1,1,2-Triphenyl-1,2-ethanediol: A Host for Carboxylic Acids and Amides in Coordinatoclathrates☆

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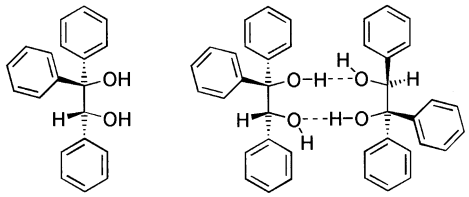
The chiral diols (*R*)- and (*S*)-**1** are found to form inclusion compounds with carboxylic acids and amides, as indicated by the relevant IR spectra. Two clathrates, (*R*)-**1** · CH_3CO_2H and (*S*)-**1** · CH_3NHCHO have been characterized by their crystal structures. The interaction between the diol **1**, which functions as the host compound, and the guest compounds, is based on hydrogen bonds. Enantiomerically pure **1** can serve as chiral solvating agent in NMR spectroscopy.

Inclusion compounds formed by crown ethers and cryptands are the most prominent representatives of the supramolecular structures that rely on non-covalent bonding.[1] In addition, clathrates, which exist only in the solid state, have attracted considerable interest in recent years.[2] Clathrates are becoming more and more important, not only because of their novel and unprecedented structures, but also due to their potential application in the separation of different compounds or isomers. Chiral host molecules, which are either found among natural products or are designed and synthesized, have proved to be suitable for performing enantioselective reactions[2f][2i] and for the resolution of racemates,[2b][2c][2i][2j][2k] as a result of enantio-differentiating clathration. Many of the synthetic host compounds used for these purposes are C_2-symmetric. The tartaric acid derived α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols ("TADDOLs")[3] have found particularly widespread application.[4] Although 1,1-diaryl-1,2-propanediols lack a moiety similar to the rigid backbone of the TADDOLs, they also form clathrates with various types of compounds and facilitate the separation of enantiomers.[5] It seems that the diarylhydroxymethyl group[6] present in both the TADDOLs and the 1,1-diaryl-1,2-propanediols plays a crucial role. Recently, methanol has been shown to form clathrates with the diol **1**, and the crystal structures of *rac*-**1** and (*R*)-**1** have been determined.[7] In this paper, we report for the first time on the preparation, spectroscopy and X-ray structure determination of clathrates in which (*R*)- or (*S*)-1,1,2-triphenyl-1,2-ethanediol (**1**) serves as the host compound.

Monoesters derived from triphenylglycol **1**, available in both enantiomeric forms from (*R*)- and (*S*)-mandelic acid, have found wide application in asymmetric aldol additions[8] and ester enolate−imine condensations.[9] When these reactions are performed, the chiral auxiliary reagent **1** is usually liberated at the end and has to be removed from a mixture of organic compounds.[10] We learned that this is easily accomplished by the addition of acetic acid, which causes the precipitation of the diol **1**. It was this unexpected reaction that prompted the present study.



(*R*)-**1** (*R*)-**1** • (*S*)-**1**

The crystal structure of racemic (*R*)-**1**·(*S*)-**1**[7] reveals that the vicinal hydroxy groups are orientated in a *gauche* conformation, so that one of the phenyl groups of the diphenylhydroxymethyl moiety and the phenyl group at the stereocenter occupy antiperiplanar positions. Hydrogen bonds are directed from the tertiary OH group of one molecule of the diol **1** to the oxygen atom of the secondary OH group in its enantiomer, and vice versa. We have found the IR spectrum, measured in KBr, to be in accordance with this arrangement; only two absorptions due to OH stretching vibrations are seen, one attributable to the non-associated secondary (3559 cm^{-1}) and the other due to the associated tertiary (3458 cm^{-1}) hydroxy group.

