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Circular Dichroism of Optically Active 1,2-Disubstituted 1,2-Diphenyl Ethanes Part II: Compounds without COOR-group at Benzylic C.[1,2]

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(R,R)-Hydrobenzoin and homochirally analogous *threo*-compounds of formula Ph-CHX—CHY-Ph (X = Y; X ≠ Y; Y = H) show a negative 0—0 — CD-line below 37200 cm^{-1} and/or a positive one just above it, which can be explained by conformational equilibria around the Ph-C — bonds. The Cotton effect at 220—210 nm is negative for this same configuration, if X ≠ Y (also Y = H), in these other cases there no such simple correlation. Cotton effects within the E_{1g}- or the E_{2g}-transitions might be the reason for this, although otherwise no indication of them could be found. The same rules hold if a ring is closed between X and Y, the Cotton effect at 220—210 nm has thus the same sign as the torsional angle (Ph-)C-C(-Ph), and the same is also true of the next Cotton effect at 198—191 nm. The temperature dependence of the CD can be explained only by assuming conformational as well as solvational equilibria. Introduction of a single *p*-chloro substituent shifts the borderline between the two 0—0 — CD-lines of opposite signs to 36200 cm^{-1}. It causes a sign inversion of the CD within the α-band of a »half-molecule« of type Cl—C_6H_4—C(H, Bn)—OZ, not however in the case of Cl—C_6H_4(H, Bn)—CH_2OZ. Such *p*-chloro substitution does not influence the Cotton effects below 220 nm. *p,p'*-Disubstitution by the CH_3CO--group shifts the p-band strongly bathochromically, the corresponding intense CD-couplet prooves the preponderance of that conformation deduced already from NMR-spectra, and prooves as well the absolute configuration.

Compounds of *erythro*-series mostly show much weaker Cotton effects, which do not correlate in a simple manner with the absolute configuration. However, the sign of the first branch of the CD-couplet at 220—210 nm (p-band) always agrees with that deduced from molecular mechanical calculations. Internal H-bonds have hardly any effect on the CD (and therefore also on conformational equilibria), protonation of amino groups leads, however, in some cases to great changes of the CD. The phthalimide moiety is not useful for the chiroptical determination of the configuration of such diphenyl ethanes.

INTRODUCTION

Since many years diastereoisomeric 1,2-disubstituted 1,2-diphenyl ethanes have been synthesized in Sofia in order to study the stereochemistry and mechanism of aldol-type reactions.[3] Optically active compounds are made mostly by using (—)menthyl phenylacetate as starting material and by separation of the four possible diastereomers, eventually followed by a modification of the substituents.[4–10] In a few cases racemic carboxylic acids have also been resolved with optically active amines. The relative configurations (threo, erythro) have been determined mostly by chemical correlations with compounds of know stereochemistry, in a few cases by means of (mainly) IR- and ^{1}H-NMR spectroscopy. The absolute configurations have always been determined by chemical correlations. In this and a following paper[11] we discuss the chiroptical properties of such diphenyl ethanes, and their possible application to the independent determination of the absolute configuration at both chiral centers, as well as to the analysis of conformational equilibria.

CONFORMATION OF MONOSUBSTITUTED BENZENE DERIVATIVES

For a bond between a phenyl group and an sp^3-C atom a sixfold relatively small energy barrier hinders free rotation.[12] The more the three substituents differ from one other in size and electronegativity the more unsymmetrical this potential function will become. In the case of a substituent $-CX_3$ the lower minima correspond to torsional angles of 0° between the X—C — bond and the direction of the respective p-orbital of the benzene π-system, and the second type of minima to a torsional angle of appr. 90°. Many X-ray studies show that (at least in the solid state) also for a substituent of the —CHXY type one of the torsional angles (X—)C—C(-p) or (Y—)C—C(-p) approaches 0° in the preferred conformation. p-π-interaction (hyperconjugation) and steric interaction of the substituent groups with the *o*-hydrogen atoms of the benzene ring are the main factors determining the shape of the potential curves. ^{1}H-NMR spectra can be applied successfully to the determination of the preferred torsional angle ω_{Ph-C}, only in a few special cases e. g. if long-range couplings or NOE-s between aliphatic and aromatic protons can be observed. CD-spectroscopy may give, however, information about the preferred conformations with the help of well established sector rules.[13]

CONFORMATION OF 1,2-DIPHENYL ETHANES

For a full description of the conformation of a 1,2-disubstituted 1,2--diphenyl ethane PhXHC—CHYPh three torsional angles must be known: two of the type mentioned above (ω_2, ω_3) and one (ω_1) along the middle bond (Ph—)C—C(—Ph).[a] In the three preferred staggered conformations along this latter bond ω_1 adopts values of approximately ± 60° (syn-clinal, sc) or 180° (anti-periplanar, ap); ^{1}H-NMR-spectroscopy will usually give information (using the Karplus-equation) about the ratio of the populations with (H—)C—C(—H) sc and ap geometry, but cannot differentiate between the two possible sc

[a] In papers on ^{1}H-NMR-spectroscopy gauche/trans or synclinal/antiperiplanar usually refers to the torsional angle (H—)C—C(—H). As we are discussing the interactions between two of the benzene rings these stereochemical descriptors apply to the (Ph—)C—C(—Ph) — bond if not specifically mentioned otherwise.

forms; it is the CD-spectroscopy which could solve this problem besides giving information about the absolute configuration.

In 1,2-dialkyl derivatives of 1,2-diphenylethanes with smaller alkyl groups it has been shown experimentally[14,15] and by molecular mechanical calculations[14,15] that for both the threo- and the erythro-form the conformation with a torsional angle (H—)C—C(—H) of appr. 180° prevails, i. e. in the threo--series the two phenyl groups prefer the sc conformation, in the erythro-series the ap. The energy difference between these two forms is somewhat larger in the erythro than in the threo series.[15] Similar results have been obtained when the alkyl groups are substituted[16] or if one of them is replaced by the —COOR — moiety.[17] If X and/or Y a substituted heteroatom (—OR, NRR'), these regularities break down, $^3J_{H,H}$ for both stereoisomers may become very similar or even indicate, that one sc arrangement of the hydrogens in the threo form becomes the dominating one.

UV- AND CD-SPECTRA

In the normally accessible wavelength range benzene gives three absorption bands, around 265 nm (α-band, $\varepsilon \approx 200$), 203 nm (p-band, $\varepsilon \approx 8000$), and 185 nm (β,β'-bands, $\varepsilon \approx 56000$), which in point group D_{6h} correspond to the electric dipole forbidden $^1A_{1g} \rightarrow {}^1B_{2u}$-, the forbidden $^1A_{1g} \rightarrow {}^1B_{1u}$- and the doubly degenerate allowed $^1A_{1g} \rightarrow {}^1E_{1u}$-transitions, resp. All these $\pi \rightarrow \pi^*$--transitions are magnetically dipole forbidden. The α-band shows a very pronounced fine structure even in solution, but does not contain a line for the 0—0-transition. It consists of several vibronic series and the most prominent one of these has been characterized[18] as $1_0{}^n6_0{}^1$. The p-band also shows some fine structure which however can not be resolved well enough to allow detailed assignments to individual vibronic series.

Monosubstitution lowers the symmetry of the perturbed π-system to C_{2v} and by this all four transitions become formally electrically dipole allowed ($B_{2u} \rightarrow B_2$; $B_{1u} \rightarrow A_1$, $E_{1u} \rightarrow A_1 + B_2$), furthermore, the $^1A \rightarrow {}^1B_2$ transitions are now also magnetically dipole allowed ($m_x \neq 0$, $\mu_y \neq 0$). In spite of this, for alkyl substituents the order of magnitude of the intensity of the 0—0-lines is approximately the same as for the $1_0{}^0 6_0{}^1$ line of benzene. Therefore the UV-spectra of such compounds resemble very much those of benzene itself, except for a small bathochromic shift of all the bands.

The CD-spectra of chirally monosubstituted benzene derivatives show very small Cotton effects for the α-band with the 0—0-line around 268.5 nm and a sector rule is known for the correlation of its sign with the absolute configuration.[13] With the p- and the β,β'-bands the signal/noise ratio in the CD-spectra is usually very small for such flexible molecules; rigid systems, as e. g. octahydrophenanthrenes, show Cotton effects of medium magnitude within the p-band and two strong Cotton effects of opposite signs for the β- and β'-transitions. Not many good CD-data are, however, available for such simple systems in this wavelength range.

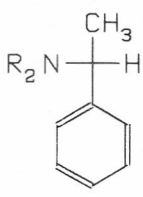
The CD-spectra within the α-band absorption of compounds with diarylmethane and 1,2-diphenylethane moieties are sometimes bisignate and have occasionally been interpreted as being caused by exciton coupling.[19] However, this is improbable at least for compounds of the type described here, since the electric transition moment for the $^1A_{1g} \rightarrow {}^1B_{2u}$ ($^1A_1 \rightarrow {}^1B_2$) transition is much too

small, so that superpositions of the two independent Cotton effects for the two phenyl chromophores, each in its own chiral surrounding, are observed. We usually found a very distinct fine structure for this α-band-CD, with either all individual Cotton effect lines of the same signs, or of the bisignate type. Even for one and the same compound uni- or bisignate CD-curves may be recorded, depending on the choice of the solvent. The series built upon the 0—0-transition will reflect directly the chirality of the »rigid« molecule, whereas the sign of those series having another vibronic origin will be determined also by chiral non-totally symmetric vibrations. Any correlation between CD and absolute configuration must thus be based on the sign of the 0—0-Cotton effect line.

The positions of the two 0—0—CD-lines for the two chromophores of a PhXHC—CHYPh compound will either coincide or at least be very close to each other, and they may have the same or opposite signs. In general the two separate vibronic series (1_0^n) can not be identified with certainty, thus from such a CD-spectrum of a 1,2-disubstituted 1,2-diphenylethane within the α-band, it seems at first impossible to get information on the absolute configurations at both chiral centres. On the other hand, as there is no appreciable interaction between the two chromophores for this transition the sum- and difference-curves for any pair of threo/erythro diastereomers should be characteristic for each »half-molecule«. Indeed, this proved to be the case and the results for 26 such pairs are described in Part I[1] of this series.

Some time ago two additional CD-couplets at 217.5/215 and 198.1/194.3 nm were reported for 1-methylindane in the gas phase and interpreted as corresponding to the doubly degenerated electric dipole forbidden $^1A_{1g} \rightarrow {}^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{2g}$-transitions, resp., of benzene ($\sigma \rightarrow \pi^*$ and/or $\pi \rightarrow \sigma^*$).[20] We have also observed an additional Cotton effect around 220 nm in solution spectra several times, which shows that the appearance of such CD-bands in the indane spectrum was not a singular case.

Most of the substituents present in our compounds do not absorb above 190 nm, with the exception of —COOR and some »Cottonogenic groups« (e. g. in **18**). In general the $n \rightarrow \pi^*$ Cotton effect of the COOR-chromophore is



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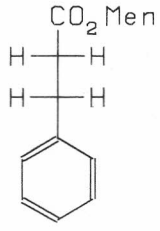
E-2: R = Phth



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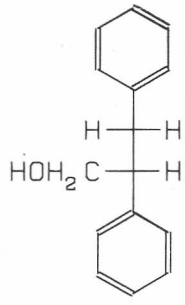

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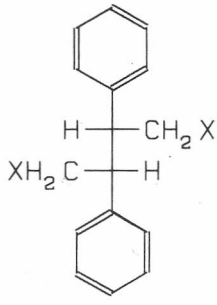
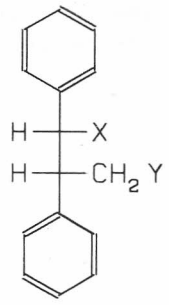
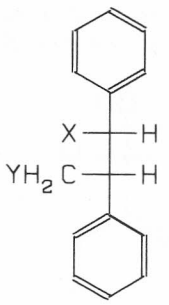


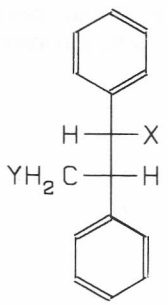
5: X = H
6: X = CN
7: X = OH
8: X = OMe
9: X = OAc
10: X = OTs
11: X = CO_2Me



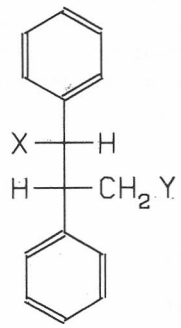
	X	Y
12	OH	OH
13	OAc	OAc
14	NH_2	H
15	NH_2	Br
16	NH_2	OH
17	NHAc	OAc



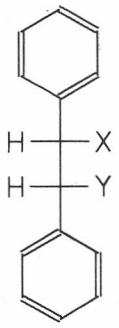
	X	Y
18	NPhth	OH
19	NH_2	NH_2
20	NPhth	NPhth



