CROATICA CHEMICA ACTA CCACAA **60** (2) 243—262 (1987)

CCA-1722

YU ISSN 0011-1643
UDC 541.653
Original Scientific Paper

Circular Dichroism of Optically Active 1,2-Disubstituted 1,2-Diphenyl Ethanes. Part III. Compounds with a COOR-group at Benzylic C

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Received July 2, 1986

Optically active 1,2-diphenyl ethanes containing a COOR — group on one of the benzylic C-atoms give a relatively strong $n \rightarrow \pi^*$ — Cotton effect around 225 nm in addition to those found for 1,2-diphenyl ethanes lacking this type of substitution, and for which the usual regularities hold which were described in our previous paper. Its sign follows the rule known for such optically active phenyl acetic acid derivatives. This additional band is often detectable only from a broader halfband width of the Cotton effect present in this wavelength range, can, however, clearly be seen when the CD-curve of the analogue containing the moiety CH_2OH instead of the COOR-group is subtracted from the original CD-curve. Effect of the solvent (isooctane vs. acetonitrile) and temperature was studied, as well as the influence of salt formation on the position and fine structure of some Cotton effects.

INTRODUCTION

The CD-curve of any chiral 1,2-diphenyl ethane consists of a superposition of individual Cotton effects of each aromatic chromophore, as well as of bands arising from an interaction between these two. In parts I[3] and II[1] of this series we have shown that the CD-bands between appr. 300 and 250 nm (α-band) are of the first type, whereas at shorter wavelengths interactions of the second type dominate the spectra. Especially from sum- and difference — CD-spectra of pairs of diastereomers the absolute configuration at each centre of chirality can be determined,[3] whereas the Cotton effects within the *p*- and β,β'-bands give valuable information about the absolute conformation. Other chromophores present will of course also interact with the benzene absorptions; as there are many compounds with previously determined absolute configuration where a carboxylic group is attached directly to one centre of chirality of a 1,2-diphenyl ethane, and this combined moiety represents a special type of chromophore, their CD-spectra are discussed separately.

CD WITHIN THE $n \rightarrow \pi^*$-BAND OF THE PHENYLACETATE MOIETY

As it is known[4], the $n \rightarrow \pi^*$-band of a β,γ-unsaturated carbonyl compound is very intense when the moiety C=C—C—C=O can acquire a conformation as shown in Figure 1 (or its mirror image), i. e. if there is a good overlap between two *p*-orbitals (at C_β and C of the oxo group); the magnitude of the molar decadic absorption coefficient for this band may even be of the order of 10^3. Since the rotational strength is proportional to the square root of the dipole strength, the unusually strong Cotton effect within the same absorption band, which is observed in case of chiral molecules, is easily explained.[5] The absolute conformation which is depicted in Figure 1 leads to a strong positive, its mirror image to a strong negative, Cotton effect ($|\Delta\varepsilon_{max}|$ up to 35). Similar effects are also found when the double bond is part of an aromatic π-system[6] and/or when the oxo-group is connected to a hetero atom (acids and esters, amides . . .).[7]

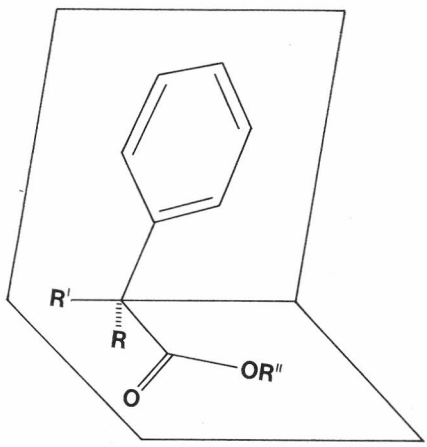


Figure 1. Geometry of a phenylacetic moiety leading to a strong positive Cotton effect within the $n \rightarrow \pi^*$-transition of the —COOR″-chromophore (around 225 nm).

Molecules containing an oxo group prefer to adopt a conformation in which one of the three neighbouring bonds is syn-periplanar to the C=O.[8] Of these, the energetically disfavoured syn-periplanar conformation with the C—Ph-bond cannot give rise to any increased CD, whereas the other two lead to the conformation in Figure 1 or its mirror image, provided that the torsional angle around the C—Ph-bond allows it. If both were of similar energy, then the two strong Cotton effects expected would approximately compensate and no exceptionally large CD-band for the $n \rightarrow \pi^*$ absorption around 230—220 nm could be measured. If one of the two substituents at C (R or R′ in Figure 1) is hydrogen, then the sign of the respective Cotton effect of such a compound indicates that it is rather the bond to the substituent than the C—H bond which prefers this syn-periplanar arrangement. It is immaterial whether R (or R′) stands for an alkyl or a hetero atom (e. g. alkyl substituted phenyl acetates[9], mandelic acid derivatives[10]) This is in agreement with molecular mechanical calculations[11] and X-ray diffraction measurements.[8c] Taking this preference into account, the absolute confi-

guration of such a substituted phenyl acetic acid (or its derivative) can thus be determined unequivocally from its CD-spectrum.

For the 1,2-diphenyl ethanes discussed here this characteristic band falls nearly into the range of the strong Cotton effects arising from the interaction between the two phenyl chromophores, so that in general it cannot be observed isolated. However, if one compares, where possible, these CD-spectra with those of analogues containing the CH_2OH group instead of the COOR moiety, one can in all but one case (*29*, in acetonitril; but in isooctane solution this band can be spotted again) clearly identify, in the respective range, an additional CD-band of the correct sign with $|\Delta\varepsilon_{max}|$ of appr. 4. For illustration, Figure 2 presents the CD-spectrum of *33* and the difference CD-spectrum after substracting that of the corresponding diol (*28* of Part II[1]). Only for the lactone *39* this $n \rightarrow \pi^*$-Cotton effect can be seen distinctly, because its sign is opposite to that of the nearby Cotton effect; its magnitude is the same as for the other compounds.

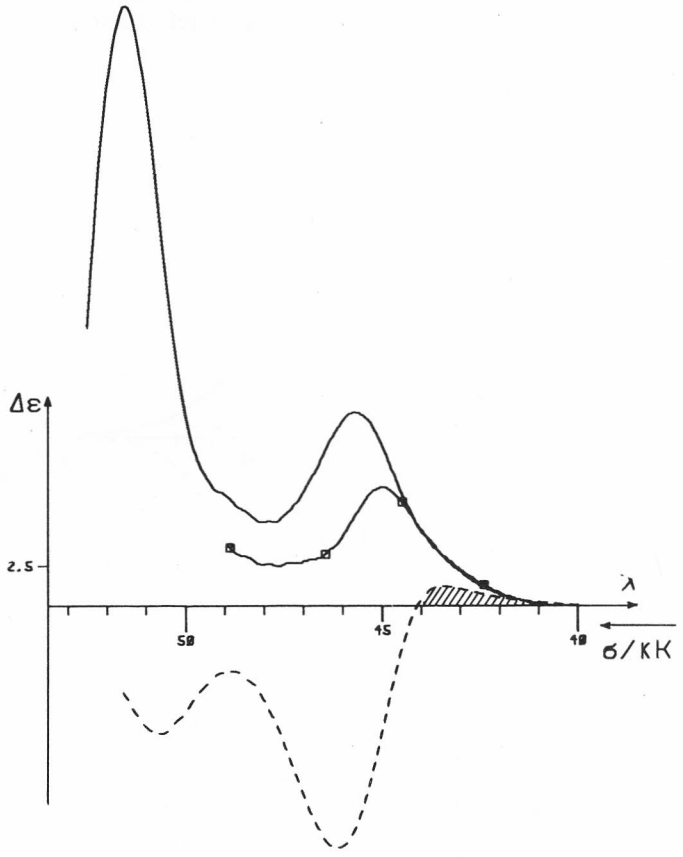


Figure 2. CD of *33* (———), the difference-CD-spectrum of *33* and the analogous compound in which —COOR is replaced by $—CH_2OH$ (-□-□-□-), and CD of *39* (- - - - - -). The characteristic —COOR—$n \rightarrow \pi^*$-band in the spectrum of *33* can be inferred only from the larger halfband width of the Cotton effect around 45 000 cm^{-1}, whereas for *39* it can be clearly recognized and is marked by hatching.