However, the crystal structure of enantiomerically pure (*R*)-**1**, determined independently by Weber's group[7] and ourselves, reveals that diol **1** does not show a preference for one single conformation. Both the *anti* and the *gauche* conformations are found in the asymmetric unit, as shown in Figure 1. There are both hydrogen-bonded and free hydroxy groups, a result which again corresponds to the IR spectrum of (*R*)-**1** measured in KBr. The spectrum shows sharp absorption peaks due to the free secondary and ter-

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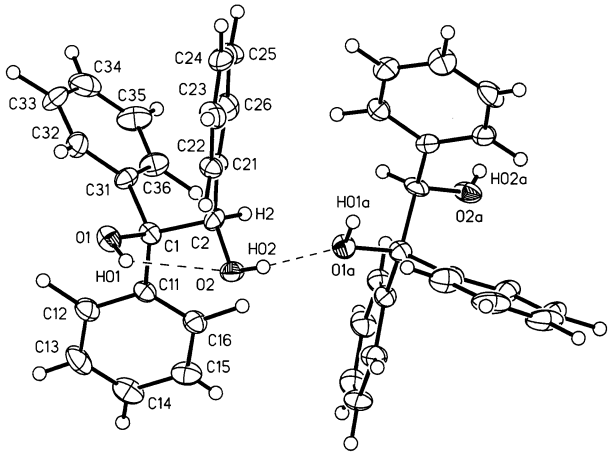
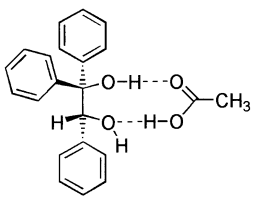
tiary OH groups (3564 and 3536 cm^{-1}), which are assigned to the *anti* conformer, as well as broad absorptions at 3449 (tertiary OH group) and 3328 cm^{-1} (secondary OH group) due to the *gauche* conformer. No cavities can be detected in the crystal structure of (*R*)-**1** and thus, at first glance, this molecule does not appear to be capable of acting as a suitable host for the formation of inclusion compounds.

Figure 1. Crystal structure of (*R*)-**1**; displacement ellipsoids at 25% probability level for all non-hydrogen atoms; in the second molecule of the asymmetric unit only the OH groups are labelled

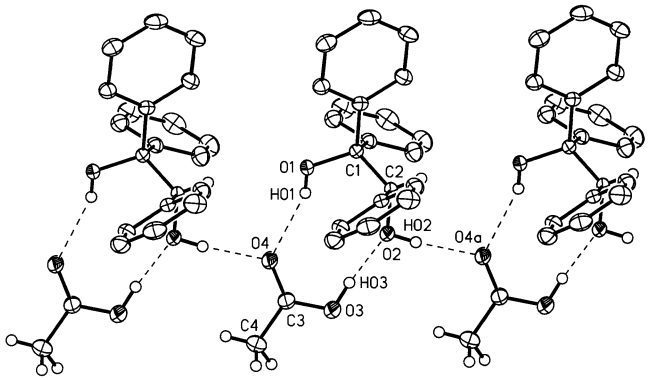


When, however, acetic acid is added to solutions of (*R*)-**1** in aprotic solvents (cyclohexane or diethyl ether), a voluminous, white precipitate forms immediately. The ^1H-NMR spectra, measured in $CDCl_3$, of all samples thus prepared, reveal a 1:1 ratio of (*R*)-**1** and acetic acid. The crystal structure unambiguously confirms this stoichiometric ratio of the clathrate (*R*)-**1** · CH_3CO_2 H, three asymmetric units of which are shown in Figure 2. Clearly, a nine-membered ring is formed as a result of two hydrogen bonds between the diol and the carboxyl moiety. The carboxylic proton bonds to the oxygen atom of the secondary hydroxy group, while the tertiary hydroxy proton is linked to the carbonyl oxygen atom. Since the proton of the secondary alcohol is not involved in the nine-membered ring, it is able to form another, even stronger hydrogen bond, directed toward the carbonyl oxygen atom of the neighboring triphenylglycol−acetic acid unit, and thereby connects the (*R*)-**1** · CH_3CO_2H chelate units together. A view along the *a* axis of the resulting stacks is given in Figure 3. The acetic acid is located in channels, and each molecule of the acid is surrounded by five phenyl groups of the staggered diol (*R*)-**1**. The distance between the guest molecule and the nearest carbon atom of the respective host molecule ranges from 2.916 to 3.847 Å.