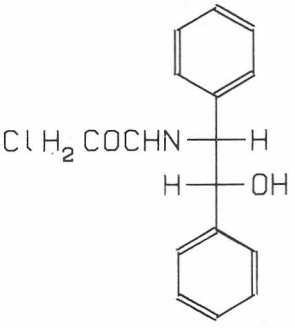
	X	Y
21	NH_2	H
22	NH_2	Br
23	NH_2	OH
24	NHAc	OAc
25	NPhth	OH
26	NH_2	NH_2
27	NPhth	NPhth



	X	Y
28	OH	OH
29	OAc	OAc
30	NH_2	OH
31	NHMe	OH



	X	Y
32	OH	NH_2
33	OH	$NHCOCH_2Cl$
34	OAc	NHAc



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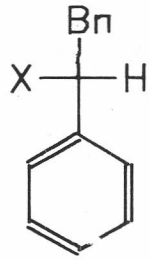
relatively weak. However in the presence of a β,γ-double bond (isolated or as a part of a benzene system) it can acquire appreciable rotational strength if the geometry is favourable for orbital interaction.[21] The chiroptical properties of these carboxylic derivatives are, therefore, discussed separately (Part III).[11]

α-BAND CD

This CD with pronounced fine structure is actually a superposition of several vibronic CD-series and will be further complicated by the presence of at least two conformations in solution. From the difference- and sum-CD-

-spectra we[1] could nevertheless show that consistently the »half-molecule« of absolute configuration I (Fischer-projection, Bn is the second [substituted]



I

benzyl moiety, X any group) gives a negative 0—0-line CD at 37 230 cm^{-1} or somewhat larger wavenumbers, which mostly is accompanied by a second one (for another conformer) of opposite sign at smaller wavenumbers, which is generaly less intense. A change of the solvent sometimes drastically alters the intensities of these two 0—0 line Cotton effects and the series built upon them. The benzene vibration ν_6 should, however, be scarcely influenced by this and the two CD-lines can, therefore, safely be ascribed to two different conformers A and B (Figure 1). It is, therefore, essential that any comparisons of CD-spectra should be made only for the same solvents or solvent mixtures.

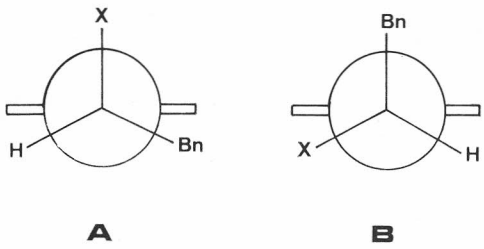


Figure 1. Idealized NEWMAN projections of the two most preferred conformations of a molecule **I** (Bn = [substituted]benzyl moiety, X = any group). **A** leads to a negative CD series with 0—0 — line at 37 200 cm^{-1} or larger wavenumbers, **B** to a positive one with 0—0 — line below this value.

That these 0—0-line CDs are not just computational artifacts is born out by the fact that simple model compounds like (R)-1-phenyl ethanol[22] or (R)-1-phenyl ethylamine (**1**, Bn of formula I replaced by methyl, X = NH_2) give also a negative Cotton effect series built upon the 0—0 line at 37 430 cm^{-1} (in ethanol) or 37 470 cm^{-1} (in isooctane). Protonation of the amino group (in ethanol solution) does not practically change the magnitude of this Cotton effect, the negative 0—0 line CD appearing at 37 610 cm^{-1}.

If the 1,2-diphenylethane is only monosubstituted like **4** then the sign of the 0—0 line CD can be used directly to determine the absolute configuration at the single chiral center: the negative Cotton effect of (R)-**4** is in agreement

with the prediction from formula I (X = CH_2OH). In this spectrum besides the main 0—0 line at 37 300 cm^{-1} ($\Delta\varepsilon$ = —0.093), the above mentioned second (very small one can also be detected (36 830 cm^{-1}, $\Delta\varepsilon$ = +0.007); these values refer to acetonitril solution and are very similar for isooctane as solvent. The CD-contribution of the second phenyl chromophore is much smaller although not completely negligible even if the benzene ring is separated from the chiral part of the molecule by two methylene groups and the planar COO-moiety as in **3**, where a Cotton effect can still be measured for the benzene α-band ($\Delta\varepsilon$ = —0.012 at 37 370 cm^{-1}). Therefore, it can not be completely be excluded that the 36 830 cm^{-1} CD-line of **4** actually stems from the second phenyl ring. For an analogous product (—CH_2OH of **E-4** replaced by NHAc) of opposite absolute configuration to that of **4** we have found a positive Cotton effect within the α-band-CD (in methanol solution), again in full agreement with the given correlation.[23]

Compounds **5** through **11** contain two identical halves of absolute configuration I and show mostly either bisignate CD-curves or sometimes Cotton effects of apparently »wrong« (positive) sign. One has, however, to take into account that two 0—0-line CDs of opposite sign always characterize each half-molecule; since a substituent X = CH_2R in general formula I resembles very much the (substituted) benzyl rest, it seems reasonable that the two preferred conformations A and B (Figure 1, cf. also I and V in Figure. 2 of PART I[1]) have similar populations and thus the 0—0-line CD below 37 200 cm^{-1} becomes larger than usual. Indeed, if such a positive 0—0-line CD appears in any of these CD-spectra its position is always at a smaller wavenumber than 37 200 cm^{-1}, which is then followed by a negative CD-line above this borderline value of 37 200 cm^{-1}. Only in one CD-spectrum (**6**, in isooctane solution) this negative maximum appears as a (positive) minimum between two positive CD-lines. In this solvent the two CD-series nearly compensate for one another, since the $\Delta\varepsilon$-values are at least one order of magnitude smaller than for each other case, and also for the same compound **6** in acetonitril solution.

Only after having found[1] these bisignate 0—0-line Cotton effects in the sum- and difference-CD-spectra, which indicated the presence of the two conformers A and B (Figure 1) it became clear how important the exact identification of both the 0—0 lines is for the determination of the absolute stereochemistry of any optically active phenyl compound, even if apparently only one vibronic series seems to show up in the CD-spectrum.

The absolute configuration of all these compounds of PhCHX—CHXPh structure can, therefore, be deduced unequivocally from their α-band Cotton effects, provided that one carefully identifies both 0—0-lines. Needless to stress that very accurate wavelength calibration is necessary for such studies. The method of sum- and difference-CD-spectra can not of course be applied here, because the corresponding erythro-compounds are optically inactive meso-forms. Also for compound **10** the CD-spectroscopy cannot be applied in this streightforward manner for the determination of its absolute configuration since two more aromatic chromophores are present in the molecule; all CD-lines are very unsymmetric and therefore no unequivocal identification of the two 0—0-lines for the diphenylethane moiety is possible. The published[24] spectrum of (*R,R*)-hydrobenzoin, which contains twice the halfmolecule **E—I**

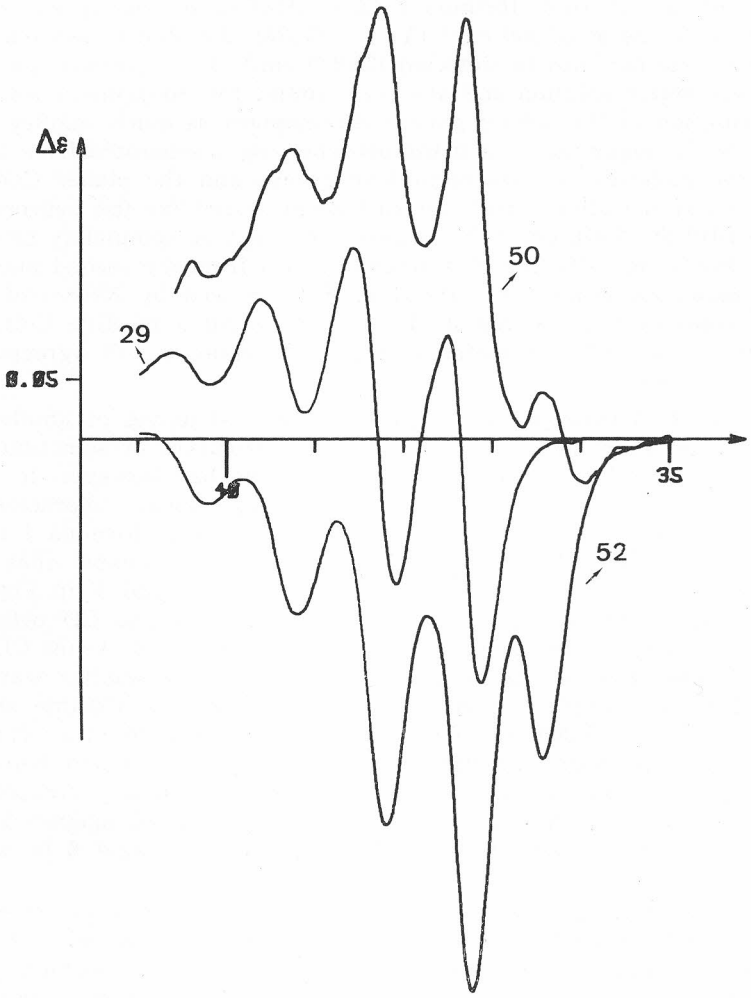
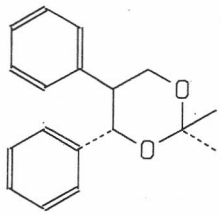


Figure 2. CD within the α-band of **29**, **50** and **52** (acetonitril solution). Abscissa linear in wavenumbers (unit: 10^3 cm^{-1}).

(X = OH), shows in agreement with these rules a positive Cotton effect with fine structure within the α-band (0—0 line at appr. 37 244 cm^{-1}; as usual, the enantiomer of **Q** is called **E**—**Q**).

In order to disentangle the CD-series of the two halfmolecules, in a few examples a *p*-chloro substituent was introduced into one of the two benzyl moieties (**45** through **52**). In this way only the Cotton effects of the substituted moieties are shifted bathochromically, so that the signs of their 0—0-lines can be read off the spectrum unequivocally, whereas the conformational equilibrium is hardly effected by such a p-substitution. Only for **49** and its acetate **50** (cf. Figure 2) bisignate Cotton effects for the p-chloro phenyl chro-



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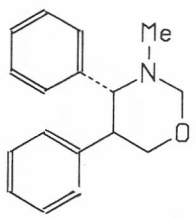

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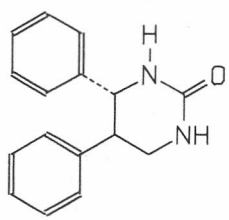

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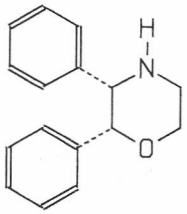

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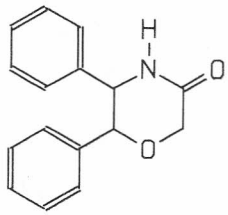

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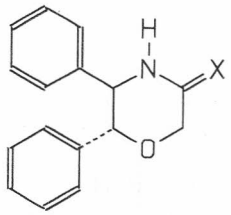
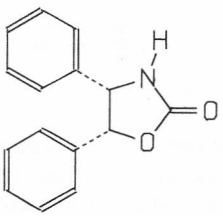


41 : X = H_2
42 : X = O



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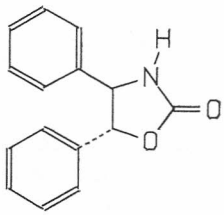

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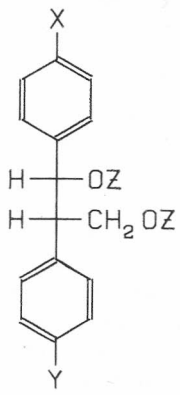
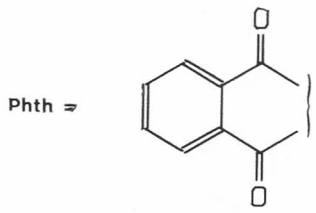
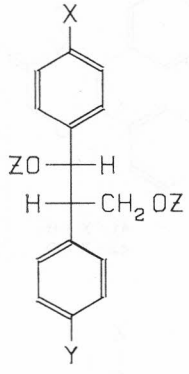


	X	Y	Z
45	H	Cl	H
46	H	Cl	Ac
47	Cl	H	H
48	Cl	H	Ac

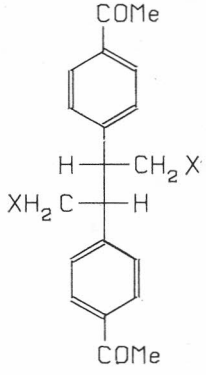
mophore could be observed between 279 and 273 nm; also the CD spectrum of **45** apparently contains such a bisignate CD, these two 0—0-CD-lines are, however, at somewhat shorter wavelengths so that the second one might already come from the unsubstituted phenyl. Empirical comparison of the bisignate 0—0 line CDs of **49** and **50** with those of their unsubstituted analogues **28** and **29** (cf. Figure 2), resp., shows that the signs of these two lines



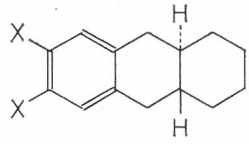
Ac = CH_3CO –
Me = CH_3 –
Men = (–) – Menthyl –
Ts = p – Tosyl –



	X	Y	Z
49	H	Cl	H
50	H	Cl	Ac
51	Cl	H	H
52	Cl	H	Ac



53: X = H
54: X = CO_2Me



55: X = H
56: X = OMe

are not inverted by *p*-chloro substitution, in contrast to many other examples for which sign inversion has been described.[25] Such reasoning implies that for **28** and **29** the two 0—0-CD-lines are determined, at least to a large extent by contributions from the »half-molecule« with a 2-phenyl-ethanol structure, which assumption is well supported by our findings[1] that all »half-molecules« of the same absolute configuration give the same signs for their 0—0 line CDs. For a compound such as **28** and **29** with threo-configuration both halves should, therefore, anyway give Cotton-effects of the same sign.

