselves in order to resolve these conflicting reports.

In addition, the gas chromatographic retention times of the diastereoisomeric amides of the acids (I–VIII) were measured.¹² The conclusions reached from these two independent series of measurements are in agreement, and are presented below.

The α -alkylphenylacetic acids were prepared by known procedures,¹³ and were resolved by crystallization of the least soluble diastereoisomeric salt formed with (+)- or (–)-1-(1'-naphthyl)-ethylamine. Part of the pure diastereoisomer was converted into the α -alkylphenylacetyl-1-(1'-naphthyl)-ethylamide by treatment with dicyclohexylcarbodiimide, and the enantiomeric purity of the amide (generally 90–98%) was determined by GLC analysis. The diastereoisomeric amides separated on GLC with a ratio of retention times of *ca* 1:10 (Table 1), and *in every case* the diastereoisomer derived from the (+)-acid had the shorter retention time and retention volume. This result was also true when the diastereoisomeric amides were formed using (+)-2-methylamino-1-phenylpropane.¹² Since (+)-hydratropic acid(I) and (+)- α -ethylphenylacetic acid (II) are known^{3–5} to have the *S*-configuration, the GLC results strongly support the conclusion that all (+)-acids of this closely related series are of the same configuration.

The UV and ORD spectra of the parent (+)- α -alkylphenylacetic acids (I–VIII) were examined in 95% ethanol solution. The isotropic absorption spectra (Table 2) showed the L_a band of benzene at 205–207 nm ($\log \epsilon$ 3.9), with shoulders at 210–211 and 216–218 nm, and the typical vibrational fine structure of the L_b transition centered at 258 nm ($\log \epsilon$ 2.3). Although the long wavelength transition of alkyl benzenes has been well investigated,¹⁴ spectral data on their farther UV region become far scarcer. However, the 210 nm transition in toluene has been shown^{15, 16} to possess vibrational fine structure in good agreement with that recorded for the acids (I–VIII), with virtually identical spectra (Table 2). The failure of the $n-\pi^*$ transition of the carboxyl chromophore to be observed at its normal location (209–211 nm)¹⁷ in the UV spectra of compounds I–VIII is readily explicable in view of the weak nature ($\log ca$ 1.7) of this forbidden transition. The ORD

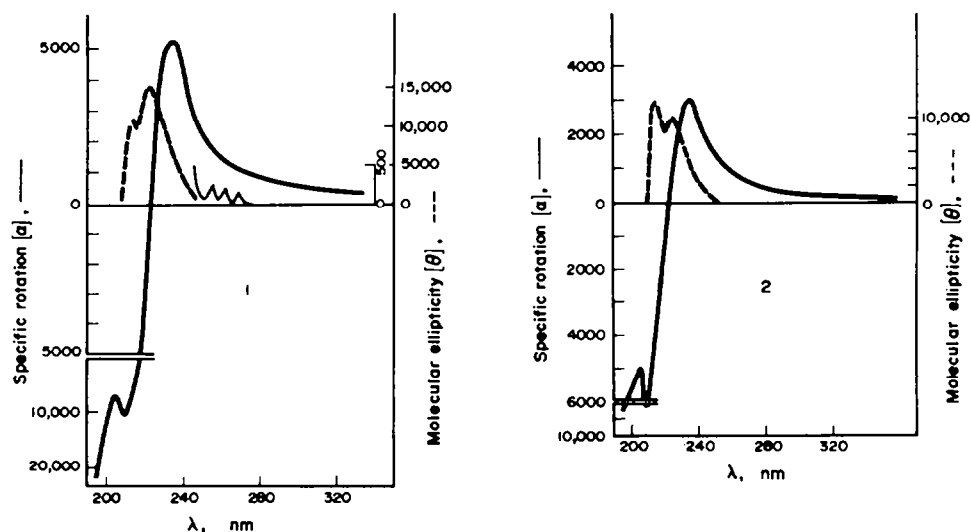


FIG 1.

spectra of the (+)- α -alkylphenylacetic acids (I–VIII), measured in the region 195–350 nm, showed (Table 3) *all* compounds of the series to possess a strong *positive* Cotton effect centered at 220 nm, as well as a weaker positive one (not shown in Table 3; see Fig. 1) located around 260 nm and exhibiting the vibrational fine structure associated with the L_b transition of toluene.¹⁴