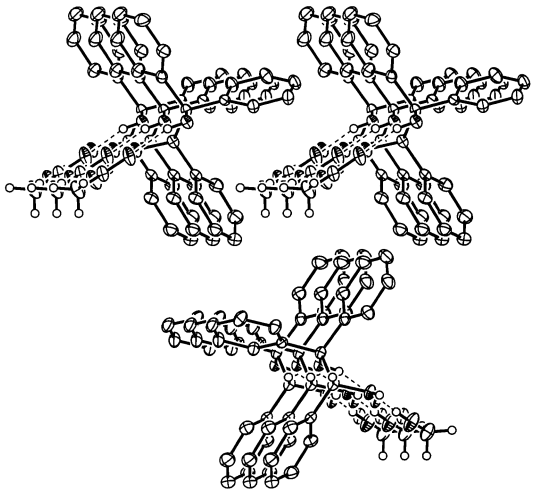
(*R*)-**1** • CH_3CO_2H

Figure 2. Crystal structure of (*R*)-**1** · CH_3CO_2H; displacement ellipsoids at 25% probability level for all non-hydrogen atoms; the aromatic H atoms are omitted for the sake of clarity[a]



[a]Selected distances [Å] and angles [°]: O1−HO1 0.95(7), O1···O4 2.855(3), HO1···O4 2.02(9), O2−HO2 0.83(3), O2···O4a 2.699(3), HO2···O4a 1.87(3), O3−HO3 0.95(10), O3···O2 2.631(3), HO3···O2 2.24(7); O1−HO1···O4 154(3), O2−HO2···O4a 175(3), O3−HO3···O2 174(4).

Figure 3. View along the *a* axis of (*R*)-**1** · CH_3CO_2H showing stacks and channels; displacement ellipsoids at 25% probability level for all non-hydrogen atoms; the aromatic H atoms are omitted for the sake of clarity



The low vibrational frequency of the secondary OH group (3255 cm^{-1}) in the IR spectrum of (*R*)-**1** · CH_3CO_2H measured in KBr also points to clathrate formation. Furthermore, the carbonyl frequency is lowered to 1678 cm^{-1} compared to the values documented for monomeric acetic acid (1788 cm^{-1} in the gas phase)[11a] and the dimeric acid (1747 in the gas phase; 1715 cm^{-1} for the liquid).[11a][11b]

The structure shown in Figure 3 suggests that other carboxylic acids might also be incorporated in the channels. Indeed, on the basis of characteristic IR shifts, we were able to prove the formation of clathrates between (*R*)-**1** and cyclohexyl-, phenyl-, 4-hydroxyphenyl-, chloro-, bromo-, iodo-, and dichloroacetic acid, cinnamic and propionic acid, as well as 2-chloro- and 2-bromopropionic acid. The short hydrogen bond of the secondary OH group is considered to make a key contribution to the stability of the coordinatoclathrates. Thus, the wavenumber $\tilde{\nu}_1$ of the O−H

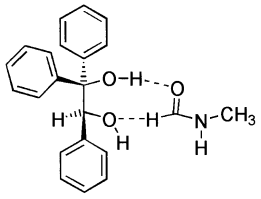
stretching vibration of the *associated* secondary hydroxy group in a *gauche* conformation gives an indication of clathrate formation when compared with the vibration of the *non-associated* secondary hydroxy group. The latter value $\tilde{\nu}_2$ is taken from the IR data of the racemic diol *rac*-**1**, which contains such a free secondary OH group, as indicated by the crystal structure. The differences in wavenumber $\Delta\tilde{\nu} = \tilde{\nu}_1 - \tilde{\nu}_2$ for the various clathrates are given in Table 1; the values are seen to range from 148 to 304 cm^{-1}.