In all other CD-spectra (**46**—**48**, **51**, **52** (cf. Figure 2)) only one 0—0 line CD can be observed for acetonitril solution. These examples and four similar ones (described in part III[11] of this series) allow the value of 36 200 cm^{-1} to be tentatively taken as the »borderline wavenumber« between the two 0—0--lines for the p-chlorophenyl derivatives. In doing so the CD of the 2-phenyl ethanol moiety and its acetate does not change sign by p-chloro substitution (**46**), whereas that of the benzyl alcohol moiety and its acetate does (**47**, **48**, **51** and **52**). The recorded CD of p,p'-dichloro hydrobenzoin[24] also fits into this scheme. These examples clearly demonstrate again that p-substitution of a chiral phenyl compound by another (achiral) substituent may or may not

influence the sign of the Cotton effect, depending on the nature of all groups; the magnitude and relative signs of Platt's »spectroscopic moments« can explain such behaviour.[26]

The change of the CD-fine structure within the α-band has been ascribed to the presence of at least two conformations with different torsional angles ω_2 or/and ω_3. This view is supported by the CD-data of ringclosed heterocyclic derivatives with trans-configuration of the two phenyl groups, as e. g. **36** and **37**. A diaxial conformation of these is excluded at least for **36** because of the 1 : 3-diaxial Ph : Me interaction,[27] and is proved (although in $CDCl_3$) by the coupling constant $^3J_{H,H} = 12.2$ Hz between the two benzylic protons. Nevertheless change of solvent from isooctane to acetonitril decreases not only the $\Delta\varepsilon$-values but induces also bisignate character into the CD-curve, which must then be caused by a change of the torsional angles ω_2 and ω_3. Similar behaviour was noticed for **37**.

In the CD-spectrum of **53** containing two CH_3CO-groups in p,p'-positions a weak negative Cotton effect with the usual finestructure for the carbonyl chromophore is observed between 370 and 300 nm. Therefore, the CD within the α-band, which should appear around 300 to 290 nm could not be identified with certainty. No such ketone $n \rightarrow \pi^*$ Cotton effect was detectable for **54**, and it also remains doubtful whether the negative CD-band at 291 nm corresponds to one line of the α-band.

In order to study conformational equilibria in more detail measurements of the temperature dependence of the CD in EPA solvent were carried out. For **13** the bisignate Cotton effect at +20 °C has an overall positive rotational strength, while at —160 °C practically only negative CD-lines were observed. Putting a chlorosubstituent into one of the two p-positions allowed the changes of the two chromophores to be monitored separately. In both cases (**46**, **48**), the CD-lines sharpen at lower temperatures as usual, and the $\Delta\varepsilon$-values increase to about double their values found at +20 °C. At least in part this must be due to the higher population of the preferred conformation of both »half-molecules« at —160 °C. As these two Cotton effects have opposite signs the change of sign of the overall rotational strength for **13** with temperature reflects quantitatively the different slopes of these conformational changes.

The diastereoisomer **29** of **13** shown similar behaviour, although small positive CD-lines persist at —150 °C. The CD of **52** (p-Cl to **E**—**I**, X = OAc) increases greatly by cooling (appr. 3 times), whereas for **50** (p-Cl to **E**—**I**, X = $= CH_2OAc$) the only detectable positive 0—0 line CD at +20 °C becomes split and bisignate at —160 °C. Obviously the two conformers of this »half-molecule«, solvated by the ethanol of EPA, have similar energies, and the same holds for the unsolvated species in dioxan and acetonitril solution, in which no hydrogen bridges are possible, even at room temperature. Thus these two solvated species are most probably desolvated at different temperatures.

In view of the practically unaltered CD of 1-phenyl ethylamine (**1**) after protonation, similar comparisons have been made also for other amines, too. The CD of the monoamine **15** as well as that of the diamine **19** is also not altered by protonation, either whereas in all other cases (**14**, **16**, **21**—**23**, **26**, **31**, **32**, **37**) drastic changes (between bisignate und unisignate Cotton effects, or with complete sign inversions) have been noted.

Most interesting is the behaviour of **14**; for the free base as well as for its hydrochloride the anti-conformation is strongly preferred.[28] As $-CH_3$ and $-NH_3^+$ are comparable in size, the salt should form a »quasi-meso form«, whereas with the amino group especially if it is hydrogen-bonded to the solvent ethanol, the difference is expected to be larger. Indeed, $\Delta\varepsilon$ of the hydrochloride of **14** is quite small (—0.07 at 267 nm), but — contrary to expectation — for the free base it is even smaller and positive (+0.01!). Whereas in UV-spectroscopy the replacement of a methyl by $-NH_3^+$ has practically no influence upon the position and intensity of the bands, in CD the charged group differs much more from the methyl than the (solvated) amino group itself. For amino ketones this difference is well known.[29] No such difference should be observable, however, in the CD-spectrum of a compound like (R)-1-phenyl ethylamine (**1**) if the $-NH_2$ and the $-NH_3^+$ groups lie preferably in a plane perpendicular to the benzene plane (conformation A of Figure 1). This is in agreement with the 0—0 line position and the negative sign of the CD of both **1** and 1-HCl.

Noteworthy is also the change of the bisignate Cotton effect of the oxazine derivative **37** by protonation, for which the torsional angle ω_1 is approximately fixed at —60°. Although both Cotton effects are bisignate, the relative intensities of the individual CD-lines are altered appreciably, which indicates either a change of torsional angles ω_2/ω_3 or very different CD-contributions of $-NR_2$ and $-NR_2H^+$.

The influence of internal hydrogen bridges in diols has been checked by comparison of these CD-spectra with those of their bis-O-derivatives. Dimethylation of **7** to **8** and diacetylation of the alcohols **12**, **28**, **45**, **47**, **49** and **51** to **13**, **29**, **46**, **48**, **50**, and **52**, resp., does in no case drastically alter the magnitudes or shapes of the Cotton effects, proving thus that such internal hydrogen bridging plays no important role in acetonitril solution. It is thus rather the torsional angle ω_2 or/and ω_3 that is somewhat altered by the derivatization of the OH, rather than it is ω_1.

A similar investigation was not possible for the aminoalcohols because they could not be dissolved in the same solvents as their diacetates. N-Methylation of **30** to **31** scarcely alter the α-band CD does at least for the hydrochlorides.

Contrary to that, N,O-diacetylation (to **34**) and N-monochloroacetylation (to **33**) of **32** invert the sign of the unisignate Cotton effect; as the same result is found for acetonitril (**33**, **34**) as for ethanol solution (**34**), significant internal hydrogen-bonding does not seem to be important for these compounds. As an amino group and its N-acetate should give contributions of the same sign to the CD, this sign inversion again indicates a change of the conformational equilibrium.

A few cyclic derivatives of 1,2-diphenyl ethanes have been prepared for comparison (**36** through **44**), because the torsional angle around the »aliphatic« C—C-bond is then fixed to appr. + 60° or — 60° for both the cis- and trans-compounds[30]. Since only for those of the open-chain analogues with threo configuration the preferred Ph—C—C—Ph torsional angle is also ± 60°, one should not expect any drastic changes of the CD-spectra by ring closure for this relative configuration, provided that 1) the sign of this preferred torsional angle is the same as that in the ring-closed compound, and 2) the torsional

angles around the Ph—C-bonds are similar in both cases .For the molar rotations, such a differentiation between threo- and erythro-isomers by comparison with their ring-closed analogues is well known.[31]

The open-chain analogues have not been available for all of these compounds; the threo-pairs **36**/**28**, **37**/**23** and **42**/**35** show similar α-band Cotton effects. The morpholine derivative **41** has the same absolute configuration as the 1,3-dioxane **36**, and indeed the Cotton effects are similar. The compounds **38** and **42** are heterochiral analogues and their Cotton effects are enantiomorphic to one other, which is in agreement with this. On the other hand, in the last two latter of the available three erythro-pairs **39**/**E-32**, **40**/**E-33** and **43**/**E-34** the α-band Cotton effects have opposite signs.

COTTONOGENIC DERIVATIVES

The phthalimide group has been suggested[32] for the determination of absolute configuration of aryl alkyl amines, although the characteristic Cotton effect around 300 nm depends very much on the preferred conformation.[33] It was hoped that at least for amines of a very similar structure this method could be used also in the 1,2-diphenylethane series, too. It turned out, however, that this was not the case. (*S*)-1-Phthalimido-1-phenylethane (**2**) gives a positive Cotton effect in dioxan or acetonitrill solution, in accord with the published data for methanol solution.[32] A replacement of the methyl group by the hydroxybenzyl rest to **18** inverts this Cotton effect, and for the similar compound **25** two (dioxan) or even three (acetonitril) Cotton effect appear around 300 nm. On the other hand, the two diastereoisomers **20** and **27**, both containing two of such phthalimido chromophores, give very similar bisignate Cotton effects, which differ only slightly in their magnitudes. No direct correlation exists, therefore, between these additional Cotton effects and the absolute configuration.

p- and β,β'-BAND CD

Substitution of benzene shifts also the p- and β,β-bands somewhat bathochromically; Cotton effects have occasionally been reported but because of the very small signal/noise ratio the data are not generally very accurate. The situation is somewhat better with rigid molecules, and from the CD--spectra of octahydro anthracene derivative **56** it can be inferred that the Cotton efects of the β- and the β'-absorption have opposite signs to one other.[35] For its parent compound **55** $\Delta\varepsilon_{max}$ within the p-band is only 2.[13,34] If two phenyl chromophores are close to one other, their transition dipoles can interact and may give rise to exciton couplets. For the α-band CD these transition moments are too small to give detectable interactions, but for the p- and both the β- and β'-absorption exciton couplets should be expected.

Although exciton CD-couplets are often quite strong and can easily be identified, the application of the coupled oscillator theory[36] to the 1,2-diphenyl ethanes is not so straightforward, because one has to take into account the mutual coupling between 3 transition moments on each phenyl ring, which gives rise to the superposition of 9 couplets between appr. 220 to 190 nm!

In other contexts it has been claimed that only the interaction of the $\| - E_{1u}$-components has to be considered, because the interaction of moments, of which at least one is perpendicular to the C—Ph-bond, should be cancelled due to slightly hindered rotation. However,as one can easily proove by model

calculation this is only the case of the torsional angle $\omega_1 = 0°$ or 180°; any other arrangement of the three consecutive bonds (Ph)—C—C—(Ph) is chiral and must, therefore, even under the assumption of completely free rotation give a nonvanishing CD. The $|\Delta\varepsilon|$-values of such couplets involving the B_{1u}--transition do not exceed 10.

The model calculation using simple point-dipole approximation and parameters, taken from a UV-spectrum of toluene, recorded under the same conditions as the CD-spectra, and with a reasonable choice of torsional angles for a cyclic compound like **41** (so as to get a CD-spectrum comparable to that of this compound), rendered the results given in Table I.

TABLE I

Individual CD-couplets of a Model 1,2-diphenyl Ethane of the Usual Bond Lengths and Bond Angles. Other Parameters Used: ω_{Ph-C} *for Each Phenyl Ring* $= +160°$, $\omega_{(Ph-)C-C(-Ph)} = +60°$; E_{1u}*-band: Dipole Strength* $= 370 \times 10^{-40}$ *cgs,* $\lambda_{max} = 193$ *nm, Halfband Width* $= 2800$ cm^{-1}; B_{1u} *Band: Dipole Strength* $= 200.4 \times 10^{-40}$ *cgs,* $\lambda_{max} = 208$ *nm, Halfband Width* $= 2600$ cm^{-1}. $\parallel$ *Refers to the Transition Polarized Parallel to the Ph—C — bond,* $\perp$ *to one Polarized Perpendicular to it. The* B_{1u}*-Transition is Parallel Polarized*

Interacting transition moment vectors	First maximum λ_{max} ($\Delta\varepsilon_{max}$)	Second maximum λ_{max} ($\Delta\varepsilon_{max}$)
B_{1u}/ B_{1u}	213 (+8.4)	203 (—8.7)
B_{1u}/ $\parallel E_{1u}{}^{a}$	208 (—15.0)	193 (+15.1)
B_{1u}/ $\perp E_{1u}{}^{b}$	208 (+11.1)	193 (—11.2)
$\parallel E_{1u}$/ $B_{1u}{}^{a}$	208 (—15.0)	193 (+15.1)
$\parallel E_{1u}$/ $\parallel E_{1u}$	198 (+79.6)	188 (—83.9)
$\parallel E_{1u}$/ $\perp E_{1u}{}^{c}$	198 (—70.1)	189 (+73.1)
$\perp E_{1u}$/ $B_{1u}{}^{b}$	208 (+11.1)	193 (—11.2)
$\perp E_{1u}$/ $\parallel E_{1u}{}^{c}$	198 (—70.1)	189 (+73.1)
$\perp E_{1u}$/ $\perp E_{1u}$	194 (+125.8)	184 (—130.9)
Sum curve: 214(+4.8), 199(+55.7), 187(—59.7)		

[a, b, c] Only with identical torsional angles ω_{Ph-C} these pairs give identical CD-couplets.