In many compounds it proved possible to extend the ORD spectrum to 195 nm, and to observe (Figs 1 and 2) a steep descent of the ORD curve indicative of the presence of an additional powerful negative Cotton effect at lower wavelengths. This may be the B_a transition of the aromatic ring, shown in toluene¹⁶ to occur at 188 nm with a high intensity ($\log \epsilon$ 4.74), but contributions from the π - π^* transition of the carboxyl group¹⁸ which exhibits rising end-absorption beginning at 185 nm (\log).

Since this work was completed, (–)- α -*t*-butylphenylacetic acid has been chemically correlated¹⁹ with *S*(+)-hydratropic acid (1) in such a manner as to show that (+)- α -*t*-butylphenylacetic acid (VIII) must have the *S*-configuration.¹⁹ In addition, a very recent communication from Červinka's laboratory²⁰ announces the assignment of the *R*-configuration to both (–)- α -isopropyl- and (–)- α -*t*-butylphenylacetic acid on the basis of chemical degradation. Physical and chemical methods are thus now in satisfactory agreement that all (+)- α -alkylphenylacetic acids possess the *S*-configuration.

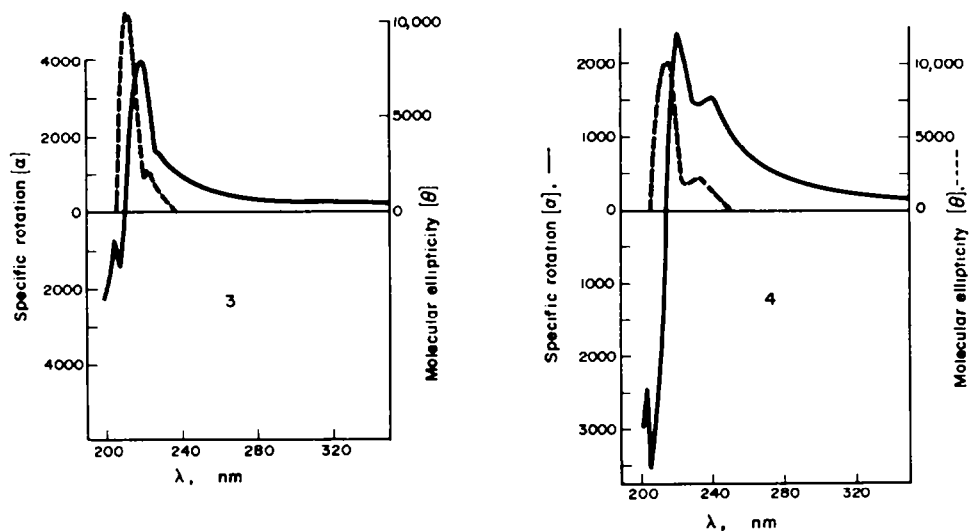


FIG 2.

Close inspection of the ORD spectra for the acids I–VIII revealed that whereas the compounds possessing a primary α -substituent (I–IV) (*cf* Fig 1) showed a simple positive Cotton effect centered at *ca.* 220nm, those acids substituted in the α -position with a secondary or tertiary alkyl group (V–VIII) (*cf* Fig 2) displayed ORD curves characteristic of two closely adjacent and identically signed Cotton effects. Since CD affords a method by which such closely spaced Cotton effects may be resolved, the CD curves of the acids I–VIII were examined. In several cases, the ORD and CD spectra of

enantiomeric acids were determined, and gave the expected mirror image curves. For convenience, all results reported are for the (+)-isomers only.

The CD spectra of compounds I–VIII confirmed (*cf* Fig 1) both the positive nature and the vibrational fine structure of weak L_b transition Cotton effect indicated by the ORD spectrum in the 260 nm region, in agreement with the observation of Legrand and Viennet²¹ for the weak positive CD of (+)- α -ethylphenylacetic acid (II) centered at 257 nm.