CD BELOW 220 nm

Compounds without the COOR-substituent show a distinctly stronger CD-band between 220 and 200 nm only if one of the rings is *p*-chloro substituted, if an O-acetyl or N-acetyl group is present instead of COOR, or in case of compound *36* of Part II[1] with a relatively fixed conformation. On the contrary, all compounds containing the mentioned COOR-group show in their CD-spectra also substantial Cotton effects in this region and, in general, the CD-band around 220 nm, as well as another one, even larger, just below 200 nm, is of the same sign as the $n \rightarrow \pi^*$ Cotton effect. At still shorter wavelengths (between 190 and 180 nm) one more, very strong Cotton effect of the opposite sign can be detected in most spectra. At appr. 210 to 205 nm these CD-spectra show also a very distinct minimum, which in some cases manifests itself even as a (weak) maximum of the opposite sign, and which must then correspond to one more Cotton effect. Consistently, it is observed that for compounds with threo-configuration the Cotton effect around 200 nm is three to five times as large as that around 220 nm, whereas for erythro-configuration this ratio is less than 2 (cf. Figure 3).

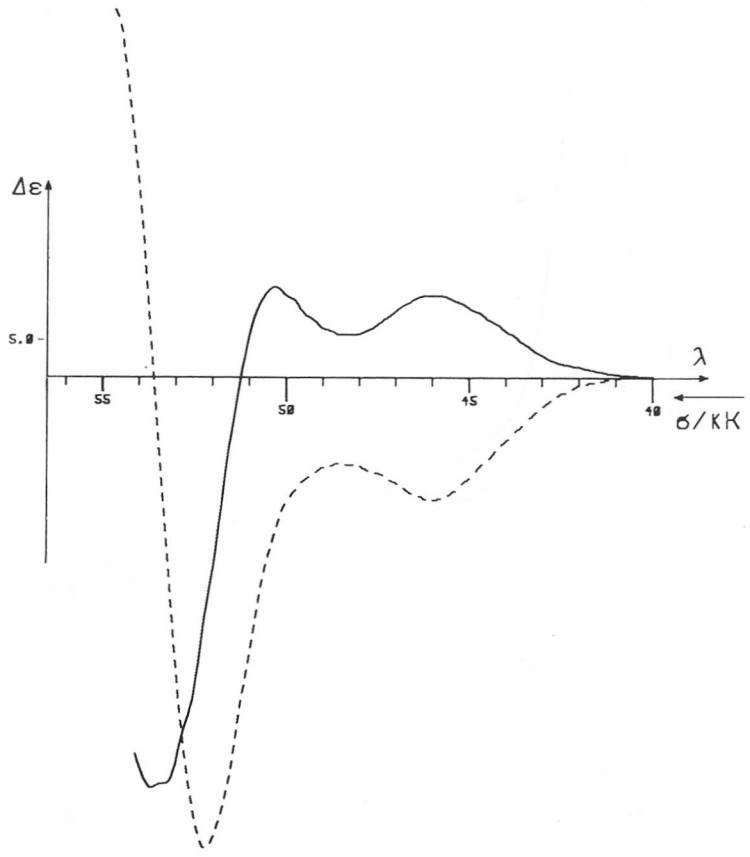


Figure 3. CD-spectra of the threo-aminoester *15* (- - - - -) and its erythro-diastereomer *30* (———).

From the magnitude of all these Cotton effects one can deduce that they are caused by exciton interaction; since, however, at least seven strong transition moments (one B_{1u} and two E_{1u} for each benzene, one $\pi \rightarrow \pi^*$ for the ester) may be involved, a straightforward correlation of these CDs with the conformation does not seem possible. We are, however, inclined to think that the observed difference in the intensity of the Cotton effects between 220—190 nm of threo- and erythro-derivatives originates from the different phenyl-phenyl dispositions in these diastereoisomers, which are preferentially synclinal for threo- and anti-periplanar for erythro.[11,12-14] As a practical rule one can state that the absolute configuration of the »phenyl acetate half« of the 1,2-diphenyl ethane can unequivocally be determined from the sings of these strong Cotton effects between 220 and 180 nm, the absolute configuration at the second center of chirality most probably results from the relative magnitudes of these individual CD-bands.

This rule cannot be applied to the two ring-closed compounds *39* and *40* because the C_α—C_β-bond is forced here into the (approximate) anti-periplanar conformation instead. The phenyl ring cannot any more adopt the ideal conformation for homoconjugation, but nevertheless $\Delta\varepsilon_{max}$ is still appr. +2 for the band around 230 nm; the positive sign is again in agreement with the absolute configuration (cf. Figure 1). The Cotton effects at wavelengths shorter than 220 nm are, however, of the opposite sign to this first Cotton effect, and this fact indicates idependently a different conformation of the three respective chromophores, relative to all other cases.

CD WITHIN THE α-BAND

Since from each phenyl ring at least two vibronic series can be expected in the CD-spectrum of any optically active 1,2-diphenyl ethane, the sum-curve of four such series will be recorded. As the associated electric transition moments are small, no interaction between the two individual phenyl chromophores should take place, and indeed we could show that from sum- and difference-spectra of corresponding pairs of threo- and erythro-compounds the absolute configuration of each »half-molecule« can be determined independently.[3] Only the 0—0-lines have been used for this purpose.[3]

In a threo-compound both »half-molecules« should then give identical or very similar patterns for the two 0—0-lines, and in such a case the CD-spectrum will also give information about the absolute configuration.[1] The same holds also, as we have now found, for threo-1,2-diphenyl ethanes derived from phenyl acetic acid (*12, 14—16, 33—38*), as well as for compounds *9—11* containing only one single center of chirality. The borderline for the separation of the two 0—0-lines is the same, viz. 37 200 cm^{-1} as for compounds without the COOR-moiety.

In the erythro-series the CD-spectra of the two »half-molecules« have opposite signs and might thus compensate each other to a great extent. In agreement with this, the CD-bands of erythro-compounds lacking the carboxylic group are generally smaller than those of the corresponding threo--analogues.[1] This is, however, not any more the case of the phenylacetic derivatives discussed here. Since very small changes of the transition energies of the two independent chromophores can lead to an exchange of the positions of the two 0—0-lines around 37 200 cm^{-1}, no prediction seems possible about

the correlation between the CD within the α-band absorption and the absolute configuration of such erythro-compounds. Furthermore, in three cases (*21*, *22* isooctane, *23*) the wavenumber of the only recognizable 0—0-line coincides exactly with the above mentioned borderline value, so that no clear identification is possible. Nevertheless, in several other cases (*22* ethanol, *25*, *27*—*31*) we observed the following regularities: again only one such 0—0-line can be detected at slightly larger wavenumbers than 37 200 cm^{-1}, whose sign corresponds formally to the absolute configuration of the »upper half-molecule« which does not contain the COOR-grouping. The presence of the menthyl moiety is of no influence in all these spectra.

p-SUBSTITUTED 1,2-DIPHENYL ETHANES

As it has been found previously[1], *p*-substitution by Cl in one ring shifts the »borderline wavenumber« from 37 200 to 36 200 cm^{-1} for the 0—0-line within the α-band absorption. This approximately corresponds to the additional shift for *p*-Cl, as published by Petruska.[15] It was furthermore observed that the signs of the Cotton effects within the 0—0-lines are inverted for homochirally analogous compounds in the case of an OZ-grouping at the benzylic position to the *p*-Cl-phenyl, but not so for a CH_2OZ-moiety. For the erythro-compounds *44* and *46*, as well as for the threo-isomers *41* and *50*, all with OH in the benzylic position, the same behaviour has been observed, and from the spectra of the erythro- (*45*, *47*) and threo- (*42*, *51*) compounds with the mentoxycarbonyl moiety can be derived that such a sign inversion holds also for that benzylic substituent. We believe that the reason for sign inversion is the opposite sign of the *q*-values for CH_2OH and CH_2COOH in contrast to CH_2-alkyl,[15] in agreement with observations for other aromatic model compounds[16] (cf. Figure 4).