These calculations show that a) CD-couplets involving the B_{1u}-transition are generally 5 to 10 times smaller than those between E_{1u}-transition moments, and b) CD-bands at wavelengths longer than appr. 210 nm stem only from B_{1u}/B_{1u}-interactions. Any such band between 210 to 220 nm indicates, therefore, the presence of a skew conformation since the interactions of the B_{1u}--transition moments (and the $\parallel$-polarized E_{1u}-transition moments) are achiral in the anti-periplanar conformation. On the other hand, the appearance of a strong CD-couplet involving an E_{1u}-transition does not exclude anti-periplanar conformation, because chiral interactions are possible between either the two $\perp$-polarized E_{1u}- or one of them with the $\parallel$-polarized E_{1u}- or the B_{1u}-transition moment. E. g. with $\omega_{(Ph-)C-C(-Ph)} = 180°$ and both $\omega_{Ph-C} = +75°$ the two $\perp$--polarized E_{1u} moment vectors give rise to a strong negative CD-couplet ($\Delta\varepsilon_{max} = -58$ at 198 nm, $+61$ at 189 nm). These calculations showed furthermore that for several combinations of the three pertinent torsional angles relatively small changes may completely invert the appearance of the CD--spectrum (e. g.: $\omega_{(Ph-)C-C-Ph)}$ always set to $+55°$, $\omega_{Ph-C} = +45$ for both phenyls: $\Delta\varepsilon_{max} = +9.0$ (213 nm), -48.5 (197 nm), and $+50.9$ (190 nm); $\omega_{Ph-C} =$

$= +50°$: +7.1 (214 nm), −0.8 (207 nm), +9.0 (201 nm), −5.5 (196 nm), +15.1 (191 nm); $\omega_{Ph-C} = +55°$: +5.3 (215 nm), −2.0 (208 nm), +44.0 (199 nm) and −48.1 (186 nm)). Therefore, also because of the simultaneous presence of always several conformers, the CD-spectra below 230 nm will not allow the exact determination of the conformations, nor of their contributions to the equilibria. Nevertheless, some conclusions can be drawn from these CD-spectra and a few regularities have been determined. That such discussions of CD-couplets are reasonable has been proved by the synthesis and CD-investigation of **53** and **54**, for which the B_{1u}/B_{1u}-interaction could be »isolated« and increased because of the presence of the CH_3CO-substituents in p-positions. For the threo-stereoisomer **53**§ with (R,R)-configuration the skew conformation with a negative torsional angle $\omega_{(Ph-)C-C(-Ph)}$ is the preferred one, and this arrangement must lead to a negative CD-couplet for the interaction of transition moments which lie (appr.) parallel to the Ph—C bond (∥-polarized). Indeed this is found, and the strong negative CD-couplet between 260 and 240 nm increases even at lower temperatures (cf. Figure 3), in full agreement with the expectation. **54** shows a similar negative CD-couplet, but of smaller intensity; this is in accord with the NMR-data[10] which indicated that the population of this skew conformer with negative torsional angle is smaller than for **53**. Its CD-couplet is unsymmetric at room temperature, where several conformations are present, but becomes »conservative« below −100 °C.

The treatment of ring-closed derivatives with trans-configuration of the two phenyl groups (resulting from cyclization of threo-isomers) should not pose any problem for the CD between 220 and 210 nm since the torsional angle ω_1 is confined to values around +60° or −60°, depending on the absolute configuration, as has also been proved by ^{1}H-NMR-spectroscopy.[30] The first band of the B_{1u}/B_{1u} CD-couplet should be positive for a positive torsional angle $\omega_{(Ph-)C-C(-Ph)}$; the second band might already be obscured by overlap with other CD-bands. The first Cotton effect does not depend on the torsional angles ω_{Ph-C} either. Indeed such positive Cotton effects have been found for **36** and **41**, and negative ones for **37** (cf. Figure 4) and **38**. Relatively strong positive Cotton effects are also given by **42** and **44**, but these substances contain amide groupings in the ring, whose $n \rightarrow \pi^*$ CD-band may appear in the same wavelength range. For the E_{1u}/E_{1u}-couplets no prediction is possible, because some of them will depend on the torsional angles ω_{Ph-C}; however, it has been experimentally determined that in each of the mentioned cases a distinct CD-band of the same sign as the Cotton effect just described appears between 198 and 191 nm. It is five to ten times larger than the 215 nm Cotton effect for **36**, **37**, **38** and **41**, but smaller than that for **42** and **44**. It is either the excition interaction with the amide chromophore which is responsible for this difference, or the change of the torsional angle(s) ω_{Ph-C}. **38**, containing the urea moiety in the ring, behaves »normally«.

Since the preferred conformation for the **threo-compounds** without such an additional heterocyclic ring is also the one with the skew arrangement of the two phenyls, all compounds belonging to the same stereochemical family as (R,R)-2,3-diphenyl butane (**5**) should show similar CD-curves to that of **37**,

§ We use here and in the following paper[11] the stereodescriptors »threo« and »erythro« instead of lk and ul[37] in order to be independent of the type of substituents, and, therefore, of the sequence rule.

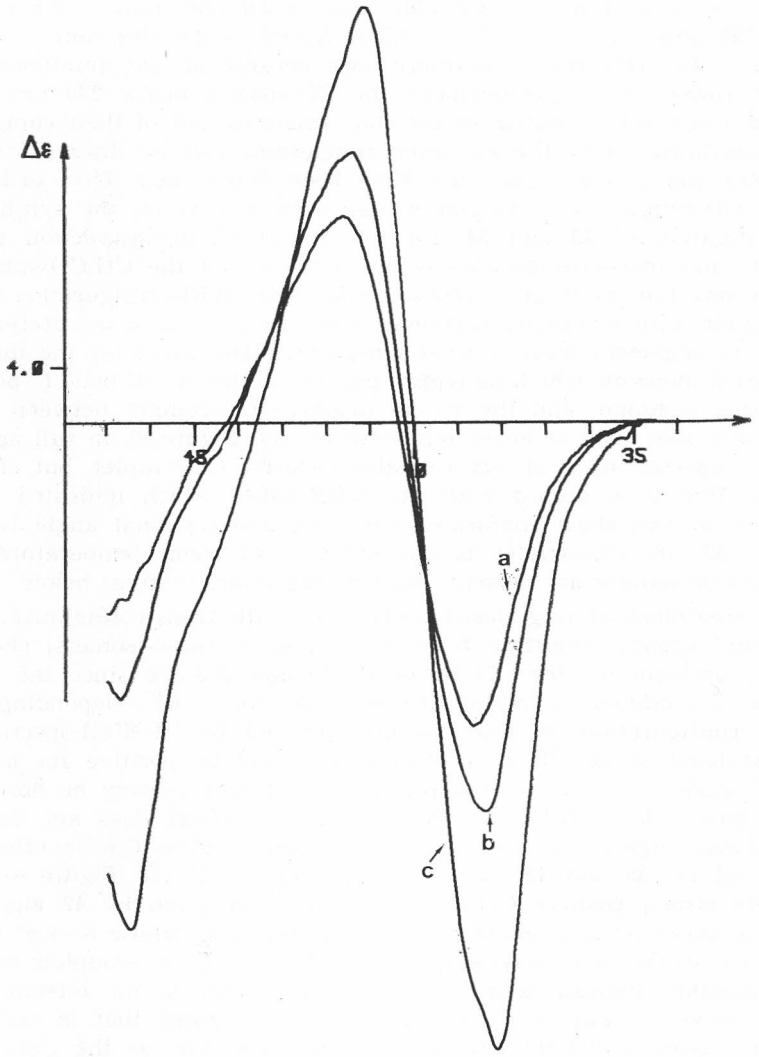
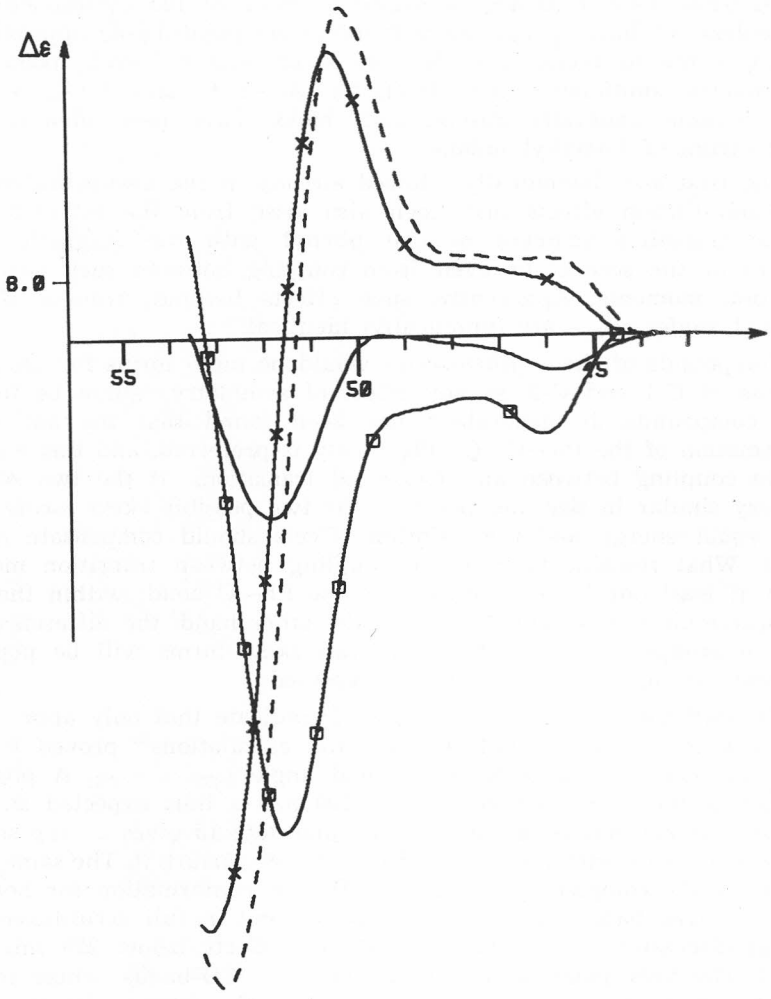


Figure 3. CD of **53** in diethyl ether/isopentane/ethanol (5 : 5 : 2) at +20 °C (a), —60 °C (b), and —160 °C (c). Abscissa as in Figure 2.

irrespective of the type of the substituents X and Y. For **5** (cf. Figure 4) this is indeed the case, and several other compounds show the same CD-properties (**21**, free base and hydrochloride; **23** free base, shape of CD is temperature dependent, **26** (hydrochloride), **E-28**, **E-29**, **E-49**, **E-50**, **E-51** and **E-52**), although some contain an additional ester function.

A few compounds of this series give, however, a completely different CD spectrum (**6**, **7**, **8** and **9** (cf. Figure 4)), which is characterized by a positive Cotton efect between 220 and 205 nm, and an additional strong positive CD-band around 200 nm. It is remarkable that these are four of the available



——— 5 (methylcyclohexane/isopentane 1:3)
--------- 8 (isooctane)
X—X—X— 9 (isooctane)
□—□—□— 37-HCl (acetonitril)

Figure 4. CD below 230 nm for **5** (methylcyclohexane/isopentane (1 : 3), **8** (isooctane), **9** (isooctane), and **37-HCl** (acetonitril). Abscissa as in Figure 2.

five compounds containing two identical substituents at C-1 and C-2, and that their parent compound **5** manifested the »usual« behaviour. It would be contrary to all other experience and to molecular mechanical calculations if one would deduce a positive torsional angle $\omega_{(Ph-)C-C-Ph)}$ from the positive CD around 215 nm. As these compounds showed no anomalities within the

α-band when their CDs are compared to those of the corresponding »half--molecules« we have to assume that the crude point-dipole approximation is not applicable to them. It could also mean that for such molecules with C_2-symmetry additional Cotton effects for $^1A_{1g} \rightarrow {}^1E_{1g}$ and/or $^1A_{1g} \rightarrow {}^1E_{2g}$ transitions become unusually strong; such bands have been identified in the CD-spectrum of 1-methyl indane.[20]

The first are magnetically allowed already in the unsubstituted benzene; additional Cotton effects may then also arise from the interaction of the electric transition moment of one phenyl with the magnetic transition moment of the second, or even from coupling between such two magnetic transition moments. Apparently, such effects become stronger if the two torsional angles ω_{Ph-C} are (practically) identical.