At shorter wavelengths, all members of the series show two *positive CD bands*. The positions and relative intensities of these bands seem to depend on the nature of the α -substituent. In those compounds bearing primary α -substituents (I–IV), the CD maxima were located around 213 and 223 nm, and were of approximately equal intensity. When the α -alkyl groups were secondary or tertiary (V–VIII), however, the separation between the two CD maxima increased slightly to an average of 15 nm, and the high wavelength maximum now had only 10–20% of the intensity of that at lower wavelength.

It is suggested that the shorter wavelength CD corresponds to the L_a transition and that at longer wavelength to a mixed transition originating from the $n-\pi^*$ transition of the carboxyl group. The mixed transition arises from an overlap of the orbitals of the benzene ring with the $2p_y$ non-bonding orbital and π^* antibonding orbital of the carbonyl portion of the carboxyl group.

Examination of space-filling models shows that the most favored position of the carboxyl group, into which it is forced by the combined steric demands of the α -alkyl substituent and the two ortho-hydrogens of the benzene ring, is one in which the plane of the carboxyl group is in the long axis of the molecule and perpendicular to the plane of the benzene ring. Allowing for the rotational mobility of the carboxyl moiety about the carboxyl- α -carbon bond, one such rotamer (Fig 3) will permit maximum interaction between carbonyl and phenyl groups.

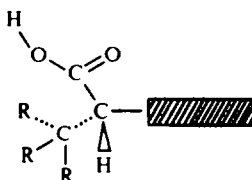


FIG 3. Conformation of α -alkylphenylacetic acids permitting maximum interaction between carbonyl and phenyl groups.

It is thus possible for the electric-dipole forbidden $n-\pi^*$ transition to overlap with the allowed $\pi-\pi^*$ transition, in which an electron is transferred from the benzene ring to an anti-bonding π^* orbital of the carbonyl group. The forbidden $n-\pi^*$ transition thus borrows intensity from the allowed $\pi-\pi^*$ transition, while the benzene transition borrows magnetic moment from the $n-\pi^*$ of the carbonyl. Rotatory character is thus conferred on the mixed transition, since the π orbitals of the benzene ring are asymmetrically disposed with respect to the symmetry planes of the carbonyl group.^{22, 23} The $n-\pi^*$ transition will therefore become more allowed, its extinction will be enhanced, and it will undergo a redshift in wavelength.

A similar phenomenon has been observed²⁴⁻²⁹ in the case of β,γ -unsaturated ketones, where non-bonding electrons of the carbonyl oxygen interact with the π -orbitals of the ethylenic system, resulting in an unusually strong $n-\pi^*$ transition with an accompanying red-shift.^{30, 31}

In the case of the α -alkylphenylacetic acids (I-VIII), the interacting transitions of the carbonyl and benzene chromophores are at almost identical wavelengths. It has been pointed out previously²⁵ that the smaller the difference in energy between the $\pi-\pi^*$ and the $n-\pi^*$ transition, the more intense the mixed $n-\pi^*$ transition will be and the larger its rotatory power will become.

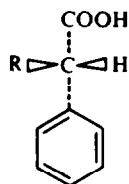
In order to assign the contributions of the two chromophores to the observed CD spectrum, *S*-(+)- α -ethylphenylacetic acid (II) was reduced to *S*-(+)-2-phenyl-1-butanol (IX)³² and thence to *S*-(+)-2-phenylbutane (X).³²

The UV spectrum of the alcohol IX and the hydrocarbon X were virtually identical with that of toluene (Table 2). The ORD curve of the alcohol showed Cotton effects at *ca.* 260 and 215 nm, and CD measurements verified the former to be positive and the latter to consist of three closely spaced negative maxima at 206, 212 and 217 nm, in agreement with the vibrational fine structure and descending order of intensity of the peaks shown in the UV spectrum. The CD in hexane showed the same effect with enhanced intensity. Such an inversion in the sign of the Cotton effect for the L_a region has been previously noted³³ on passing from *S*-(-)-2-amino-3-phenylpropionic acid to the corresponding alcohol *s*-(-)-2-amino-3-phenyl-1-propanol. In both alcohol and hexane solutions the ORD and CD spectra of the hydrocarbon X showed positive Cotton effects at 260 and 212 nm, the latter exhibiting similar evidence of vibrational fine structure of the L_a transition. The ORD curve of this compound has been reported³⁴ in isooctane solution down to 230 nm as a steeply ascending plain curve with a small Cotton effect at 260 nm. The closely related and configurationally identical *S*-(+)-2-(*p*-tolyl)butane (XI), *S*-(+)-2-methyl-6-(*p*-tolyl) heptane (XII), and *S*-(+)-4-(*p*-tolyl) pentanol-1 (XIII) all gave³⁵ ORD spectra in methanol showing a small positive Cotton effect at 260 nm and the first extremum (at 223 nm) of an intense positive one centered around 212 nm. Furthermore, the hydrocarbon *S*-(+)- α -deuterioethylbenzene (XIV) showed³⁶ CD maxima centered at about 260 and 212 nm, with fine structure at 208, 213 and 218 nm.