The bromo derivatives *48* and *49* follow the same scheme even if one takes into consideration that the »borderline« should be further redshifted (estimated at appr. 36 000 cm^{-1}). In contrast, the two methoxy derivatives *43* and *52* give practically enantiomorphous 0—0-line Cotton effects in spite of the same absolute configuration around the chiral center in benzylic position to the methoxy phenyl ring, which exception cannot be understood at the moment.

For all these compounds the four Cotton effects below 240 nm follow, however, again the rules established in this paper for 1,2-diphenyl ethanes not further substituted in the phenyl rings.

SUBSTANCES SHOWING NO FINESTRUCTURE WITHIN THE α-BAND CD

Substances *18*, *24*, and *32* are salicylidene derivatives of the primary amines *15*, *22*, and *30*, resp., and show several strong Cotton effects overriding by far those within the α-band. (*R*)-configuration at the chiral centre carrying the salicyliden amino function leads to a negative Cotton effect above 315 nm and to a positive one between 280 and 270 nm (acetonitril solution), which is in agreement with the general rule for such chromophores.[17,18] It is interesting to note that for the two erythro-compounds (*24*, *32*) the Cotton effect around 325 nm is quite small in contrast to the case of threo-compound *18* with $\Delta\varepsilon_{max} = -4{\cdot}0$ at 318 nm.

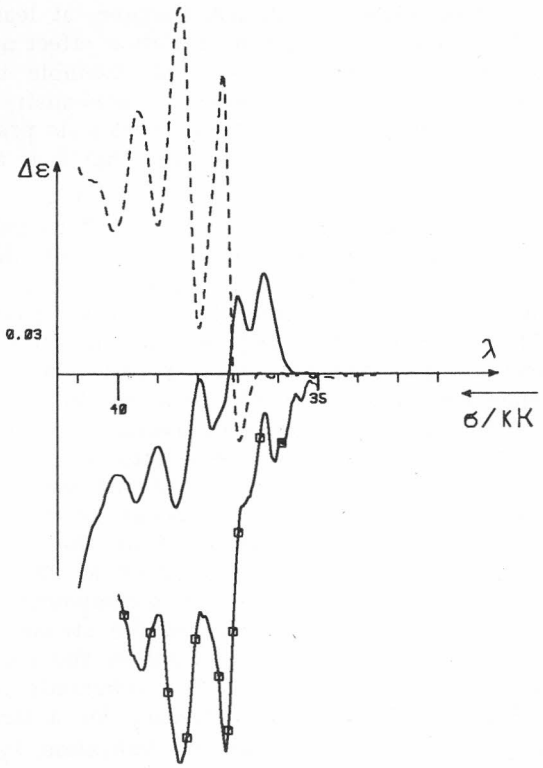


Figure 4. Cotton effects within the α-band: For the threo-compound *34* (- - - - -) we expect a negative 0—0-line at smaller, and a positive one at larger wavenumbers than 37 200 cm^{-1}, as it has been found. For its *p*-chloroderivative *41* (———) the opposite will be predicted if homochirally analogous »half-molecules« give CD-bands of identical signs. Only one of the two (namely at larger wavenumbers than 36 200 cm^{-1}) is observed, and it is of a positive sign, indicating thus a sign inversion by the *p*-chloro substitution in such a moiety.

42 (-□-□-□-) has the *p*-chloro substituent in the other half of the molecule and the first observable CD-line is at 36 000 cm^{-1}, i. e. below that »magic borderline«, and it is negative. Sign inversion takes place also in this type of substitution of the »half-molecule«.

The *N*-2,4-dinitrophenyl derivatives *8* and *19* of phenylalanin and the amine 15, resp., show no finestructure for the same reason. This is also true of the *N*-dimedonyl derivative *17* of *15*.

For the three bromo compounds *13, 20,* and *26* no fine structure band can be identifed because of an unusually strong Cotton effect around 235 to 230 nm. Furthermore, the otherwise characteristic four Cotton effects below 240 nm do not appear in the CD-spectra in the usual way: the threo--compound *13* shows a still relatively strong Cotton effect below 200 nm, but between 240 and 210 nm the CD-bands are quite different: the otherwise negative minimum around 210 nm becomes here a positive maximum, which

proves that the preferred conformation has changed, at least partially. The erythro-derivative *20* shows an even stronger Cotton effect at 233 nm (—5.8), and below 220 nm the CD-spectrum does not resemble the normal ones any more. The CD-spectrum of *26*, whose stereochemistry at the bromo--bearing carbon atom could not be determined before, is practically enantiomorphous to that of *20*, so that we can conclude that it is also the erythro--stereoisomer.

In the analogous series of β-bromo-ketones such anomalously large and somewhat bathochromically shifted $n \rightarrow \pi^*$-bands in both the UV- and CD--spectra are found only when there is an approximate antiperiplanar conformation of the (O=C)—C—C—Br train of bonds.[19] We have then to expect a similar anomality for esters, too, and ascribe, therefore, this additional strong Cotton effect at appr. 233 nm to the presence of a conformer with similar bond arrangement. For a flexible molecule this seems to be quite reasonable, because in it the dipole-dipole interaction of the two polar groups is then minimized. This conformation necessitates for *13* a syn-periplanar arrangement of the C_α-phenyl bond to C=O if one takes into account the positive Coffon effect, which is not so energetically favoured. We can, therefore, still see the usual negative CD arising from the interaction between the carboxyl and the nearby phenyl chromophore at 231 nm of the other conformer. On the other hand, for the erythro-compounds the C—H bond must be arranged syn-periplanarly to explain the strong Cotton effect at 233 nm (*20* and *26*), and for such a conformation the contribution to the $n \rightarrow \pi^*$ Cotton effect would be opposite to that commonly found. Obviously, the respective C-phenyl torsional angle necessary for a strong contribution of the latter type is not possible, because no indication for it is found in the CD-spectra of these two compounds. The observed H—H-coupling constants are in agreement with the assumption of these conformations.[20]

CHANGES OF CD BY SALT FORMATION

Transformation of an amine into its corresponding salt may change the CD at least for two reasons, viz. by changing the contribution of a neutral group into that of a cation, and by change of the conformational equilibrium. Both effects are very weak because most of the CD-spectra (*12*, *15*, *22*, and *35*) are scarcely changed by acidification of the solution. For the menthyl esters it has also been proved by NMR-spectroscopy[11b] that the torsional angle around the central C—C-bond is not drastically changed under these conditions. Only for *30* the ratio of the intensities of positive to negative CD-lines is strongly influenced by such salt formation (*cf.* Figure 1 of ref.[3]). *30* is an erythro-compound for which the contributions from both rings to the CD within the α-band more or less compensate and, as already mentioned, minimal changes of band positions can then lead to big changes of intensities or even signs.