Compounds of the *erythro-series* would be meso forms for identical substitution at C-1 and C-2, so any effect of symmetry cannot be tested with these compounds. In general, it has been found that the anti-periplanar conformation of the Ph—C—C—Ph moiety is preferred, and this will exclude exciton coupling between all ||-polarized transitions. If the two substituents are very similar in size and polarity, the two possible skew forms will have appr. equal energy and their Cotton effects should compensate to a great extent. What remains then is the coupling between transition moments of which at least one is perpendicular to the Ph—C bond; within the B_{1u}-band no appreciable CD is expected. If, on the other hand, the difference between the two groups is greater, then the two skew forms will be populated to different extents and a larger CD is expected.

^{1}H-NMR-spectra[28] of **12** (cf. Figure 5) indicate that only appr. 1/3 of the molecules adopt the ap conformation, and calculations[28] proved that this is solely the one with a positive torsional angle $\omega_{(Ph-)C-C-Ph)}$. A positive CD--couplet in the range between 220 to 200 nm is thus expected and its first (positive) branch has been observed. Its diacetate **13** gives a very similar CD, although coupling with the ester transitions may perturb it. The same methods[28] proved nearly complete preference of the ap conformation for both **14** and **19** as the free base and the hydrochloride, and in full accordance with the general discussion only very weak Cotton effects below 220 nm were recorded. The very polar amino alcohol **16** gives CD-bands, whose magnitudes and even signs depend on the solvent and on the presence of charge on the nitrogen. Ordinary calculations cannot include solvent interaction in more detail than as a bulk property, and NMR-measurements have not been done in different solvents.[28] The sign of the 215 nm Cotton effect can tentatively be taken as an indication of the preference for the (+ sc) vs. (— sc) conformation. Its diacetate **17** gives a CD which is comparable to that of the free base of **16** in hydrocarbon solvent, and to that of the diacetate **13**. For these two analogous diacetates a very similar distribution of their conformations is expected.

Only appr. 40% of the amino alcohol moiety **32** adopt the ap conformation[38], the ratio of (+ sc)- to (— sc)-form is calculated [39] to be larger than 2 : 1. A positive CD is then expected around 216 nm and this is indeed found. The sign of the next, stronger Cotton effect below 200 nm depends on the solvent, but this might also be due to different preferred torsional angles ω_{Ph-C}. The erythro-compounds **33** and **34** contain an additional amide chromo-

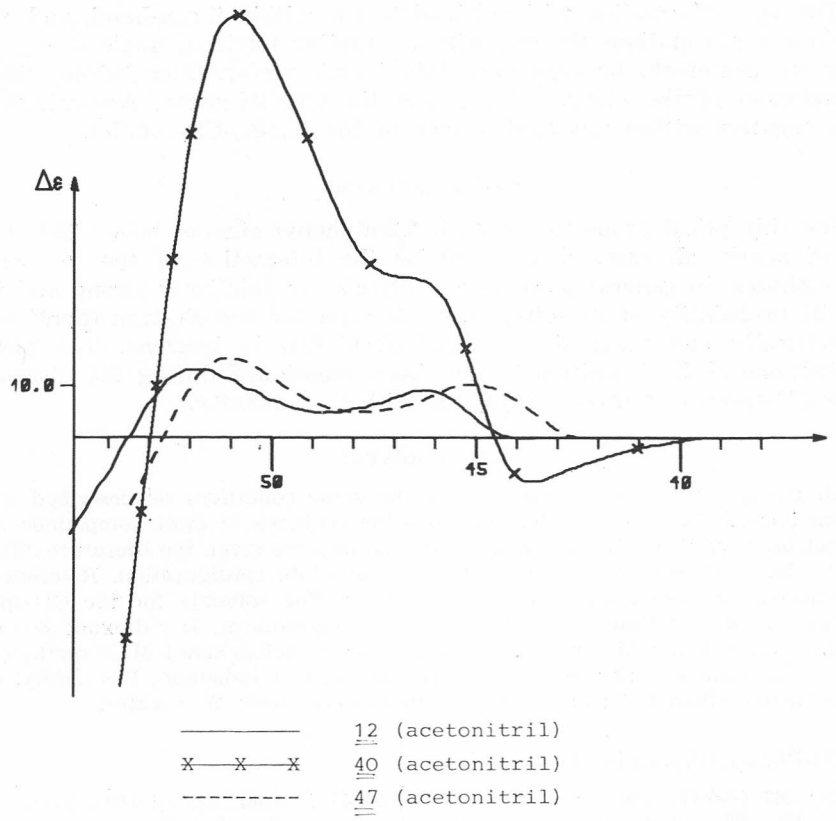


Figure 5. CD of **12**, **40**, and **47** below 260 nm (acetonitril solution). Abscisa as in Figure 2.

phore, which gives its own Cotton effect but may also perturb by exciton interaction; no conclusions can be drawn from these CD-spectra.

The compounds **45** to **48** (cf. Figure 5) are p-substituted by Cl in one of the two phenyl rings; their CD-spectra below 220 nm are virtually identical with those of the unsubstituted diphenyl ethanes, as one would expect, since Cl is a relatively weak perturber of the aromatic π-system.

The ring-closed morpholine derivative **39** should show a preference for the (— sc) conformation according to discussions in the literature.[30,40] In accordance with this a negative Cotton effect within the first branch of the CD-couplet has been measured. The CD of the morpholinone **40** (cf. Figure 5) is extremely strong below 220 nm and shows an additional (negative) CD at 229 nm; within the α-band no exceptionally large Cotton effect was noticed, however. We take this as a clear indication of the μ,μ-interaction between the amide $\pi \rightarrow \pi^*$- and the benzene E_{1u}-transitions. Because of similar interactions in the oxazolidinone **43** no conclusions about its preferred conformation can be made from the CD.

As the CD-spectrum of **4** shows, even the presence of one single substituent in the ethane moiety suffices to give strong Cotton effects below 220

nm. The ap conformation will not lead to CD within the p-band, and of the two skew conformations the one with a negative torsional angle $\omega_{(Ph-)C-C(-Ph)}$ should be preferred, because only this (— sc) conformation allows the ap--arrangement of the phenyl at C-2 and the CH_2OH-group. Accordingly the CD is negative within this first branch of the B_{1u}/B_{1u}-CD-couplet.

OTHER CD-BANDS

The chiroptical properties of such 1,2-diphenyl ethanes below 220 nm are thus in nearly all cases determined by the interaction of the two phenyl chromophores; in general these Cotton effects are relatively strong and there is small probability of detecting any CD-band for the E_{2g}-transition[20] which is electrically and magnetically dipole-forbidden in benzene. The possible contributions of E_{1g}-transitions[20] have been mentioned during the discussions of the CD-spectra of threo-compounds with C_2-symmetry.

EXPERIMENTAL

All CD-spectra were recorded under the same conditions as described in our previous paper.[1] The following text presents the synthesis of those compounds which have not been published before. When only CD-data are given the literature citations refer to the syntheses and determinations of absolute configuration. References to NMR-spectra are given separately, if necessary. The solvents for the CD-spectra are abbreviated as follows: A = acetonitril; C = chloroform; D = dioxan; E = ethanol; H = cyclohexane; M = methanol; MH = methylcyclohexane; MI = methylcyclohexane + isopentane (1 : 3); ML = dichloromethane; O = isooctane; P = diethyl ether + isopentane + ethanol (5 : 5 : 2); TF = trifluoroacetic acid; W = water.

(+)-(R)-Phenylethylamin (**1**)

(O): 267 (—0.11), 260 (—0.12), 255 (—0.09), 249 (—0.06), 225 (+0.04), 211 (—1.06), 208 (—1.22), 202 (—1.08), 198 (—1.02), negative at shorter wavelengths.

(E): 267 (—0.09), 261 (—0.09), 255 (—0.06), 249 (—0.04), 217 (+0.16), 213 (+0.19), 210 (+0.13), 207 (+0.08), negativ below 205 nm.

(E + H^+): 266 (—0.05), 259 (—0.06), 255 (—0.03), 253 (—0.03), 213 (+0.10).

(—)-(S)-1-Phenyl-1-phthalimido-ethane (**2**)

(A): 315 (+0.48), 305 (+0.48), 289sh (+0.40) 261sh (+0.07), 255sh (+0.04), 237 (—1.70), 221 (+2.42), 232sh (—1.58), 211 (—3.28), 205 (—2.42).

(D): 320 (+0.45), 237 (—3.12).

(—)-Menthyl-3-phenyl-propanoate (**3**)

(A): 267 (—0.01), 263 (—0.01), 260 (—0.01), 256 (—0.01), 254 (—0.01), 252 (—0.01), 221 (+0.63), 213sh (+0.56), 209sh (+0.52), negative at shorter wavelengths.

(—)-(R)-2,3-Diphenyl-1-propanol (**4**)

Prepared by reduction of (-)-menthyl-(R)-2,3-diphenylpropanoate[6] with LAH in Et_2O for two hours at room temp.; oil with $[\alpha]_D^{19} = -71.54$ ($CHCl_3$), lit.[41] for E-**4** $[\alpha]_D = +117.3$ (ether).

(A): 271 (+0.01), 268 (—0.09), 260 (—0.11), 255 (—0.09), 219 (—12.40), 211sh (—5.30), 195 (—19.40), positive at shorter wavelengths.

(O): 269 (—0.16), 262 (—0.16), 256 (—0.11), 218 (—9.80), 196 (—18.50), positive at shorter wavelengths.

(—)-(2R,3R)-2,3-Diphenylbutane (**5**)[6] *(NMR*[42]*)*

(A): 269 (+0.07), 266 (—0.18), 259 (—0.22), 252 (—0.16), 217 (—7.18), 212 (—3.38), 206 (—3.34), 203 (—4.38), negative at shorter wavelengths.

(D): 272 (+0.03), 268 (—0.29), 262 (—0.31), 255 (—0.24), 219 (—6.04), 206 (—2.40).

(C): 272 (+0.02), 268 (—0.27), 261 (—0.40).

(MI): 268 (—0.31), 262 (—0.40), 255 (—0.30), 250 (—0.24), 246 (—0.20), 219 (—5.94), 210sh (—1.37), 205sh (—1.26), 193 (—25.20).

(—)-(2R,3R)-1,4-Dicyano-2,3-diphenylbutane (**6**)[10] *(NMR*[10,43]*)*

(A): 270 (+0.31), 267 (—0.05), 263 (+0.23), 260 (—0.09), 256 (+0.04), 253 (—0.04), 217 (—0.94), 214sh (+3.30), 211 (+3.56), 198 (+10.04), 190 (—38.60).

(O): 269 (+0.01), 266 (+0.002) 262 (+0.01), 219 (+0.42), 209sh (+1.02), 196 (+7.17), 186 (—12.70).

(—)-(2R,3R)-1,4-Dihydroxy-2,3-diphenylbutane (**7**)[6] *(NMR*[10,43]*)*

(A): 269 (+0.49), 266 (—0.002), 262 (+0.42), 255 (+0.18), 248 (+0.07), 221 (+2.94), 215 (+3.68), 210 (+3.06), 198 (+11.34).

(A + TF): 220 (+4.24), 214 (+5.12), 211 (+4.86), 198 (+9.30).

(O): 270 (+0.34), 268 (—0.17), 264 (+0.28), 261 (—0.13), 257 (+0.08), 254 (—0.05), 221 (+3.50), 214sh (+2.90), 206sh (+3.60), 199 (+17.40), 191 (—47.20).

(D): 270 (+0.47), 268 (—0.03), 264 (+0.43), 257 (+0.20), 251 (+0.10), 222 (+7.76), 216 (+7.88), 213 (+7.86).

(C): 269 (+0.42), 266 (—0.07), 262 (+0.34), 259 (—0.08), 255 (+0.12).

(—)-(2R,3R)-1,4-Dimethoxy-2,3-diphenylbutane (**8**)[10]

(A): 270 (+0.27), 267 (—0.06), 263 (+0.22), 260 (—0.07), 257 (+0.06), 254 (—0.02), 220sh (+2.60), 215 (+3.40), 205 (+3.90), 190 (—45.33).

(O): 270 (+0.13), 267 (—0.13), 264 (+0.12), 261 (—0.11), 257 (+0.07), 254 (—0.04), 251 (+0.06), 220 (+12.00), 211 (+11.80), 208 (+12.20), 198 (+50.00), 190 (—86.40).