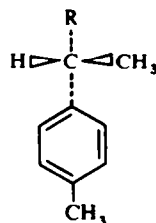
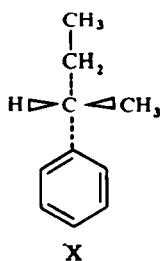
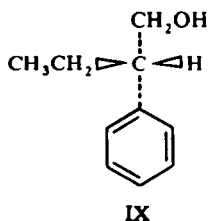
In summary, it may then be noted that compounds IX-XIV are uniform in possessing Cotton effects centered around 212 nm, with evidence of vibrational fine structure at *ca.* 206, 212 and 218 nm, which may clearly be ascribed solely to the L_a transition of benzene in these cases since primary alcohols have an $n-\sigma^*$ transition below 200 nm.³⁷ None of the compounds IX-XIV showed any circular dichroism maxima between 220 and 240 nm.

The positive low wavelength CD maximum at 212 nm observed in the acids I-VIII, with molecular ellipticity $[\theta]$ *ca.* 10,000, may thus be assigned to the aromatic L_a band. The higher wavelength positive CD maximum in these acids must therefore have its origin in the enhanced mixed transition of the carbonyl group, which has undergone the anticipated red-shift in wavelength.

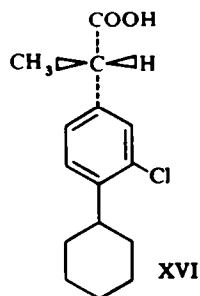
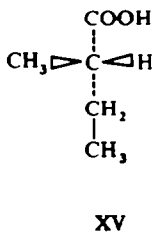
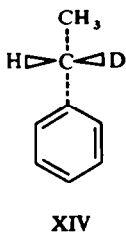
The $n-\pi^*$ transition of simple aliphatic acids devoid of α -substituents possessing non-bonding electrons is located in the 210-212 nm region and shows CD maxima at this wavelength, e.g. *S*-(+)- α -methylbutyric acid (XV) has¹ λ_{max} 212 nm, $[\theta] + 267$ in 95% ethanol while α -amino, α -hydroxy, and α -alkoxy acids and esters have CD maxima of $[\theta]$ 2000-3000 in this solvent.¹ The positive CD maxima in the 222 nm region for the



- I: R = Me
 II: R = Et
 III: R = n-Pr
 IV: R = n-Bu
 V: R = isopropyl
 VI: R = cyclopentyl
 VII: R = cyclohexyl
 VIII: R = Bu



- XI: R = Et
 XII: R = (CH₂)₃CH(CH₃)₂
 XIII: R = n-Pr



acids I–IV, which possess primary alkyl α -substituents, without non-bonding electrons, have $[\theta] \text{ ca. } 10,000$, representing an enhancement of the mixed transition by about 50 times compared with the rotational strength of the aliphatic acid XV. Space-filling models show that when the α -substituent in the α -alkylphenylacetic acids is an *n*-alkyl group, the steric constraint imposed upon the carboxyl group increases only slightly with the size of the α -substituent. The rotational mobility of the carboxyl moiety about the carboxyl- α -carbon bond thus permits maximum overlap to occur between the carbonyl and phenyl groups in compounds I–IV (Fig 1). However, when the α -substituent is secondary or tertiary in nature (acids V–VIII), steric interference of the bulky branched α -alkyl group with the non-bonding orbitals of the hydroxyl group of the acid may force the carboxyl group to adopt a conformation in which the plane of the carboxyl is at 120° to the plane of the benzene ring, and at right angles to the long axis of the molecule. The possibility of overlap between the carbonyl and phenyl orbitals will be