Table 1. Differences between the wavenumbers of the secondary OH vibration in the clathrates and that in diol **1**

Clathrate	$\Delta\tilde{\nu} = \tilde{\nu}_1 - \tilde{\nu}_2$[a]
(*R*)-**1** · CH_3CO_2H	−304
(*R*)-**1** · $PhCH_2CO_2H$	−265
(*S*)-**1** · 4-$HOC_6H_4CH_2CO_2H$	−312
(*R*)-**1** · *c*-C_6H_{11}-CH_2CO_2H	−299
(*R*)-**1** · $ClCH_2CO_2H$	−193
(*R*)-**1** · $BrCH_2CO_2H$	−211
(*R*)-**1** · ICH_2CO_2H	−222
(*R*)-**1** · Cl_2CHCO_2H	−148
(*R*)-**1** · $CH_3CH_2CO_2H$	−252
(*R*)-**1** · *rac*-$CH_3CH(Cl)CO_2H$	−155
(*R*)-**1** · *rac*-$CH_3CH(Br)CO_2H$	−172
(*R*)-**1** · $PhCH{=}CHCO_2H$	−267
(*S*)-**1** · CH_3NHCHO	−199
(*S*)-**1** · $(CH_3)_2NHCHO$	−189

[a] $\tilde{\nu}_1$ = associated *sec.* OH in clathrate (*gauche* conformation); $\tilde{\nu}_2$ = non-associated *sec.* OH in *rac*-**1** (*gauche* conformation) = 3559 cm^{-1}.

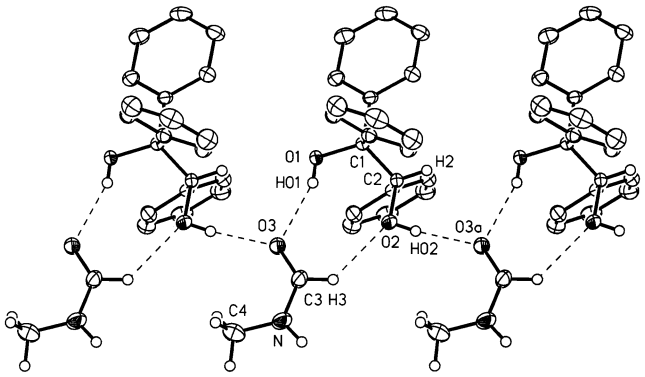
Coordinatoclathrates were also formed between the enantiomerically pure diol **1** and carboxylic amides. In the case of *N*-methylformamide, the host/guest ratio of 1:1 (*S*)-**1** · CH_3NHCHO was not only proved by ^{1}H-NMR spectroscopy, but also by thermogravimetry, which indicated the loss of 17 mass percent for *N*-methylformamide. A differential thermoanalysis (DTA) shows a sharp melting point at 83−84°C, indicating considerable thermostability of the clathrate.



(*S*)-**1** • CH_3NHCHO

Unambiguous proof of the structure of the inclusion compound (*S*)-**1** · CH_3NHCHO was again provided by the crystal structure (Figure 4). A remarkable hydrogen bond between the formyl proton[12] and the oxygen atom at the stereocenter, and a second hydrogen bond of the tertiary hydroxy group to the carbonyl oxygen, result in the formation of an eight-membered ring. Here again, the stability of the clathrate is distinctly enhanced by a hydrogen bond of the secondary hydroxy group directed toward the carbonyl oxygen atom of the neighboring chelate. Despite the different character of the guest molecules, acetic acid and *N*-methylformamide, a similar arrangement of hydrogen bonds is seen in both clathrates. Therefore, it is assumed that the lattice of the host, diol **1**, is similar in both cases, apart from the fact that (*R*)-glycol **1** is used for clathration of acetic acid, whereas the *N*-methylformamide adduct is formed with (*S*)-**1**. Indeed, isotypy results by transformation into the clathrates with identical isomers. Besides *N*-methylformamide, *N*,*N*-dimethylformamide also forms a clathrate when treated with diol (*S*)-**1**; it is characterized by the relatively low frequencies of the hydrogen-bonded hydroxy groups in the IR spectrum (see Table 1 and the Experimental Section).