(—)-(2R,3R)-1,4-Diacetoxy-2,3-diphenylbutane (**9**)[10] *(NMR*[10,43]*)*

(A): 269 (+0.37), 267 (—0.08), 263 (+0.31), 260 (—0.04), 256 (+0.11), 249 (+0.05), 219 (+3.90), 212 (+5.50), 197 (+14.70), 190 (—47.00).

(O): 270 (+0.21), 267 (—0.16), 263 (+0.16), 260 (—0.13), 257 (+0.06), 254 (—0.04), 250 (+0.03), 218 (+8.60), 197 (+43.60), 188 (—81.00).

(—)-(2R,3R)-1,4-Di-p-tolylsulfonyloxy-2,3-diphenylbutane (**10**)[6]

(A): 269 (+0.41), 262 (+0.28), 256 (+0.06), 237 (+0.18), 234 (+0.24), 230 (—0.53), 226 (—0.43), 218 (+1.36), 214 (+1.58), 204 (—0.82), 199 (+2.30), 193 (—19.30), 187 (—13.50).

(D): 269 (+0.26), 263 (+0.13), 260 (—0.09), 253 (—0.10), 250 (—0.06), 219 (+5.74), 215 (+5.69).

(+)-(2R,3R)-1,4-Dimethoxycarbonyl-2,3-diphenylbutane (**11**)[10] *(NMR*[10,43]*)*

(A): 270 (+0.22), 267 (—0.09), 263 (+0.13), 260 (—0.14), 254 (—0.08), 222sh (—3.60), 218 (—4.90), 211 (+1.82), 208 (+1.70), 200 (+4.74), 192 (—23.70).

(O): 270 (+0.16), 267 (—0.07), 263 (+0.13), 261 (—0.05), 257 (+0.06), 220 (+5.40), 210 (+12.10), 198 (+44.50), 188 (—59.90).

(+)-(1R,2S)-1,3-Dihydroxy-1,2-diphenylpropane (**12**)[8] *(NMR*[28]*)*

(A): 267 (—0.06), 265 (+0.02), 260 (—0.06), 257 (+0.04), 254 (—0.01), 218 (+9.80), 194 (+14.70), 190 (+13.00), negative at shorter wavelengths.

(A + TF): 267 (—0.08), 265 (+0.02), 261 (—0.08), 254 (—0.02), 251 (+0.04), 217 (+11.40), 197 (+17.90).

(D): 268 (—0.06), 266 (+0.02), 262 (—0.06), 259 (+0.01), 256 (—0.04), 252 (+0.01), 219 (+5.78).

(C): 267 (—0.06), 260 (—0.06), 254 (—0.02), 250 (+0.02).

(+)-(1R,2S)-1,3-Diacetoxy-1,2-diphenylpropane (**13**)[9]

(A): 272 (+0.003), 268 (—0.02), 266 (+0.03), 262 (—0.02), 258 (+0.06), 252 (+0.04), 246 (+0.02), 217 (+11.20), 194 (+35.70), negative at shorter wavelengths.

(O): 272 (+0.002), 268 (—0.02), 264 (+0.03), 261 (—0.01), 258 (+0.05), 251 (+0.04), 246 (+0.02), 217 (+11.40), 212 (+11.40), 193 (+34.10), negative at shorter wavelengths.

(P): (+20 °C): 272 (+0.01), 269 (+0.04), 266 (+0.04), 261 (—0.01), 252 (+0.04).

(—60 °C): 271 (+0.003), 268 (—0.02), 266 (+0.04), 264 (+0.04), 261 (—0.03), 258 (+0.06), 252 (+0.05).

(—100 °C): 272 (+0.001), 268 (—0.04), 266 (+0.03), 264 (+0.04), 261(—0.05), 258 (+0.06), 255 (—0.03), 252 (+0.04).

(—160 °C): 268 (—0.11), 266 (+0.02), 261 (—0.13), 258 (—0.08), 255 (—0.08), 249 (—0.05).

(+)-(1R,2R)-1-Amino-1,2--diphenylpropane (**14**)[6] *(NMR*[28]*)*

(E): 268 (+0.01), 263 (—0.00), 259 (—0.006), 216 (+3.04), 207 (+2.54), 199 (+1.80), negative at shorter wavelengths.

(E + H^+): 267 (—0.07), 260 (—0.07), 254 (—0.05), 251 (—0.05), 219 (—0.44), 210 (—0.82), 208 (—1.12), negative at shorter wavelengths.

(+)-(1R,2R)-1-Amino-3-bromo-1,2-diphenylpropane (**15**)[6]

(E): 268 (+0.10), 261 (+0.10), 254 (+0.06), 248 (+0.04), 216 (+3.04), 208sh (+2.70), 205sh (+3.34), 201 (+4.35), negative at shorter wavelengths.

(E + H^+): 268 (+0.06), 261 (+0.05), 257 (—0.01), 254 (+0.02), 252 (—0.008), 247 207 (+3.10), 203 (+3.71), 199 (+4.82), 192 (—8.60).
(+0.008), 217 (+0.78).

(+)-(2R,3R)-3-Amino-2,3-diphenyl-1-propanol (**16**)[6,4] *(NMR*[44]*)*

(E): 269 (+0.02), 266 (+0.02), 262 (+0.01), 259 (+0.01), 219 (+3.07), 215 (+2.99), 207 (+3.10), 203 (+3.71), 199 (+4.82), 192 (—8.60).

(E + H^+): 267 (—0.11), 260 (—0.12), 254 (—0.07), 251 (—0.07), 217 (—4.90), 212 (—4.40), 203 (—6.00), 194 (—22.00).

(W + H^+): 266 (—0.10), 259 (—0.10), 253 (—0.07), 249 (—0.04), 216 (+1.80), 213 (+1.50), 203 (—1.10), negative at shorter wavelengths.

(MI_{13}): 270 (+0.06), 263 (+0.06), 256 (+0.04), 254 (+0.04), 220 (+4.50), 210 (+5.60), 206 (+6.60), 202 (+9.50), 199 (+7.70), 188 (—30.40).

(+)-(2R,3R)-O,N-Diacetyl-3-amino-2,3-diphenyl-1-propanol (**17**)

Prepared by treatment of **16** with excess of Ac_2O in the presence of Et_3N at room temp. for 40 hours; the crude product was recrystallized from dilute methanol, m. p. 154—5 °C, $[\alpha]_D^{26} = +27.34$ ($CHCl_3$) (Found: C, 73.14, H, 7.02. Calc. for $C_{19}H_{21}NO_3$: C, 73.28, H, 6.80%); ^{1}H-NMR ($CDCl_3$): $J_{2,3} = 9.8$ Hz.

(A): 268 (—0.37), 261 (—0.39), 254 (—0.24), 215 (+13.50), 198 (+20.60), 188 (—23.50).

(—)-(2,3S)-2,3-Diphenyl-3-phthalimido-1-propanol (**18**)[45] *(NMR*[45]*)*

(A): 311sh (—0.09), 297 (—0.13), 287sh (—0.11), 266 (+0.29), 259 (+0.60), 238 (+2.22), 218 (—7.06), 211 (+2.06), 202 (—1.22).

(D): 240 (+3.88), 220 (—9.20), 211 (+4.28).

(—)-(1S,2R)-1,3-Diamino-1,2-diphenylpropane (**19**)[45] *(NMR*[28]*)*

(E): 267 (+0.01), 265 (+0.006), 263 (—0.004), 261 (+0.005), 256 (—0.01), 219 (—4.05), 212sh (—1.38), 206sh (—1.80), negative at shorter wavelengths.

(E + H^+): 266 (+0.01), 260 (—0.01), 255 (—0.01), 249 (—0.01), 214 (—1.27), 208sh (—0.98), 204sh (—0.72), negative at shorter wavelengths

(+)-(1S,2R)-1,2-Diphenyl-1,3-diphthalimidopropane (**20**)[45] *(NMR*[45]*)*

(A): 326 (+0.19), 317sh (+0.15), 282 (—0.37), 263 (—0.14), 259 (+0.08), 239 (+4.12), 235sh (+2.46), 224 (+11.82), 222 (+12.54), 210 (—6.24), 205 (—7.04).

(D): 331 (+0.21), 319 (+0.20), 283 (—0.53), 265 (—0.27), 240 (+3.14), 223 (+17.16), 209 (—8.52).

(—)-(1R,2S)-1-Amino-1,2-diphenylpropane (**21**)[6] *(NMR*[28]*)*

(E): 267 (—0.42), 260 (—0.45), 254 (—0.27), 218 (—5.30), 211sh (—2.20), 204sh (—2.20), 200sh (—2.60), 193 (—11.80).

(E + H^+): 269 (+0.26), 266 (—0.25), 262 (+0.14), 259 (—0.34), 252 (—0.24), 246 (—0.12), 216 (—11.50), 211sh (—8.20), 206sh (—8.20), 201sh (—9.30), 192 (—59.10).

(W + H^+): 268 (+0.26), 265 (—0.12), 261 (+0.15) 258 (—0.19), 251 (—0.13), 216 (—4.86), 203sh (—2.74), 198sh (—5.78), negative at shorter wavelengths.

(—)-(1R,2S)-1-Amino-3-bromo-1,2-diphenylpropane (**22**)[6]

(E): 271 (+0.05), 267 (—0.21), 260 (—0.27), 254 (—0.18), 220 (—2.49), 211sh (+3.23), 209 (+3.81), 201 (+3.70), negative at shorter wavelengths.

(E + H^+): 269 (+0.26), 266 (—0.03), 262 (+0.22), 258 (—0.08), 255 (+0.08), 252 (—0.05), 222 (—0.67), 217 (—1.53), 212sh (+3.90), 210 (+4.68), 205 (+6.10), negative at shorter wavelengths.

(—)-(2S,3R)-3-Amino-2,3-diphenyl-1-propanol (**23**)[6,4] *(NMR*[28,44]*)*

(E): 270 (+0.15), 267 (—0.12), 263 (+0.07), 260 (—0.14), 253 (—0.08), 210 (+2.28), 207 (+2.30), 202 (+2.48), 193 (—17.40).

(E + H^+): 268 (+0.45), 261 (+0.39), 258 (—0.06), 255 (+0.12), 251 (—0.04), 220 (+0.52), 216 (—1.23), 213 (+1.05), 206sh (—1.53), 202 (—2.17), 190 (—56.80).

(W + H^+): 268 (+0.35), 261 (+0.28), 254 (+0.08), 247 (+0.03), 219 (+0.29), 216 (—0.14), 213 (+0.66), negative below 200 nm.

(MI) (+20 °C): 271 (+0.19), 269 (—0.41), 265 (+0.004), 261 (—0.43), 255 (—0.27), 248 (—0.13), 220 (—4.40), 211 (+2.20), 206sh (—2.00), 194 (—44.10), positive at shorter wavelengths.

(0 °C): 221 (—4.00), 213 (+1.60), 210 (+1.10), 205 (—3.60).

(—40 °C): 220 (—3.94), 213 (+1.60), 210 (+0.52).

(—80 °C): 225 (—1.14), 220 (—2.18), 213 (+4.98), 210 (+5.12), 204 (+4.02).

(—120 °C): 226 (—1.54), 221 (—1.78), 212sh (+10.40), 208sh (+12.60), 205 (+15.32).

(—160 °C): 225 (—2.10), 220 (—2.40), 213sh (+10.80), 205sh (+17.80), 203 (+19.60).

(+)-(2S,3R)-O,N-Diacetyl-3-amino-2,3-diphenyl-1-propanol (**24**)

Prepared from **23** according to the procedure described for **17**; the crude product was recrystallized from acetone/*n*-hexane, m. p. 143—144.5 °C, $[\alpha]_D^{20} = +74.9$ ($CHCl_3$) (Found: C, 73.51, H, 6.93) (^{1}H-NMR ($CDCl_3$): $J_{2,3} = 9.5$ Hz).

(A): 270 (+0.24), 267 (—0.27), 263 (+0.16), 260 (—0.30), 254 (—0.17), 247 (—0.08), 213 (+17.00), 202sh (+14.80), 194 (—19.00).

(+)-(2S,3R)-2,3-Diphenyl-3-phthalimido-1-propanol (**25**)[45] *(NMR*[45]*)*

(A): 333 (—0.13), 320sh (—0.05), 309 (+0.10), 290 (—0.08), 268 (+0.52), 261 (+0.73), 254 (+0.52), 223 (+12.60), 212 (—6.30), 202sh (+3.50), 199 (+4.20), 192 (—10.40).

(D): 336 (—0.15), 311sh (+0.24), 283 (+0.11) 270 (+0.89), 263 (+0.87), 255 (+0.63), 225 (+15.90), 212 (—8.40).

(—)-(1R,2R)-1,3-Diamino-1,2-diphenylpropane (**26**)[45] *(NMR*[28,45]*)*

(E): 271 (+0.07), 267 (—0.26), 260 (—0.32), 254 (—0.20), 248 (—0.11), 218 (—3.45), 209 (+2.80), 199 (+3.40), 194 (—9.70).

(E + H^+): 268 (+0.32), 261 (+0.33), 258 (—0.05), 254 (+0.16), 251 (—0.06), 216 (—7.80), 211sh (—4.16).