TABLE I. PROPERTIES OF DIASTEREOMERIC DERIVED FROM (-)-1-(1'-NAPHTHYL)ETHYLAMINE AND α -ALKYLPHENYLACETIC ACIDS Ph-CH(R)-COOH

R	Least soluble diastereoisomeric salt		GLC retention times ^a of diastereoisomeric α -alkylphenylacetyl-1-(1'-naphthyl) ethylamides (min)				Ratio of retention times (-)(-)	
	m.p.(°C)	$[\alpha]_D^{20}$	From (+) acid	From (-) amine	From (-) acid	From (-) amine	(-)(-)	(+)(-)
Methyl	142-143°	-19.7°	9.1	10.0	10.0	10.0	1.10	
Ethyl	137-138°	-5.4°	10.5	11.8	11.8	11.8	1.12	
n-Propyl	138-139°	-11.1°	12.4	13.4	13.4	13.4	1.08	
n-Butyl	133-134°	-25.8°	11.0	12.6	12.6	12.6	1.15	
iso-Propyl	155-156°	-8.0°	15.4	16.8	16.8	16.8	1.09	
Cyclohexyl	163-164°	-22.6°	11.3	12.0	12.0	12.0	1.06	

^a c = 2 to 5 in EtOH.

^b GLC analyses were carried out using a 5 ft. \times $\frac{1}{8}$ in column packed with 5% SE30 on chromosorb W. The N₂ flow was 35 ml/min and the separation temp 250° (cyclohexyl derivative 280°).

reduced in this conformation, and may explain the smaller intensity of the long-wavelength CD maximum in the acids V–VIII ($[\theta]$ between 1000–3000) which however still represents an approximately ten-fold increase over the value in the aliphatic acid (XV). The methyl ester of the acid VIII showed ORD and CD spectra very similar to those of the parent acid.

Inspection of molecular models of the acids I–VIII indicates that the net dipole moment of both the above conformations will be in the same direction, although with different magnitudes. No change in the *sign* of the long wavelength Cotton effect is therefore expected between the compounds with primary (I–IV) and those with secondary and tertiary (V–VIII) α -substituents. The two positive CD maxima found in the 210–230 nm region for compounds I–VIII possess different band widths. The CD band

TABLE 2. UV ABSORPTION OF α -ALKYLPHENYLACETIC ACIDS^a

Compound	λ , nm (log ϵ)			
	210 nm Band		260 nm Band	
I	205 (3.90)	211 (3.85)	217 (3.65)	258 (2.29)
II	207 (3.90)	211 (3.86)	217 (3.64)	258 (2.31)
III	206 (3.90)	211 (3.85)	217 (3.64)	258 (2.29)
IV	206 (3.91)	211 (3.85)	217 (3.64)	258 (2.30)
V	206 (3.88)	211 (3.97)	218 (3.66)	258 (2.31)
VI	207 (4.01)	211 (3.93)	217 (3.64)	258 (2.38)
VII	207 (3.91)	212 (4.00)	218 (3.76)	258 (2.32)
VIII	207 (3.89)	211 (3.88)	216 (3.67)	258 (2.38)
Toluene ^b	206.5 (3.91)	212.5 (3.85)	217 (3.67)	262 (2.3)
IX	206 (3.98)	212 (3.91)	217 (3.69)	258 (2.37)
X	206 (3.93)	212 (3.85)	217 (3.64)	258 (2.34)

^a In 95% ethanol.