Figure 4. Crystal structure of (*S*)-**1** · CH_3NHCHO; displacement ellipsoids at 25% probability level for all non-hydrogen atoms; the aromatic H atoms are omitted for the sake of clarity[a]



[a] Selected distances [Å] and angles [°]: O1−HO1 0.78(3), O1···O3 2.847(2), HO1···O3 2.11(4), O2−HO2 0.80(3), O2···O3a 2.762(2), HO2···O3a 1.96(3), C3−H3 0.99(3), C3···O2 3.131(3), H3···O2 2.46(3); O1−HO1···O3 156(3), O2−HO2···O3a 173(3), C3−H3···O2 124(2).

The fundamental difference between *rac*- or (*R*)-triphenylglycol **1** on the one hand, and the clathrates (*R*)-**1** · CH_3CO_2H and (*S*)-**1** · CH_3NHCHO on the other, is clearly evident. The host, diol **1**, does not itself contain tubular voids or channels into which the guest molecules can fit. Instead, the particular structure of the corresponding inclusion compound is only formed when host and guest are combined. Since it is the guest molecule which shapes the structure, the term "coordinatoclathrates", introduced by Weber,[13] is applied to the adducts (*R*)-**1** · CH_3CO_2H and (*S*)-**1** · CH_3NHCHO investigated here.

In our search for applications of the interaction that takes place between triphenylglycol **1** and compounds suitable for clathration, the ^{1}H-NMR spectra of several chiral compounds were recorded in the presence of (*R*)-**1**. It was found that enantiomeric 2-chloropropanoic acid (**2a**) and its amide **2b**, as well as mandelic acid (**3**) and hydroxyphosphonate **4**, show non-equivalence in their spectra; characteristic shift differences are given in the formulae. The ability of (*R*)-**1** to function as a chiral solvating agent is demonstrated in Figure 5, which shows sections of the ^{1}H-NMR spectra of racemic as well as (*S*)- and (*R*)-mandelic acid (**3**) in the presence of (*R*)-**1**. Remarkably, the determination of enantiomeric excesses based thereon is possible simply from 300-MHz ^{1}H-NMR spectra, in contrast to the TADDOLs, for which ^{13}C- or ^{19}F-NMR spectroscopy is

generally required when they are used for resolutions of alcohols.[14]

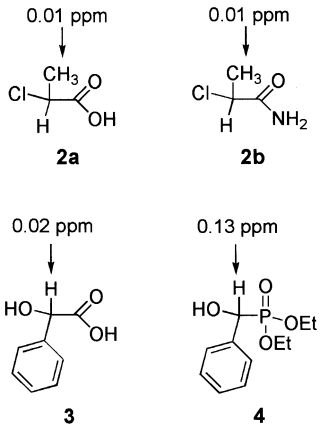
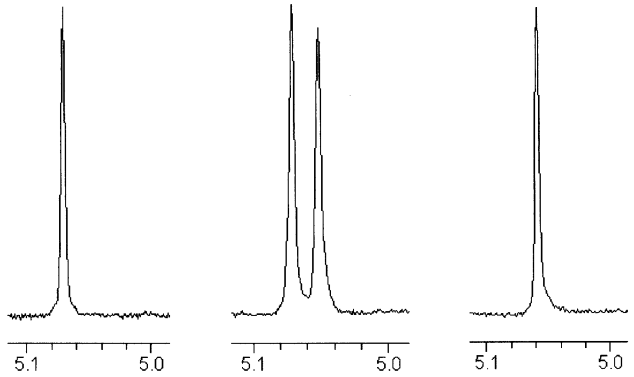