(D): 272 (+0.04), 268 (—0.12), 261 (—0.14), 253 (—0.07).

(+)-(1R,2R)-1,2-Diphenyl-1,3-diphthalimidopropane (**27**)[45] *(NMR*[45]*)*

(A): 325 (+0.33), 315 (+0.33), 300 (—0.07), 292 (—0.11), 274 (—0.03), 269 (+0.27), 265 (—0.19), 235 (—13.10), 219 (+40.90), 199 (—3.70), 191 (—17.00).

(D): 329 (+0.53), 317 (+0.65), 295 (—0.22), 274 (—0.25), 236 (—13.80), 220 (+57.70).

(+)-(1S,2S)-1,3-Dihydroxy-1,2-diphenylpropane (**28**)[9] *(NMR*[28]*)*

(A): 270 (—0.06), 267 (+0.22), 259 (+0.27), 252 (+0.17), 217 (+8.28), 200sh (+7.80), 192 (+27.60).

(A + TF): 269 (—0.09), 266 (+0.27), 259 (+0.33), 253 (+0.22), 246 (+0.12).
(E): 270 (—0.03), 267 (+0.33), 260 (+0.36), 253 (+0.23), 218 (+5.00), 198 (+4.12), 194 (+8.90).
(E + TF): 270 (—0.02), 267 (+0.35), 260 (+0.38), 253 (+0.24).
(D): 272 (—0.02), 267 (+0.33), 260 (+0.36), 254 (+0.22), 220 (+9.44).
(C): 266 (+0.38), 259 (+0.46), 252 (+0.33), 245 (+0.18).

(+)-(1S,2S)-1,3-Diacetoxy-1,2-diphenylpropane (**29**)[9] *(^{1}H-NMR ($CDCl_3$): $J_{1,2}$ = 9.4 Hz)*

(A): 269 (—0.20), 267 (+0.09), 262 (—0.12), 259 (+0.16), 252 (+0.12), 218 (+4.30), 202sh (+2.70), 200 (+4.10), 194 (+28.90).
(O): 270 (—0.10), 267 (+0.23), 263 (—0.03), 260 (+0.27), 253 (+0.18), 217 (+3.97), 209 (—1.07), 206 (—0.88), 199 (—2.67), 192 (+31.10).
(P) (+20 °C): 270 (—0.14), 267 (+0.18), 263 (—0.07), 260 (+0.23), 253 (+0.15).
(—20 °C): 269 (—0.19), 267 (+0.23), 263 (—0.11), 260 (+0.28), 253 (+0.19), 247 (+0.12).
(—60 °C): 269 (—0.27), 267 (+0.24), 262 (—0.18), 260 (+0.31), 253 (+0.20), 246 (+0.12).
(—100 °C): 269 (—0.39), 267 (+0.25), 262 (—0.27), 259 (+0.31), 252 (+0.20), 246 (+0.11).
(—150 °C): 269 (—0.61), 267 (+0.19), 262 (—0.41), 259 (+0.26), 255 (—0.08), 252 (+0.16).
(MI) (+20 °C): 270 (—0.11), 267 (+0.26), 263 (—0.04), 260 (+0.31), 253 (+0.20), 247 (+0.12).

(+)-(2R,2S)-3-Amino-2,3-diphenyl-1-propanol (**30**)[6,4] *(NMR*[28,44]*)*

(E + H^+): 269 (—0.41), 262 (—0.34), 255 (—0.13), 220 (—0.65), 214 (—1.54), 209sh (—0.78), 207sh (+0.49), 205 (+0.84).

(+)-(2R,3S)-2,3-Diphenyl-3-methylamino-1-propanol (**31**)

Prepared by conversion of **30** into the corresponding (4*S*, 5*R*)-trans-4,5-diphenyl-2-oxotetrahydro-1,3-oxazine ($[\alpha]_D^{20}$ = +143.0 ($CHCl_3$)) by reaction with phosgene according to ref.[46] and reduction of the latter with $LiAlH_4$ according to ref.[47] The crude oil product was converted into hydrochloric salt and purified by recrystallization from dry ethanol ether, m. p. 233—235 °C, $[\alpha]_D^{20}$ = +44.9 (ethanol) .
(Found: N, 4.87, Calc. for $C_{16}H_{20}ClNO$: 5.04%).

(E): 270 (—0.11), 267 (+0.19), 263 (—0.04), 260 (+0.22), 254 (+0.12), 226 (—0.74), 218 (+0.21), 213sh (—0.98), 209 (—1.12).
(E + H^+): 268 (—0.53), 262 (—0.45), 258 (+0.06), 255 (—0.15), 251 (+0.04), 248 (—0.03), 217 (+1.45), 213 (—1.67), 204 (+1.45), 198 (—1.57), 190 (+43.53).

(+)-(1S,2R)-2-Amino-1,2-diphenylethanol (**32**)[48] *(NMR*[38,39]*)*

(A): 268 (—0.08), 261 (—0.09), 255 (—0.05), 220 (+1.36), 218 (+1.54), 206sh (—1.46), 202sh (—2.14), negative at shorter wavelengths.
(E): 267 (—0.05), 261 (—0.05), 254 (—0.04), 225 (—1.12), 218 (+1.53), 215 (+1.10), 209sh (+0.75), negative at shorter wavelengths.
(E + H^+): 267 (—0.04), 264 (+0.07), 261 (—0.07), 258 (+0.13), 251 (+0.11), 244 (+0.08), 216 (+14.20), 207sh (+10.00), 195 (+20.20).
(C): 269 (—0.13), 262 (—0.14), 255 (—0.09).

(+)-(1S,2R)-2-Chloracetylamino-1,2-diphenylethanol (**33**)[48] *(NMR*[48]*)*

(A): 266 (+0.30), 259 (+0.35), 252 (+0.26), 245 (+0.21), 218sh (—2.40), 213sh (—4.28), 208 (—4.66), 205sh (—4.54), 199sh (—2.00), 192 (—7.40), 185 (—21.20).
(D): 268 (+0.34), 260 (+0.31), 254 (+0.08).
(C): 267 (+0.17), 260 (+0.18), 253 (+0.11).

(+)-(1S,2R)-O,N-Diacetyl-2-amino-1,2-diphenylethanol (**34**)

prepared from **32** according to procedure described for **17** and **24**, the crude product recrystallized from methanol, m. p. 232—3 °C, $[\alpha]_{546}^{20}$ = +12.30 ($CHCl_3$). (Found: C, 72.91, H, 6.58, Calc. for $C_{18}H_{19}NO_3$: C, 72.50, H, 6.47%).

(A): 267 (+0.19), 260 (+0.21), 253 (+0.14), 247 (+0.08), 223 (—1.42), 212sh (—1.14), 207sh (—2.66), 200 (—5.80), 192 (+21.30).

(E): 267 (+0.17), 260 (+0.17), 253 (+0.11), 247 (+0.05), 218 (—4.40), 211sh (—5.30), 203sh (—7.30), 199 (—9.30), 189 (+30.13).

(+)-(1R,2R)-2-Chloracetylamino-1,2-diphenylethanol (**35**)[48] *(NMR*[48]*)*

(A): 267 (+0.50), 260 (+0.54), 253 (+0.40), 246 (+0.33), 220 (+2.10), 208 (—4.46), 202sh (—3.90), 198sh (—3.70), 191 (—9.00).

(D): 268 (+0.64), 261 (+0.68), 255 (+0.49), 248 (+0.35), 222 (+6.08), 210 (—7.84).

(C): 268 (+0.34), 261 (+0.34), 254 (+0.21).

(+)-(4S,5S)-2,2-Dimethyl-trans-4,5-diphenyl-1,3-dioxane (**36**), prepared from **28** according to ref.[27]. The crude product was purified by preparative TLC on silicagel (n-hexane/ether = 17 : 1) and recrystallized afterwards from methanol: m. p. 81—3 °C, 40% yield, $[\alpha]_D^{30} = +118.8$ ($CHCl_3$) (Found: C, 80.76, H, 7.68, Calc. for $C_{18}H_{20}O_2$: C, 80.56, H, 7.51%).

(A): 273 (+0.01), 269 (—0.05), 266 (+0.13), 259 (+0.19), 252 (+0.15), 246 (+0.10), 218 (+11.30), 191 (+56.80).

(O): 268 (+0.45), 261 (+0.52), 255 (+0.37), 218 (+15.50), 197sh (+24.80), 189 (+38.90).

(—)-(4R,5S)-trans-4,5-Diphenyl-3-methyl-tetrahydro-1,3-oxazin (**37**), *(CD in (M)*[49]) prepared from **23** according to ref.[50]. The corresponding crude hydrochloric salt was purified from ethanol/ether, yield 62%, m. p. 218—20 °C, $[\alpha]_D^{20} = -140.3$ (ethanol) (Found: N, 4.68, Calc. for $C_{18}H_{19}ClNO$ 4.80%). The free base is an oil with $[\alpha]_D^{24} = -83.7$ ($CHCl_3$).

(Ac + H^+): 218 (—16.80), 213sh (—10.00), 209sh (—9.40), 194 (—74.00), positive at shorter wavelengths.

(E): 269 (+0.10), 267 (—0.24), 259 (—0.29), 252 (—0.19), 247 (—0.09), 230 (+0.64), 226sh (+0.48), 217 (—7.02), 210sh (—2.40), 201sh (—3.30).

(E + H^+): 268 (+0.31), 264 (—0.08), 261 (+0.26), 258 (—0.14), 254 (+0.06), 251 (—0.11), 217 (—6.90), 208sh (—3.90), 204 (—3.30), 201 (—3.40), 198sh (—3.90).

(D): 270 (+0.11), 267 (—0.19), 263 (+0.04), 260 (—0.22), 253 (—0.11), 233 (+0.46), 219 (—4.67), 210sh (—1.10).

(—)-(4R,5R)-trans-4,5-Diphenyl-2-oxo-hexahydro-1,3-diazine (**38**), prepared from **26** according to ref.[51]. The resulting crude crystalline product was purified twice from benzene/n-hexane, yield 57% pure **38**, m. p. 225—6 °C, $[\alpha]_D^{20} = -124.0$ ($CHCl_3$). (Found: N, 11.1, Calc. for: $C_{16}H_{16}N_2O$: 10.82%) (NMR[52]).

(A): 267 (—0.21), 260 (—0.25), 253 (—0.19), 247 (—0.10), 218 (—6.60), 208sh (—2.80), 205sh (—3.70), 193 (—21.10).

(D): 267 (—0.31), 260 (—0.36), 253 (—0.28), 219 (—6.78), 206sh (—2.00).

(—)-(2R,3S)-cis-2,3-Diphenyl-morpholine (**39**)[48] *(NMR*[48]*)*

(A): 269 (+0.17), 266 (—0.05), 263 (+0.06), 259 (—0.10), 256 (—0.09), 216 (—4.78), 206sh (—2.32), 195 (—9.10), 191sh (—5.14), 186 (+9.88).

(E): 269 (+0.14), 266 (—0.03), 262 (+0.05), 260 (—0.08), 257 (—0.09), 219 (—2.20), 203 (—2.34), 194sh (—6.14).

(E + H^+): 267 (—0.05), 265 (—0.08), 225 (+1.24), 223sh (+1.16), 218 (—5.53), 209sh (—2.38), 206sh (—2.67).

(D): 270 (+0.18), 267 (—0.07), 263 (+0.10), 259 (—0.12), 256 (—0.09), 253 (—0.15).

(C): 270 (+0.23), 263 (+0.15), 258 (—0.03), 253 (—0.11).

(+)-(2S,3R)-cis-2,3-Diphenyl-5-morpholone (**40**)[48] *(NMR*[30]*)*

A): 267 (+0.51), 259 (+0.62), 252 (+0.44), 229 (—9.40), 216sh (+31.20), 202sh (+66.33), 196 (+84.40), negative below 190 nm.

(D): 268 (+0.66), 259 (+0.73), 253 (+0.56).

(C): 266 (+0.32), 259 (+0.53), 252 (+0.43).

(+)-(2R,3R)-trans-2,3-Diphenyl-morpholine (**41**)[48] *(NMR*[30]*)*

(A): 267 (+0.40), 260 (+0.41), 254 (+0.20), 234 (—0.53), 217 (+7.60), 193 (+66.40), negative at shorter wavelengths.

(E): 268 (+0.44), 260 (+0.46), 255 (+0.30), 231 (—0.72), 216 (+5.2), 205sh (+7.7).

(E + H^+): 267 (—0.15), 264 (+0.11), 261 (—0.28), 258 (+0.09), 254 (—0.18), 235 (—0.05), 217 (+12.80), 207sh (+8.4), 204sh (+11.23).

(D): 268 (+0.52), 261 (+0.52), 255 (+0.30), 218 (+2.56), 215 (+2.82), 210 (+2.68), 208 (+2.38).

(C): 268 (+0.40), 261 (+0.40), 255 (+0.20).