^b Ref. 16; in isopentane/3-methylpentane mixture.

associated with the L_a transition of benzene shows a band width of *ca.* 15–20 nm, while that due to the $n-\pi^*$ transition of acids and esters¹ is considerably broader, with a band width of 45–50 nm. The two closely spaced curves will therefore overlap, and (treating them as approximately Gaussian) their superposition will give a resultant CD curve in which the amplitudes of the two maxima will no longer be those of the original contributing curves. (The analogous situation when two oppositely signed Cotton effects of similar amplitudes are superimposed has been investigated³⁸ and has led to important

TABLE 3. ORD AND CD OF S-(+)- α -ALKYLPHENYLACETIC ACIDS Ph—CH(R)—COOH IN 95% ETHANOL

R	ORD: λ (nm) and $[\alpha]_D^{20}$ (°)		CD: λ (nm) and $[\theta]$	
	ORD	$[\alpha]_D^{20}$	CD	$[\theta]$
Methyl	234 pk	—	204 pk	212
	+5300	209 tr	195	+10,800
	233 pk	-12,250	-21,000	213
Ethyl	+3100	209 tr	195	+12,200 ^(a)
	233 pk	-6300	-7200	216
	+3300	208 tr	200	+9800
Butyl	+3200	-8300	-6000	213
	234 pk	210 tr	196	+9100
	+3200	-4750	-9500	212
Isopropyl	232 sh	208 tr	—	+10,300
	+2000	-3500	232	215
	232 pk	209 tr	202	+11,500
Cyclohexyl	+5300	-6000	-6500	213
	230 sh	208 tr	200	-10,700
	+1500	-1450	-2400	215
t-Butyl	240 pk	206 tr	202	+10,050
	+1550	-3500	-2900	216
	231 pk	212 tr	—	+7800
Methyl ^b	+1500	-1100	-750	212
	236 pk	213 tr	204	+6300
	+3100	-5900	-8500	

^a In hexane $[\theta]_{222} + 22,500$, $[\theta]_{213} + 18,000$, $[\theta]_{208} 0$, $[\theta]_{205} 0$, $[\theta]_{205} - 6,600$.^b Methyl ester.^c α -Methyl-(4-cyclohexyl-3-chlorophenyl) acetic acid¹⁹; $[\alpha]_D^{20} + 38.7^\circ$ (c 0.4 in 95% ethanol).

conclusions). This phenomenon may explain the difference in the appearance of the curves for compounds I–IV from those for compounds V–VIII.

It is of interest that the closely related compound α -methyl-(4-cyclohexyl-3-chlorophenyl) acetic acid (XVI) was recently reported³⁹ to possess anti-inflammatory activity, which resided in the (+)-enantiomer, assigned the *S*-configuration.³⁹ The ORD spectrum of this compound shows the expected positive Cotton effect for this configuration, and the CD curve has two positive maxima like the parent acid I and in the same ratio.

Since our work was completed, a very recent publication⁴⁰ reports the CD spectra of a series of phenylacetic acids disubstituted in the α -position with hydroxy, methoxy, and other substituents. These disubstituted compounds showed, in addition to the expected positive CD maxima in the 220 and 260 nm region, a further CD band of *opposite* sign in the vicinity of 240 nm. The authors⁴⁰ use excellent arguments to assign the oppositely-signed bands at 220 and 240 nm to two different conformations of these highly hindered molecules. Phenylacetic acids monosubstituted in the α -position with various substituents did not show this 240 nm CD band. The same authors⁴⁰ report the CD spectra in ethanol of the acids I and II down to 219 nm. While their results are in agreement with ours over this range, their observations did not extend to lower wavelengths. In the case of the acid VIII and its methyl ester, the same authors⁴⁰ reported only the larger of the two positive CD maxima found by us, and made no mention of the smaller positive CD peak in the 230 nm region.

These authors⁴⁰ also indicate the possibility of interaction between $n-\pi^*$ and phenyl transitions and coupling between the two chromophores in their series. They assign the strongly positive CD around 220 nm to the $n-\pi^*$ transition of the acid, and predict an equally intense *negative* Cotton effect (associated with the L_a aromatic transition) in the 200–215 nm region.

Our present evidence suggests that this transition is indeed situated in this region, but is represented in the α -monosubstituted phenylacetic acids (I–VIII) examined by us, by the *positive* CD which is observed around 212 nm. However, at still lower wavelengths it was possible to detect the beginning of a further negative CD, e.g. in compound IV and particularly when the CD spectrum of the acid II was examined in hexane solution. This is in agreement with the conclusions arrived at from the ORD curves.