We also studied the influence of salt formation from carboxylic acids upon the CD. For *25*, *33*, and *37* no remarkable change of the Cotton effect within the α-band absorption is noticeable, whereas for *9*, which contains only one single centre of chirality, sign inversion takes place for all lines

in the same wavelength range, and this resembles the behaviour of model compounds *1* and *3*, also containing only one asymmetric C-atom. As expected, the $n \rightarrow \pi^*$-band of the COOH-group is shifted to the blue and, therefore, cannot any more be observed for *9* and *33* because of the presence of Cotton effects caused by the two aromatic chromophores; no such change is noticeable for *37*, but there is still another ester moiety present, nor for *25*, which contains an additional ureido chromophore.

INFLUENCE OF THE SOLVENT UPON THE CD

In the cases where the solvent dependence was checked (one center of chirality: *9, 10, 11*; two centers of chirality: *12, 14, 15, 16, 21—23, 25, 27, 30, 31, 33—38*; cyclic compounds: *39, 40; p*-substituted in one ring: *41—52*), only very seldom have changes of the CD, even within the α-band, been observed. The most striking case is that of the hydrochloride of *30*, whereas the CD of the free amine *30* is scarcely influenced by a change of solvent. The case of *22* was already discussed earlier in this paper, and only for *23* and *27* small variations of the $\Delta\varepsilon_{max}$-values could be found. One generality could be observed: with the exception of *44*, where the contrary is the case, in acetonitrile solutions the first 0—0-line CD is usually more distinctly visible than in isooctane solution (especially for *14, 33—35, 41* and *50*).

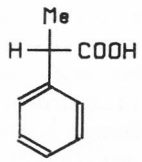
Of the model compounds with only one phenyl ring, whose molecules are more flexible than the 1,2-diphenyl ethanes, only mandelic acid (*3*) shows a medium, and the ester of (*R*)-mandelic acid with (—)-menthol (*4*) a strong influence of the solvent upon the CD, whereas the O-methyl ether *5* of the latter and the diastereomeric menthyl ester *6* give very similar enlargement of the $\Delta\varepsilon_{max}$-values (EPA as solvent).

INFLUENCE OF TEMPERATURE UPON CD

For *38* we have investigated the influence of lowering the temperature in order to find out whether the interaction between the four chromophores, which should be highly sensitive to conformational changes, is altered. We observed some enlargement of the already at room temperature quite strong Cotton effects between 240 and 200 nm, but no other drastic alteration of the CD.

For *41, 46*, and *47* the behaviour of the CD within the α-band was investigated in a similar way, and we observed the usual sharpening of the CD-bands at lower temperature, better resolution of adjecent lines, and enlargement of the $\Delta\varepsilon_{max}$-values (EPA as solvent).

Change of temperature with the model compounds *4* and *6* conforms with the behaviour when changing the solvent: the CD of *6* is almost not influenced by the temperature, whereas the initially negative CD of *4* becomes bisignate below —60 °C, and at —50 °C the positive series is already larger than the negative one. The reason for these differences of sensitivity of the Cotton effects towards changes of solvents or temperature must reflect different mobilities of the molecules of these two diastereomers. Empirical force field calculations support this view.[11c]



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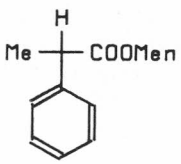

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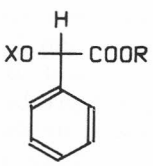
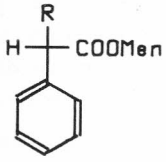
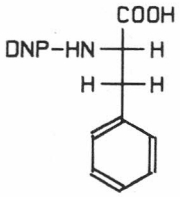


	R	X
3	H	H
4	Men	H
5	Men	Me



6: R = OH
7: R = H



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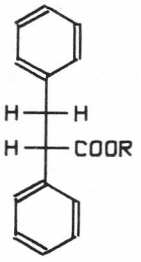
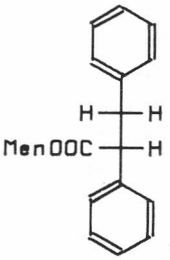


9: R = H
10: R = Men



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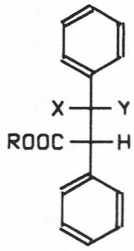
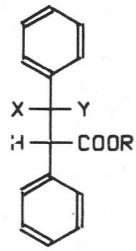
EXPERIMENTAL

All CD-spectra have been recorded under the same conditions as described in our previous papers.[1,3]

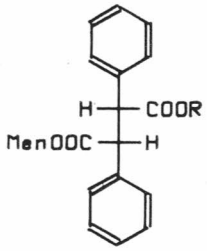
When only CD-data are given, the literature citation refers to the synthesis and determination of absolute configuration. The solvents for the CD-spectra are abbreviated as follows: A = acetonitrile; C = chloroform; D = dioxane; E = ethanol; H = cyclohexane; M = methanol; MH = methylcyclohexane + isopentane (1:3), ML = dichloromethane; O = isooctane; P = diethyl ether + isopentane + ethanol (5:5:2); TF = trifluoro acetic acid; W = water.



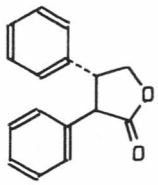


	R	X	Y
12	Me	H	NH_2
13	Men	H	Br
14	Men	H	OH
15	Men	H	NH_2
16	Men	H	$NHCONH_2$
17	Men	H	NH-DIM
18	Men	H	N=SAL
19	Men	H	NH-DNP
20	Men	Br	H
21	Men	HO	H
22	Men	H_2N	H
23	Men	H_2NCONH	H
24	Men	SAL=N	H

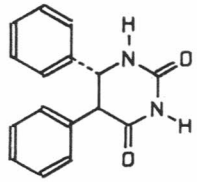
	R	X	Y
25	H	H	$NHCONH_2$
26	Men	(H, Br)	
27	Men	H	OH
28	Men	H	OMe
29	Men	H	OAc
30	Men	H	NH_2
31	Men	H	$NHCONH_2$
32	Men	H	N=SAL
33	H	HO	H
34	Men	HO	H
35	Men	H_2N	H
36	Men	H_2NCONH	H



37 R = H
38 R = Me



39



40

(+)-(S)-Hydratropic acid (1)

(A): 267 (+0.04), 260 (+0.05), 222 (+3.7), 204 (—0.98).

(O): 267 (+0.05), 261 (+0.06), 253 (+0.05), 222 (+3.83), 204 (—0.59), negative below 200 nm.

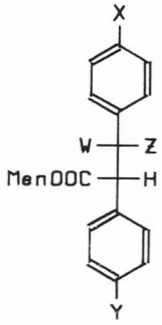
(E): 267 (+0.03), 260 (+0.04), 253 (+0.04), 221 (+3.06), 203 (—0.84).

(E + OH^-): 268 (—0.14), 262 (—0.15), 255 (—0.09), 230 (+0.34), 218 (—0.68).

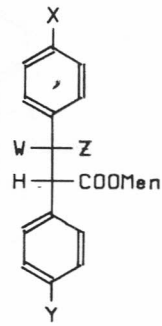
(—)-Menthyl ester of (R)-hydratropic acid (2)

(A): 269 (—0.16), 262 (—0.18), 225 (—4.26), 205 (+1.92).

(O): 268 (—0.26), 262 (—0.28), 255 (—0.20), 225 sh (—6.24), 222 (—6.54), 203 (+1.90).