(+)-(2R,3R)-trans-2,3-Diphenyl-5-morpholone (**42**)[48] *(NMR*[30]*)*

(A): 267 (+0.38), 260 (+0.39), 252 (+0.28), 231sh (+4.00), 217 (+18.80), 210sh (+10.30), 206sh (+8.00), 197 (+13.10), negative at shorter wavelengths.

(D): 267 (+0.42), 261 (+0.44), 253 (+0.34), 220 (+12.40), 211sh (+5.32).

(C): 268 (+0.25), 265 (+0.23), 259 (+0.33), 252 (+0.25).

(—)-(4S,5R)-cis-4,5-Diphenyl-2-oxazolidone (**43**)[48] *(NMR*[30]*)*

(A): 269 (—0.04), 264 (—0.09), 259 (—0.11), 253 (—0.08), 246 (—0.06), 218 (—6.32), 215 (—6.04), 210sh (—5.96), 203sh (—8.22), negative at shorter wavelengths.

(D): 269 (+0.05), 266 (—0.04), 262 (+0.03), 258 (—0.09), 253 (—0.07), 246 (—0.05).

(C): 269 (+0.11), 262 (+0.09), 259 (—0.05), 256 (+0.02), 251 (—0.05).

(+)-(4R,5R)-trans-4,5-Diphenyl-2-oxazolidone (**44**)[48] *(NMR*[30]*)*

(A): 267 (+0.20), 260 (+0.23), 254 (+0.17), 218 (+14.50), 196 (+3.70), negative at shorter wavelengths.

(D): 267 (+0.23), 261 (+0.28), 255 (+0.20).

(C): 267 (+0.23), 261 (+0.27), 255 (+0.18).

(+)-(1R,2S)-1,3-Dihydroxy-2-(p-chlorphenyl)-1-phenylpropane (**45**)[9]

(A): 279 (—0.01), 275 (—0.02), 272 (+0.01), 268 (—0.15), 262 (—0.13), 222 (+12.40), 216sh (+7.80), 208sh (+8.60), 204sh (+9.90), 201sh (+14.80), 198 (+18.70).

(+)-(1R,2S)-1,3-Diacetoxy-2-(p-chlorphenyl)-1-phenylpropane (**46**)[9]

(A): 274 (—0.03), 268 (—0.09), 261 (—0.07), 255 (—0.03), 227sh (+4.10), 220 (+8.90), 213sh (+7.10), 206sh (+7.10), 197 (+18.90), negative below 190 nm.

(O): 276 (+0.01), 268 (—0.06), 265 (+0.01), 262 (—0.06), 258 (+0.02), 256 (—0.02).

(P) (+20 °C): 276 (+0.02), 272 (+0.03), 267 (—0.06), 264 (+0.03), 261 (—0.07), 258 (+0.04).

(—60 °C): 277 (+0.03), 271 (+0.03), 268 (—0.08), 264 (+0.04), 261 (—0.07).

(—100 °C): 274 (+0.03), 268 (—0.09), 264 (+0.04), 261 (—0.10).

(—140 °C): 274 (+0.03), 268 (—0.17), 264 (+0.03).

(—160 °C): 274 (+0.08), 268 (—0.18).

(—180 °C): 274 (+0.03), 268 (—0.21).

(+)-(1R,2S)-1,3-Dihydroxy-1-(p-chlorphenyl)-2-phenylpropane (**47**)[9]

(A): 275 (+0.05), 267 (+0.16), 260 (+0.16), 253 (+0.12), 222 (+11.10), 196 (+16.30), negative at shorter wavelengths.

(+)-(1R,2S)-1,3-Diacetoxy-1-(p-chlorphenyl)-2-phenylpropane (**48**)[9]

(A): 275 (+0.11), 267 (+0.19), 260 (+0.17), 253 (+0.11), 219 (+12.70), 195 (+24.20), negative below 190 nm.

(O): 276 (+0.12), 267 (+0.20), 260 (+0.17), 253 (+0.11), 217 (+12.30), 196 (+22.70), negative below 190 nm.

(P) (+20 °C): 275 (+0.14), 267 (+0.22), 260 (+0.20), 254 (+0.14).

(—20 °C): 275 (+0.16), 267 (+0.26), 260 (+0.24), 254 (+0.14).

(—60 °C): 275 (+0.18), 267 (+0.30), 260 (+0.25), 253 (+0.16).

(—100 °C): 275 (+0.19), 267 (+0.32), 260 (+0.26), 253 (+0.16).

(—160 °C): 274 (+0.21), 267 (+0.35), 260 (+0.25), 253 (+0.16).

(+)-(1S,2S)-1,3-Dihydroxy-2-(p-chlorphenyl)-1-phenylpropane (**49**)[9]

(A): 278 (—0.03), 275 (+0.04), 268 (+0.34), 261 (+0.37), 255 (+0.24), 222 (+10.90), 197 (+22.10), negative below 190 nm.

(+)-(1S,2S)-1,3-Diacetoxy-2-(p-chlorphenyl)-1-phenylpropane (**50**)[9]

(A): 278 (—0.04), 274 (+0.04), 268 (+0.35), 261 (+0.36), 255 (+0.24), 223 (+10.40), 213 (—3.10), 204sh (+7.10), 197 (+24.50), negative at shorter wavelengths.
(D): 275 (+0.10), 268 (+0.51), 262 (+0.47).
(P) (+ 20°C): 276 (+0.14), 268 (+0.53), 261 (+0.50), 255 (+0.32).
(—40 °C): 275 (+0.16), 268 (+0.65), 261 (+0.58).
(—100 °C): 278 (—0.01), 275 (+0.16).
(—140 °C): 277 (—0.03), 274 (+0.13).
(—160 °C): 276 (—0.04), 274 (+0.08).

(+)-(1S,2S)-1,3-Dihydroxy-1-(p-chlorphenyl)-2-phenylpropane (**51**)[9]

(A): 275 (—0.07), 270 (—0.22), 267 (+0.05), 263 (—0.14), 259 (+0.07), 256 (—0.02), 252 (+0.06), 247 (+0.04), 222 (+10.30), 195 (+28.5), negative below 190 nm.

(+)-(1S,2S)-1,3-Diacetoxy-1-(p-chlorphenyl)-2-phenylpropane (**52**)[9]

(A): 274 (—0.27), 269 (—0.46), 262 (—0.32), 255 (—0.15), 249 (—0.05), 221 (+3.90), 196 (+22.90), 194 (+24.00), negative at shorter wavelengths.
(O): 275 (—0.26), 269 (—0.37), 262 (—0.23), 259 (+0.02), 256 (—0.08), 252 (+0.03), 230 (—0.85), 220 (+2.41), 213 (—2.08), 194 (+26.70), negative at shorter wavelengths.
(P) (+20 °C): 275 (—0.28), 269 (—0.41), 262 (—0.27), 256 (—0.11).
(—20 °C): 275 (—0.33), 269 (—0.50), 262 (—0.32), 255 (—0.11).
(—60 °C): 275 (—0.41), 269 (—0.59), 262 (—0.39), 256 (—0.15), 249 (—0.04).
(—100 °C): 275 (—0.51), 269 (—0.75), 262 (—0.49), 255 (—0.17).
(—160 °C): 274 (—0.79), 269 (—1.06), 262 (—0.68), 255 (—0.24).

(—)-(2R,3R)-2,3-Di-(p-acetylphenyl)-butane (**53**)[10]

(A): 259 (—22.30), 241 (+15.40), 214 (—16.60), 199 (—8.03), 190 (+15.10), positive below 195 nm.
(O): 257 (—21.90), 239 (+12.80), 212 (—11.50), 197 (—8.90), positive below 195 nm.
(P) (+20 °C): 259 (—21.90), 240 (+14.90), 213 (—13.80).
(—20 °C): 259 (—25.00), 241 (+16.60), 214 (—16.90).
(—60 °C): 261 (—28.00), 242 (+19.50), 214 (—20.00).
(—100 °C): 261 (—32.20), 242 (+22.60), 214 (—24.40).
(—130 °C): 261 (—39.60), 243 (+22.80), 214 (—34.10).
(—160 °C): 262 (—45.10), 243 (+29.90), 215 (—36.40).
(MI) (+20 °C): 257 (—23.00), 238 (+13.80), 212 (—12.40).
(—20 °C): 258 (—25.40), 239 (+14.93), 212 (—14.47).
(—60 °C): 258 (—27.77), 239 (+16.40), 212 (—16.00).
(—90 °C): 259 (—27.40), 240 (+15.80), 212 (—16.70).
(—110 °C): 260 (—13.00), 241 (+8.00), 213 (—7.30).
(—130 °C): 261 (—7.00), 243 (+5.00), 218 (—5.70).
(—150 °C): 265 (—7.22), 245 (+5.6), 218 (—6.14).

(+)-(2R,3R)-2,3-Di-(p-acetylphenyl)-1,4-dimethoxycarbonyl-butane (**54**)[10]

(A): 291 (—0.17), 258 (—7.08), 240 (+7.60), 202 (+2.06), 197 (—0.78), 189 (+5.78).
(P) (+20 °C): 261 (—0.87), 241 (+5.90), negative below 230 nm.
(—20 °C): 261 (—1.25), 241 (+6.18), negative below 230 nm.
(—60 °C): 262 (—2.24), 242 (+6.55), negative below 230 nm.
(—100 °C): 261 (—5.16), 242 (+6.94).
(—160 °C): 262 (—12.98), 243 (+8.36).
(E): 262 (—3.72), 243 (+7.48), negative below 230 nm.
(E : A = 1 : 3): 259 (—5.96), 240 (+7.32).
(E : A = 1 : 1): 260 (—4.80), 243 (+6.26), 241 (+6.22).
(E : A = 3 : 1): 261 (—5.12), 242 (+6.88), 240 (+6.88).
(D): 258 (—4.52), 241 (+7.12), 239 (+6.74), negative below 230 nm.

(4aR,9aR)-6,7-Dimethoxy-trans-1,2,3,4,4a,9,9a,10-octahydroanthracene (**56**) (O): 295.5 (—0.71), 289.5 (—1.02), 285 (—1.07), 280.5 (0.96), 232 (—3.50), 205 (—13), 194 (+14).

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SAŽETAK

Cirkularni dikroizam optički aktivnih 1,2-disupstituiranih 1,2-difeniletana. Dio II. Spojevi bez skupine COOR na benzilnom C-atomu

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(R,R)-hidrobenzoni i homohiralno analogni threo-spojevi opće formule Ph—CHX—CHY-Ph (X = Y; X ≠ Y; Y = H) pokazuju negativnu 0—0—CD-liniju ispod 37200 cm^{-1} i/ili pozitivnu neposredno iznad te vrijednosti, što se može objasniti konformacijskim ravnotežama oko veze Ph—C. Za navedenu je konfiguraciju Cottonov efekt kod 220—210 nm negativan, ako je X ≠ Y (ili ako je Y = H), u drugim slučajevima ne postoji tako jednostavna korelacija. Razlog tomu mogao bi biti Cottonov

efekt unutar E_{1g} ili E_{2g}-prijelaza, premda drugih indikacija za njegovo postojanje nema. Ista pravila vrijede i kada je između X i Y zatvoren prsten, te tako Cottonov efekt kod 220—210 nm ima isti predznak kao i torzijski kut (Ph-)C-C-(-Ph), a isto vrijedi i za Cottnov efekt kod 198—191 nm. Temperaturna ovisnost CD-spektara moguće je objasniti jedino uzimajući u razmatranje kako konformacijske tako i solvatacijske ravnoteže. Uvođenje samo jednog p-kloro-supstituenta pomiče granice između dvije 0—0- CD-linije suprotnog predznaka na 36200 cm^{-1}. Taj pomak dovodi do promjene predznaka CD unutar α-vrpce »polu-molekule« tipa Cl—C_6H_4—C(H, Bn)-OZ, ali ne i u slučaju Cl—C_6H_4—C(H, Bn)—CH_2OZ. p-Kloro-supstitucija ne utječe na Cottonov efekt ispod 220 nm. p,p-Disupstitucija acetilnom skupinom vodi do snažnog batokromnog pomaka p-vrpce. Intenzivni CD-couplet koji odgovara toj vrpci potvrdio je kako apsolutnu konformaciju tih spojeva, ranije određenu s pomoću NMR, a također i apsolutnu konfiguraciju.

Spojevi iz erythro-niza pretežno su pokazivali slabiji Cottonov efekt, koji ne korelira na jednostavan način sa apsolutnom konfiguracijom. Predznak prvog ogranka CD-coupleta kod 220—210 nm (p-vrpca) slaže se pak s onima dobivenim računima molekulske mehanike. Intramolekulska vodikova veza vrlo slabo utječe na CD, kao i na konformacijsku ravnotežu, dok protonacija amino-skupine dovodi u nekim slučajevima do velikih promjena u CD. Ftalimidna skupina nije se pokazala upotrebljivom za kiroptičko određivanje konfiguracije difeniletana opisanih u ovom radu.