Figure 5. Sections of the ^{1}H-NMR spectra (δ values) of mandelic acid (**3**) in the presence of (*R*)-**1**; left: (*S*)-**3**; middle: *rac*-**3**; right: (*R*)-**3**



In conclusion, inclusion compounds with novel structures are obtained from 1,1,2-triphenyl-1,2-ethanediol (**1**) and polar guest molecules, namely carboxylic acids and amides. The interaction between host and guest molecules is largely determined by hydrogen bonding, as indicated by crystal-structure analyses as well as IR spectroscopy. Comparison of the crystal structures of the diol (*R*)-**1** with those of the adducts (*R*)-**1** · CH_3CO_2H and (*S*)-**1** · CH_3NHCHO shows the latter to be coordinatoclathrates, in which the polar guests are incorporated in channels formed by the host due to aryl stacking and hydrogen bonding between the chelates.

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Experimental Section

(*R*)-, (*S*)- and *rac*-1,1,2-triphenyl-1,2-ethanediol (**1**) were prepared according to ref.[15] Hydroxyphosphonate **4** was obtained by the addition of diethyl phosphite to benzaldehyde; for non-racemic samples of **4**, the reaction was mediated by chiral additives.[16] Diethyl ether was distilled from sodium and stored under nitrogen. Cyclohexane p.a. was purchased from Janssen Chimica. All chemicals used for clathrate formation are commercially available. They were purified by distillation or recrystallization. ^{1}H- and ^{13}C-NMR spectra were recorded with a Varian VXR 300 instrument, FT-IR spectra with Bruker Vektor 22 or Bruker IFS 66 spectrometers, and differential thermoanalyses with a Mettler TG-DTA TA 1 apparatus. Melting points (uncorrected) were determined with a Büchi B-540 melting point apparatus.

(*R*)-*1,1,2-Triphenylethane-1,2-diol* [(*R*)-**1**] *or (S)-1,1,2-Triphenylethane-1,2-diol* [(*S*)-**1**]: Obtained according to ref.[15] as colorless crystals, m.p. 127−128°C; (*R*)-**1**: $[\alpha]_D^{20}$ = +219 (*c* = 1.0, chloroform); (*S*)-**1**: $[\alpha]_D^{20}$ = −220 (*c* = 1.0, chloroform). We do not recommend reaction of methyl mandelate with phenyllithium[7] instead of phenylmagnesium bromide because the lithium reagent causes partial racemization. This is clearly shown by the low optical rotation of (*R*)-**1** obtained in ref.[7]. − IR (KBr): $\tilde{\nu}$ = 3564 cm^{-1} (m, *sec.* OH, non-associated), 3536 (m, *tert.* OH, non-associated), 3449 (m, *tert.* OH, associated), 3328 (m, *sec.* OH, associated), 3056 (m), 3026 (m), 1491 (m), 1446 (s), 1166 (m), 1061 (m), 1007 (m), 766 (m), 750 (m), 736 (s), 715 (m), 697 (s), 613 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.6 [d, *J*(H,H) = 3 Hz, 1 H, CH(O*H*)], 3.2 [s, 1 H, C(OH)Ph_2], 5.5 [d, *J*(H,H) = 3 Hz, 1 H, C*H*(OH)Ph], 7.0−7.4 (m, 13 H, Ar-H), 7.5−7.6 (m, 2 H, Ar-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 77.44 [CH(OH)Ph], 80.70 [C(OH)Ph_2], 126.13 (C of Ar), 126.65 (*para*-C of Ar), 127.01 (C of Ar), 127.29 (*para*-C of Ar), 127.38 (C of Ar), 127.55 (C of Ar), 127.62 (*para*-C of Ar), 128.06 (C of Ar), 128.37 (C of Ar), 138.78, 143.32 and 145.07 (3 *ipso*-C of Ar).

rac-1,1,2-Triphenylethane-1,2-diol (*rac*-**1**): Prepared from racemic methyl mandelate according to the procedure given in ref.[15], colorless needles, yield 66%, m.p. 165.5−167°C. − IR (KBr): $\tilde{\nu}$ = 3559 cm^{-1} (s, *sec.* OH, non-associated), 3458 (m, *tert.* OH, associated), 3059 (m), 3027 (m), 1492 (m), 1448 (s), 1186 (m), 1059 (m), 1039 (s), 1020 (m), 764 (m), 747 (s), 699 (s), 614 (m).