	W	X	Y	Z
41	H	Cl	H	OH
42	H	H	Cl	OH
43	H	OMe	H	OH
44	HO	Cl	H	H
45	HO	H	Cl	H



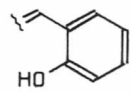
	W	X	Y	Z
46	H	Cl	H	OH
47	H	H	Cl	OH
48	H	Br	H	OH
49	H	Br	H	OAc
50	HO	Cl	H	H
51	HO	H	Cl	H
52	H	OMe	H	OH

Ac = CH_3CO

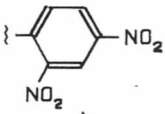
Me = CH_3

Men = (–)-Menthyl

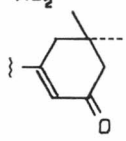
SAL =



DNP =



DIM =



(—)-(R)-Mandelic acid (3)

(E): 268 (+0.06), 261 (+0.07), 252 (+0.03), 223 (—7.88), 203 (+0.42), 198 (+0.78).
(E + OH^-): 269 (—0.03), 261 (—0.03), 255 (—0.02), 219 (—5.09), 201 (—6.18).
(D): 272 (—0.01), 268 (+0.03), 266 (—0.02), 263 (+0.04), 260 (—0.02), 224 (—12.54).

(—)-Menthyl ester of (R)-mandelic acid (4)

(A): 267 (+0.03), 265 (—0.02), 262 (+0.04), 258 (—0.02), 255 (+0.02), 251 (—0.03), 222 (—12.50), 201 sh (+2.30), 190 (+32.40).

(O): 268 (—0.07), 260 (—0.11), 253 (—0.10), 222 (—24.10), 204 (—3.80), 192 (+57.20).
(MI) (+20 °C): 268 (—0.05), 260 (—0.07), 253 (—0.06).
(—60 °C): 268 (—0.08), 260 (—0.12), 253 (—0.09).
(—100 °C): 269 (+0.01), 265 (—0.07), 259 (—0.07).
(—150 °C): 269 (+0.09), 265 (—0.04), 263 (+0.18), 260 (—0.10), 257 (+0.13).

(—)-Menthyl ester of (R)-O-methyl-mandelic acid (5)

(A): 268 (+0.08), 261 (+0.09), 255 (+0.07), 225 (—7.02), 201 sh (+1.56), 192 (+18.16).
(O): 268 (+0.07), 262 (+0.08), 255 (+0.08), 226 (—7.70), 205sh (+2.50), 192 (+30.1).

(—)-Menthyl ester of (S)-mandelic acid (6)

(A): 267 (—0.10), 261 (—0.10), 255 (—0.08), 222 (+11.20), 203 (+2.8), 190 (—27.30).
(O): 268 (—0.10), 262 (—0.12), 256 (—0.08), 222 (+30.80), 189 (—73.20).
(MI): (+ 20 °C): 268 (—0.04), 262 (—0.06), 255 (—0.04). Inessential change at lower temperature.

(—)-Menthylphenylacetate (7)

(A): 268 (—0.04), 261 (—0.04), 255 (+0.03), 226 (—0.33), 209 (+0.18).

(+)-(S)-2-(N-2,4-dinitrophenyl)-amino-3-phenyl-propanoic acid (8)

(A): 409 (—2.50), 334 (+2.88), 271 (+0.62), 247 (—0.64), 213 (+6.10).

(+)-(S)-2,3-Diphenylpropanoic acid (9)[21]

(A): 267 (+0.13), 264 (0.08), 260 (+0.16), 234 sh (+2.20), 218 (+14.70), 202 sh (+7.70), 195 (+24.87), negative below 190 nm.
(E): 267 (+0.15), 261 (+0.16), 253 (+0.13), 218 (+9.60), 205 sh (+4.00), 199 sh (+5.00), 197 (+8.00), negative below 193 nm.
(E + OH^-): 269 (—0.09), 266 (+0.03), 262 (—0.09), 259 (+0.05), 255 (—0.02), 222 (+7.41), 211 sh (+2.52), 208 (+3.09).
(D): 268 (+0.12), 261 (+0.12), 251 (0.10), 220 (+7.25).

(—)-Menthyl-(S)-2,3-diphenylpropanoate (10)[21]

(A): 268 (+0.06), 260 (+0.07), 258 (+0.07), 255 (+0.06), 219 (+12.70), 203 sh (+7.10), 196 (+19.40), negative below 192 nm.
(O): 268 (—0.31), 261 (—0.32), 255 (—0.24), 218 (—15.80), 205 sh (—8.50), 195 (+26.40).

(—)-Menthyl-(R)-2,3-diphenylpropanoate (11)[21]

(A): 268 (—0.17), 261 (—0.21), 254 (—0.17), 218 (—12.00), 195 (—21.30), 186 (+19.80).
(O): 268 (—0.31), 261 (—0.32), 255 (—0.24), 218 (—15.80), 205 sh (—8.50), 195 (—30.80), 186 (+34.6).

(—)-Methyl-(2S, 3R)-3-amino-2,3-diphenyl-propanoate (12)[22]

(A): 270 (+0.09), 267 (—0.19), 260 (—0.26), 253 (—0.18), 221 (—6.2), 193 (—49.3).
(D): 272 (+0.05), 269 (—0.34), 261 (—0.43), 254 (—0.28), 220 (—10.50).
(E): 271 (+0.02), 267 (—0.29), 260 (—0.35), 253 (—0.25), 218 (—8.50), 208 sh (—5.2), 194 (—20.00).
(E + H^+): 269 (+0.18), 262 (+0.16), 258 (—0.15), 251 (—0.13), 218 (—9.74), 204 sh (—5.08), 200sh (—4.34), 193 (—17.46).

(—)-Menthyl-(2R, 3R)-3-bromo-2,3-diphenyl-propanoate (13)[20,21]

(A): 269 (+0.62), 246 (+2.18), 231 (—2.40), 214 (+9.50), 197 (—20.20).

(—)-Menthyl-(2S, 3R)-2,3-diphenyl-3-hydroxy-propanoate (14)[14]

(A): 268 (—0.18), 260 (—0.22), 253 (—0.16), 221 (—7.20), 210 sh (—2.70), 195 (—25.20).

(O): 269 (—0.46), 261 (—0.51), 255 (—0.35), 219 (—13.20), 196 (—27.90), positive below 190 nm.

(—)-Menthyl-(2S, 3R)-3-amino-2,3-diphenylpropanoate (15)[21]

(A): 271 (+0.06), 267 (—0.27), 260 (—0.36), 253 (—0.27), 221 (—4.00), 204 sh (—5.00), 191 (—40.30).

(A + H^+): 269 (+0.08), 265 (—0.13), 260 (—0.26), 251 (—0.22), 215 (—19.20), 202 sh (—11.00), 191 (—45.40).

(O): 267 (—0.65), 260 (—0.73), 253 (—0.49), 216 (—14.80), 210 sh (—10.50), 191 (—58.70).

(M): 268 (—0.41), 260 (—0.48), 253 (—0.36), 219 (—10.38), 211 sh (—5.90), 193 (—17.10).

(—)-Menthyl-(2S, 3R)-2,3-diphenyl-3-ureidopropanoate (16)[23]

(A): 270 (+0.03), 267 (—0.44), 260 (—0.48), 253 (—0.30), 225 (—2.44), 214 (+1.28), 206 sh (—2.2), 195 (—27.20), 185 (+10.90).

(D): 271 (+0.04), 268 (—0.37), 261 (—0.35), 254 (—0.19).