EXPERIMENTAL

ORD and CD curves were determined on a JASCO spectropolarimeter in 95% EtOH at 25°. Since curves of enantiomers agreed within 5%, only one isomer is described. CD was recorded in molecular ellipticity units [θ]. Wherever necessary, measurements of ORD and CD were corrected to optical purity.

Chemical resolution of alkylphenylacetic acids

The racemic α -alkylphenylacetic acid (0.03 mole) was added to a soln of (–)-1-(1'-naphthyl) ethylamine (0.03 mole) in MeOH (15 ml) and the soln allowed to stand at room temp for several hr. The diastereoisomer, which was derived from the (–)-acid, was removed by filtration and recrystallized from MeOH to constant m.p. and rotation. The enantiomeric purity of the sample was determined as described below and was between 90 and 98%. The diastereoisomer was then hydrolysed by dissolving in *N* NaOH (20 ml) and extracting the soln with ether. The aqueous layer was then acidified (6*N* HCl) and the liberated acid extracted into ether. The dried (Na_2SO_4) ethereal extracts were concentrated and the resolved acid distilled *in vacuo* at ca 1 mm Hg. The results are summarised in Table 1. In the same manner, the use of the (+)-amine resolving agent afforded the (+)-acids.

GLC analysis of diastereoisomeric salts. To a soln of the above diastereoisomeric salt (0.01 mmole) in THF (0.5 ml) was added dicyclohexylcarbodiimide (0.011 mmole) and the soln stirred for several hr at room temp. The mixture was then diluted with EtOAc (5 ml) and the dicyclohexylurea removed by filtration. The filtrate was concentrated *in vacuo* to about 1 ml, and ca 1 μ l of the resulting α -alkylphenylacetyl-1-(1'-naphthyl) ethylamide was injected into the gas chromatograph. Results are summarised in Table 1. All amides were characterized by mass spectrometry, using a Varian 600-D gas chromatograph coupled to a Finnigan 1015 quadrupole mass spectrometer; and gave molecular ions in agreement with their structure.

S-(+)- α -*t*-Butylphenylacetic acid methyl ester. Prepared from the (+)-acid with diazomethane, the ester had b.p. 70°/0.025 mm, IR 1745 cm^{-1} (ester), $[\alpha]_D^{25} + 25.2^\circ$ (c 0.37 in 95% EtOH). It showed a single peak on GLC.

S-(+)-2-Phenyl-1-butanol.³² $[\alpha]_D + 25.3^\circ$ (c 1.0 in 95% EtOH). ORD $[\alpha]_{232} = +335^\circ$ pk, $[\alpha]_{218} - 245^\circ$ tr, $[\alpha]_{213} + 1500^\circ$; CD $[\theta]_{267} + 48$, $[\theta]_{260} + 57$, $[\theta]_{254} + 48$, $[\theta]_{247} + 39$, $[\theta]_{225} 0$, $[\theta]_{217} - 950$ (max), $[\theta]_{212} - 1450$ (max), $[\theta]_{206} - 1650$ (max), $[\theta]_{200} - 700$. In hexane, $[\theta]_{217} - 2000$ (max), $[\theta]_{213} - 3000$ (max), $[\theta]_{209} - 4000$ (max).

S-(+)-2-Phenylbutane.³² $[\alpha]_D + 22.7^\circ$ (c 1.0 in 95% EtOH). ORD $[\alpha]_{267} - 284^\circ$ pk, $[\alpha]_{218} + 1780^\circ$ pk, $[\alpha]_{213} + 1780^\circ$ pk, $[\alpha]_{209} + 1500^\circ$ pk, $[\alpha]_{205} + 800^\circ$ tr, $[\alpha]_{203} + 1100^\circ$; CD $[\alpha]_{221} 0$, $[\theta]_{217} + 2700$ (max), $[\theta]_{212} + 3800$ (max), $[\theta]_{207} + 4600$ (max); $[\theta]_{200} 0$. In hexane, $[\theta]_{223} 0$, $[\theta]_{211} + 3000$, $[\theta]_{203} 0$.

Acknowledgement—We thank Dr. H. S. Mosher for samples of several α -alkylphenylacetic acids, and Dr. A. Moscovitz for helpful discussion.

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