(—)-Menthyl-(2S, 3R)-3-(N-dimedonyl)-amino-2,3-diphenylpropanoate (17)[18]

(A): 283 (+7.08), 268 sh (+4.00), 217 (—7.16).

(—)-Menthyl-(2S, 3R)-3-(N-salicylidene)-amino-2,3-diphenylpropanoate (18)[18]

(A): 318 (—4.02), 276 (+2.96), 250 (—6.08), 226 (+18.80), 209 (—12.20).

(—)-Menthyl-(2S, 3R)-3-(N-2,4-dinitrophenyl)-amino-2,3-diphenyl-propanoate (19)[18]

(A): 407 (—1.39), 340 (+2.64), 277 (—2.18), 253 (+0.48), 233 (+2.68), 215 (—5.88).

(—)-Menthyl-(2R, 3S)-3-bromo-2,3-diphenylpropanoate (20)[20,21]

(A): 264 (—1.50), 233 (—5.82), 211 (—1.78), 203 (+1.50), negative below 200 nm.

(—)-Menthyl-(2S, 3R)-2,3-diphenyl-3-hydroxypropanoate (21)[14]

(A):269 (—0.03), 262 (—0.04), 257 (—0.05), 220 (—5.90), 215 sh (—5.30), 207 sh (—3.30), 195 (—11.60), positive below 192 nm.

(O): 269 (—0.22), 261 (—0.23), 259 (—0.19), 219 (—16.40), 206 (—8.10), 197 (—25.30), positive below 192 nm.

(—)-Menthyl-(2S, 3S)-3-amino-2,3-diphenylpropanoate (22)[21]

(A): 270 (—0.03), 267 (+0.04), 263 (—0.04), 260 (—0.05), 218 sh (—3.80), 215 (—4.90), 203 (—5.90), 197 (—7.90), 185 (+29.80).

(A + H^+): 268 (+0.04), 265 (—0.04), 261 (+0.05), 257 (—0.05), 218 (—6.28), 211 sh (—5.72), 203 sh (—3.83).

(E): 270 (—0.01), 266 (—0.06), 260 (—0.08), 254 (—0.06).

(E + H^+): 274 (+0.01), 266 (—0.06), 260 (—0.08), 254 (—0.06).

(M): 270 (—0.01), 266 (—0.07), 257 (—0.08), 225 sh (—4.62), 217 sh (—5.38), 211 sh (—5.70), 205 (—6.48), 196 (—11.90), positive below 192 nm.

(O): 269 (—0.04), 265 (—0.04), 259 (—0.05), 218 (—10.60), 207 sh (—7.50), 197 (—16.70), 186 (+40.40).

(—)-Menthyl-(2S, 3S)-2,3-diphenyl-3-ureido-propanoate (23)[23]

(A): 269 (—0.03), 267 (+0.09), 260 (+0.08), 256 (—0.04), 253 (+0.03), 227 sh (—2.30), 212 (—7.72), 201 sh (—7.00), 189 (+20.00).
(D):269 (—0.07), 267 (+0.03), 262 (—0.09), 256 (—0.07).

(—)-Menthyl-(2S, 3S)-2,3-diphenyl-3,-(N-salicylidene)-aminopropanoic acid (24)[18]

(A): 325 (+0.33), 273 (—4.40), 255 (+2.71), 224 (—9.30), 211 (—8.78).

(+)-(2R, 3R)-2,3-Diphenyl-3-ureidopropanoic acid (25)[23]

(A + E): 267 (—0.14), 260 (—0.14), 253 (—0.06), 232 sh (+2.12), 214 (+12.20), 203 sh (+10.10).
(E): 267 (—0.11), 260 (—0.11), 253 (—0.05), 213 (+5.60), 204 sh (+4.10), 200 sh (+4.00), negative below 197 nm.
($E + OH^-$): 269 (—0.32), 262 (—0.36), 255 (—0.24), 212 (+5.70), 207 sh (+4.80), 200 sh (+2.50).
(D): 268 (—0.11), 261 (—0.11), 254 (—0.08), 216 (+7.32).

(+)-Menthyl-(2S, 3R)-3-bromo-2,3-diphenylpropanoate (26)[21]

(A): 232 (+7.30), 211 (+4.70), 197 (+4.50), 191 (+4.90).

(—)-Menthyl-(2R, 3R)-2,3-diphenyl-3-hydroxypropanoate (27)[24]

(A): 268 (—0.04), 261 (—0.03), 253 (—0.01), 215 (+9.10), 206 sh (+6.70), 202 sh (+7.10), 194 (+18.20), 184 (—45.60).
($A + H^+$): 267 (—0.04), 261 (—0.04), 253 (—0.02), 230 sh (+1.08), 217 (+6.64), 210 (+7.50), 197 (+13.40).
(D): 268 (—0.05), 261 (—0.06), 257 (—0.05), 224 sh (+3.40), 220 (+3.58), 214 sh (+2.83), 206 sh (+1.25).
(E): 272 (+0.01), 266 (—0.02), 261 (—0.03), 254 (—0.03), 219 sh (+2.44), 214 (+2.62).

(—)-Menthyl-(2R, 3R)-2,3-diphenyl-3-methoxypropanoate (28)

Prepared by treatment of *27* with CH_3I and Ag_2O according to ref.[25]; the crude product was recrystallized from dilute methanol, m. p. 96—97° C, $[\alpha]_D^{20} = -6.83$ (acetone). (Found: C, 79.20, H, 8.71. Calc. for $C_{26}H_{34}O_3$: C, 79,12, H, 8.68).
(A): 268 (—0.08), 260 (—0.07), 253 (—0.04), 215 (+8.40), 206 sh (+5.30), 195 (+14.00), 187 (—32.10).

(+)-Menthyl-(2R, 3R)-3-acetoxy-2,3-diphenyl-propanoate (29)[24]

(A): 267 (—0.04), 261 (—0.04), 254 (—0.03), 228 sh (+1.04), 211 (+9.98), 206 sh (+8.40), 192 (+19.10).
(O): 267 (—0.08), 260 (—0.08), 253 (—0.04), 218 sh (+10.10), 211 (+11.50), 202 sh (+6.30), 191 (+20.70), negative below 189 nm.

(—)-Menthyl-(2R, 3R)-3-amino-2,3-diphenylpropanoate (30)[21]

(A): 268 (—0.12), 261 (—0.10), 254 (—0.05), 218 sh (+7.30), 214 (+8.14), 211 sh (+8.06), 199 (+9.70), negative below 193 nm.
($A + H^+$): 267 (—0.08), 261 (—0.10), 254 (—0.06).
(E): 268 (—0.06), 262 (—0.06), 256 (—0.02), 221 (+4.38), 216 (+4.26), 204 sh (+2.28).
($E + H^+$): 266 (+0.05), 259 (+0.04), 252 (+0.03), 220 (+6.50), 214 sh (+6.40), negative below 198 nm.
($(E + A)\ (1:3) + H^+$): 269 (—0.03), 266 (+0.03), 262 (—0.05), 259 (+0.02), 256 (—0.02), 252 (+0.02).
($(E + A)\ (1:1) + H^+$): 269 (+0.03), 266 (+0.03), 262 (—0.05), 255 (—0.03).
($(E + A)\ (3:1) + H^+$): 272 (+0.01), 269 (—0.01), 266 (+0.04), 262 (—0.03), 259 (+0.04), 252 (+0.03).
(O): 268 (—0.10), 262 (—0.08), 255 (—0.03), 218 (+11.30), 199 (+12.00), 186 (—56.70).

(MI) (+20 °C): 219 (+13.03), 205 (+8.02), 202 (+10.49).
(—20 °C): 220 (+14.27), 217 sh (+13.70), 201 (+8.57).
(—60 °C): 220 (+14.04), 217 (+14.06), 200 (+6.97).
(—100 °C): 220 sh (+13.42), 217 (+14.15), 215 sh (+13.65), 200 (+2.95).
(—150 °C): 223 sh (+9.33), 220 sh (+10.14), 215 (+11.31), 201 sh (—2.47).

(—)-Menthyl-(2R, 3R)-2,3-diphenyl-3-ureidopropanoate (31)[23]

(A): 267 (—0.16), 260 (—0.17), 253 (—0.09), 213 (+11.60), 204 sh (+8.50), 197 sh (+6.20), 187 (—36.50).
(D): 268 (—0.18), 261 (—0.18), 254 (—0.11), 217 (+10.96), 214 sh (+10.62), 205 sh (+8.50).

(+)-Menthyl-(2R, 3R)-3-(N-salicylidene) amino-2,3-diphenylpropanoate (32)[18]

(A): 333 (—0.37), 273 (+4.16), 251 (—1.57).

(+)-(2R, 3S)-2,3-diphenyl-3-hydroxypropanoic acid (33)[14]

(A):269 (—0.10), 267 (+0.22), 259 (+0.29), 252 (+0.22), 219 (+12.80), 194 (+42.90), negative below 190 nm.
(E): 271 (—0.01), 267 (+0.35), 260 (+0.39), 253 (+0.27), 220 (+10.30), 205 sh (+4.70), 196 (+10.40).
($E + OH^-$): 268 (+0.46), 261 (+0.49), 254 (+0.30), 221 (+8.50), 204 sh (+1.54).
(D): 267 (+0.31), 260 (+0.37), 253 (+0.25), 220 (+9.34).
(ML): 270 (—0.02), 267 (+0.19), 260 (+0.25), 252 (+0.19).

(+)-Menthyl-(2R, 3S)-2,3-diphenyl-3-hydroxy-propanoate (34)[14]

(A): 270 (—0.05), 268 (+0.22), 260 (+0.27), 253 (+0.20), 221 (+10.40), 211 sh (+4.30), 194 (+37.30), negative below 189 nm.
(O): 268 (+0.53), 261 (+0.57), 254 (+0.38), 218 (+16.80), 205 sh (+11.00), 196 (+30.00).

(+)-Menthyl-(2R, 3S)-3-amino-2,3-diphenylpropanoate (35)[21]

(A): 271 (—0.10), 267 (+0.24), 260 (+0.30), 253 (+0.19), 221 (+6.78), 192 (+51.00).
($A + H^+$): 270 (—0.11), 266 (+0.09), 262 (—0.09), 258 (+0.19), 218 (+19.60), 204 sh (+11.40).
(E): 268 (+0.41), 260 (+0.45), 253 (+0.31).
($E + H^+$): 270 (—0.10), 265 (+0.11), 262 (—0.08), 258 (+0.21), 252 (+0.17).
(O): 267 (+0.65), 260 (+0.69), 253 (+0.47), 218 (+14.60), 207 sh (+7.80), 193 (+50.40).

(—)-Menthyl-(2R, 3S)-2,3-diphenyl-3-ureidopropanoate (36)[23]

(A): 270 (—0.08), 267 (+0.39), 260 (+0.39), 253 (+0.24), 222 (+3.27), 213 (—1.28), 195 (+22.30).
(D): 270 (—0.12), 267 (+0.25), 261 (+0.22), 255 (+0.08).

(—)-Monomenthyl-(2R, 3R)-2,3-diphenylsuccinate (37)[21]

(A): 267 (—0.34), 260 (—0.40), 252 (—0.31), 217 (—24.70), 192 (—39.00), 184 (+32.80).
(E): 267 (—0.44), 260 (—0.50), 253 (—0.37), 219 (—27.60), 195 (—48.40).
($E + OH^-$): 268 (—0.47), 261 (—0.50), 254 (—0.33), 222 (—21.90), 207 sh (—10.00), 192 (—36.00).
(MH): 267 (—0.41), 260 (—0.47), 254 (—0.31), 220 (—18.50), 211 sh (—13.40), 195 (—20.70).

(—)-Menthyl-methyl-(2R, 3R)-2,3-diphenylsuccinate (38)[21]

(A): 267 (—0.33), 259 (—0.38), 252 (—0.27), 220 sh (—23.50), 217 (—25.20), 209 sh (—18.17), 201 sh (—13.60), 192 (—39.33), 183 (+33.10).

(O): 268 (—0.29), 260 (—0.32), 253 (—0.22), 218 (—30.20), 195 (—58.60), 185 (+52.20).
(MI): (+20 °C): 219 (—42.60), 215 sh (—40.20), 212 sh (—36.80).
(—20 °C): 219 (—46.00), 214 sh (—43.10), 212 sh (—34.20).
(—60 °C): 219 (—50.40), 216 (—46.40).
(—100 °C): 219 (—53.60), 211 (—51.20).
(—150 °C): 219 (—55.00), 211 (—53.20).

(—)-(3R, 4R)-trans-3,4-Diphenyl-tetrahydro-furanone-2 (39)[21]

(A): 268 (—0.24), 262 (—0.22), 258 (—0.12), 229 (+1.64), 216 (—14.36), 202 sh (—7.50), 195 (—13.70), positive below 190 nm.
(O): 269 (—0.26), 262 (—0.22), 257 (—0.13), 230 (+0.94), 218 (—17.08), 196 (—10.02).

(—)-(5S, 6R)-trans-5,6-Diphenyl-dihydrouracil (40)[23]

(A): 268 (+0.37), 261 (+0.60), 254 (+0.57), 224 (+2.28), 216 (—5.08), 207 sh (—2.40), 193 (—19.40).
(D): 268 (+0.29), 261 (+0.46), 255 (+0.38), 225 (+2.32), 217 (—3.14), 210 sh (—1.46).

(—)-Menthyl-(2S, 3R)-3-hydroxy-3-(p-chlorophenyl)-2-phenylpropanoate (41)[14]

(A): 275 (+0.08), 270 (+0.06), 266 (—0.04), 260 (—0.10), 253 (—0.10), 226 (—9.50), 196 (—24.60), 188 (+24.20).
(O): 276 (+0.03), 269 (—0.37), 262 (—0.45), 255 (—0.34), 222 (—21.80), 197 (—38.20), 189 (+43.70).
(MI) (+20 °C): 269 (—0.44), 262 (—0.52), 255 (—0.38).
(—60 °C): 268 (—0.64), 262 (—0.68), 254 (—0.46).
(—100 °C): 276 (+0.05), 268 (—0.40), 260 (—0.44), 253 (—0.34).
(—150 °C): 275 (+0.10), 269 (—0.36), 266 (—0.27), 262 (—0.40).
(P) (+20 °C): 268 (—0.19), 260 (—0.21), 253 (—0.17).
(—100 °C): 275 (—0.05), 268 (—0.26), 260 (—0.26).
(—160 °C): 277 (+0.01), 268 (—0.18), 266 (—0.18), 260 (—0.23).

(—)-Menthyl-(2S, 3R)-3-hydroxy-2-(p-chlorphenyl)-3-phenylpropanoate (42)[14]

(A): 277 (—0.07), 268 (—0.28), 260 (—0.29), 225 (—12.60), 217 sh (—7.70), 214 (+2.40), 197 (—26.90), positive below 190 nm.
(O): 277 (—0.25), 269 (—0.48), 261 (—0.45), 253 (—0.34), 226 (—18.60), 198 (—19.14).

(—)-Menthyl-(2S, 3R)-3-hydroxy-3-(p-methoxyphenyl)-2-phenylpropanoate (43)[14]

(A): 281 (—0.28), 275 (—0.33), 267 (—0.34), 260 (—0.26), 228 (—9.00), 210 sh (—4.33), 196 (—26.50), positive below 190 nm.
(O): 280 (—0.24), 275 sh (—0.30), 269 (—0.71), 262 (—0.69), 254 (—0.46), 224 (—17.30), 211 sh (—7.00), 197 (—37.30), 188 (+45.67).

(—)-Menthyl-(2S, 3S)-3-hydroxy-3-(p-chlorphenyl)-2-phenylpropanoate (44)[14]

(A): 275 (—0.05), 268 (—0.09), 262 (—0.08), 254 (—0.07), 223 (—5.54), 198 (—8.56), positive below 192 nm.
(O): 277 (+0.02), 274 sh (—0.03), 268 (—0.28), 261 (—0.32), 254 (—0.25), 223 (—18.60), 208 sh (—6.30), 197 (—13.90), 191 (+33.30).

(—)-Menthyl-(2S, 3S)-3-hydroxy-2-(p-chlorphenyl)-3-phenylpropanoate (45)[14]

(A): 276 (—0.05), 269 (—0.08), 265 (—0.05), 263 (—0.05), 223 (—6.78), 221 sh (—6.22), 203 sh (—4.22).
(H): 278 (—0.09), 270 (—0.11), 264 (—0.13), 258 (—0.19), 222 (—19.70), 208 sh (—9.40), 202 (—14.30), 196 sh (—11.40).

(+)-Menthyl-(2R, 3R)-3-hydroxy-3-(p-chlorphenyl)-2-phenylpropanoate (46)[14]

(A): 275 (+0.11), 267 (+0.11), 259 (+0.08), 251 (+0.06), 221 (+8.22), 212 sh (+6.18), 196 (+10.38), negative below 192 nm.

O): 275 (+0.15), 268 (+0.27), 261 (+0.25), 253 (+0.18), 223 (+15.00), 197 (+15.30).
(MI): (+20 °C): 275 (+0.16), 268 (+0.29), 260 (+0.27), 253 (+0.20).
(—20 °C): 274 (+0.21), 268 (+0.33), 261 (+0.29), 253 (+0.22).
(—60 °C): 274 (+0.25), 267 (+0.34), 261 (+0.29), 253 (+0.14).
(P): (+20 °C): 275 (+0.14), 267 (+0.15), 261 (+0.12), 258 (+0.12).
(—20 °C): 275 (+0.19), 267 (+0.17), 258 (+0.12).
(—60 °C): 275 (+0.24), 267 (+0.20), 256 (+0.12).
(—100 °C): 274 (+0.29), 267 (+0.23), 258 (+0.13).
(—160 °C): 274 (+0.34), 266 (+0.26), 258 (+0.13).

(+)-Menthyl-(2R, 3R)-3-hydroxy-2-(p-chlorphenyl)-3-phenylpropanoate (47)[14]

(A): 275 (—0.01), 271 (+0.01), 267 (—0.03), 260 (—0.02), 223 (+8.00), 211 sh (+2.80), 207 sh (+4.00), 200 (+8.90), 188 (—26.40).

(H): 276 (—0.06), 273 (+0.03), 268 (—0.05), 266 (+0.04), 258 (+0.08), 225 (+15.20), 200 (+12.40).

(P): (+20 °C): 276 (—0.03), 272 (+0.02), 268 (—0.10), 260 (—0.06).
(—60 °C): 275 (—0.08), 271 (+0.04), 267 (—0.16).
(—100 °C): 275 (—0.12), 272 (+0.04), 267 (—0.16).
(—130 °C): 275 (—0.22).

(+)-Menthyl-(2R, 3R)-3-hydroxy-3-(p-bromphenyl)-2-phenylpropanoate (48)[14]

(A): 275 (+0.15), 267 (+0.15), 258 (+0.10), 221 (+7.54), 207 sh (+4.78), negative below 200 nm.

(O): 274 (+0.20), 267 (+0.35), 260 (+0.30), 222 (+14.66), 207 sh (+7.80), 199 (+12.70).

(E): 274 (+0.18), 267 (+0.17), 263 (+0.11), 257 (+0.08), 220 (+3.49), 215 sh (+3.03).

(+)-Menthyl-(2R, 3R)-3-acetoxy-3-(p-bromphenyl)-2-phenylpropanoate (49)[14]

(A): 274 (+0.15), 266 (+0.18), 259 (+0.12), 251 (+0.07), 218 (+7.60), 210 sh (+1.80), 188 (—6.80).

(O): 274 (+0.30), 267 (+0.28), 260 (+0.18), 253 (+0.12), 222 (+5.80), 207 (+0.70), 202 (—2.60), 193 (—7.76).

(+)-Menthyl-(2R, 3S)-3-hydroxy-3-(p-chlorphenyl)-2-phenylpropanoate (50)[14]

(A): 275 (—0.08), 270 (—0.11), 266 (+0.05), 260 (+0.12), 253 (+0.11), 224 (+12.30), 196 (+30.30), 187 (—26.90).

(O): 276 (+0.06), 269 (+0.43), 262 (+0.45), 255 (+0.32), 223 (+21.60), 198 (+32.30), 191 (—20.20).

(+)-Menthyl-(2R, 3S)-3-hydroxy-2-(p-chlorphenyl)-3-phenylpropanoate (51)[14]

(A): 267 (+0.19), 260 (+0.23), 253 (+0.17), 224 (+14.20), 198 (+31.00).

(H): 277 (+0.14), 268 (+0.36), 261 (+0.37), 254 (+0.28), 224 (+18.10), 199 (+18.30), 187 (—35.40).

(+)-Menthyl-(2R, 3R)-3-hydroxy-3-(p-methoxyphenyl)-2-phenylpropanoate (52)[14]

(A): 281 (+0.14), 274 (+0.16), 265 (+0.12), 257 (+0.07), 224 (+5.72), 213 (+5.74), 198 sh (+3.62), 193 (+4.44), negative below 190 nm.

(O): 280 (+0.28), 274 (+0.33), 268 (+0.30), 259 (+0.27), 255 (+0.18), 224 (+11.00), 211 sh (+8.70), 200 (+11.70).

Acknowledgement. — G. S. thanks the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and Hoechst AG for financial support; N. B. the Bulgarian Academy of Sciences, the Deutsche Forschungsgemeinschaft and the German Academic Exchange Service for grants and Dr. M. Palamareva, Dr. R. Rakovska and Mr. S. Bojadžijev for the help in the preparation of some samples.

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SAŽETAK

Cirkularni dihroizam optički aktivnih 1,2-disupstituiranih 1,2-difenil-etana. Dio III. Spojevi sa COOR-skupinom na benzilnom C-atomu

N. Berova, B. Kurtev i G. Snatzke

Optički aktivni 1,2-difeniletani, koji sadrže COOR skupinu na jednom od benzilnih C-atoma, pokazuju snažan $n \rightarrow \pi^*$ Cottonov efekat kod približno 225 nm. Njegov predznak slijedi pravilo poznato za optički aktivne spojeve izvedene iz fenilacetatne kiseline. Ova dodatna vrpca može se jasno uočiti kad se odbiju CD-krivulje spojeva koji sadrže COOR i CH_2OH skupinu. Promatran je utjecaj otapala (izooktan *vs.* acetonitril) i temperature, te prevođenje karboksilnih kiselina u odgovarajuće soli na položaj Cottonovih efekata i finu strukturu vrpci.