General Procedures for the Preparation of Clathrates from (*R*)- *or* (*S*)-**1**. − *Procedure A:* (*R*)- or (*S*)-1,1,2-triphenylethane-1,2-diol (**1**; 290.3 mg, 1.0 mmol) was dissolved in the minimum amount of dry diethyl ether and 1.0 mmol of the respective neat guest compound was added. After slow, partial evaporation of the solvent, a crystalline or amorphous precipitate formed, which was filtered off, washed with a small amount of dry diethyl ether, and dried at room temp. at oil-pump pressure (1 mbar). The formation of the clathrate was verified by FT-IR spectroscopy and/or crystal-structure analyses, and the host/guest ratio was determined by ^{1}H-NMR spectroscopy (300 MHz, $CDCl_3$). − *Procedure B:* A mixture of (*R*)- or (S)-*1,1,2-triphenylethane-1,2-diol* (**1**; 290.3 mg, 1.0 mmol) and 1.0 mmol of the appropriate guest compound was stirred in 20 ml of cyclohexane. The resulting amorphous and voluminous precipitate was filtered off, washed twice with cyclohexane, and dried at room temp. at oil-pump pressure (1 mbar). The clathration was verified by FT-IR spectroscopy, and the host/guest ratio was determined as described above. −According to these procedures, the following were obtained:

(*R*)-**1** · *CH_3CO_2H* (Procedure A): The product crystallized in colorless needles; yield: 290 mg (83%), m.p. 121−124°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3459 cm^{-1} (s, *tert*. OH, associated), 3255 (m, *sec*. OH, associated), 1678 (s), 1450 (m), 1289 (m), 1035 (m), 898 (m), 755 (m), 743 (s), 698 (s), 612 (m).

(*R*)-**1** · *$PhCH_2CO_2H$* (Procedure B): Colorless, amorphous product was obtained; yield: 360 mg (84%), m.p. 105.5−106.5°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3508 cm^{-1} (m, *tert*. OH, weakly associated), 3294 (m, *sec*. OH, associated), 1677 (s), 1495 (m), 1449 (m), 1013 (m), 752 (m), 748 (m), 745 (m), 725 (m), 697 (s), 611 (m).

(*S*)-**1** · *4-HOC$_6$H$_4$CH$_2$CO$_2$H* (Procedure A): Thin, colorless needles were obtained; yield: 410 mg (93%), m.p. 142.5−143.5°C; molar host/guest ratio = 1:1 (300 MHz, [D$_6$]DMSO). − IR (KBr): $\tilde{\nu}$ = 3489 cm^{-1} (s, *tert*. OH, associated), 3294 (s, *sec*. OH, associated), 1672 (s), 1511 (s), 1448 (m), 1235 (s), 1171 (m), 896 (m), 752 (m), 742 (m), 698 (s), 612 (m).

(*R*)-**1** · *c-C$_6$H$_{11}$-CH$_2$CO$_2$H* (Procedure A): The product crystallized in thin, colorless needles; yield: 320 mg (74%), m.p. 121.5−123°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3508 cm^{-1} (m, *tert*. OH, weakly associated), 3260 (m, *sec*. OH, associated), 2924 (s), 2852 (m), 1684 (s), 1666 (m), 1449 (m), 1167 (m), 1064 (m), 748 (m), 743 (m), 698 (s), 613 (m).

(*R*)-**1** · *ClCH$_2$CO$_2$H* (Procedure A): The clathrate crystallized in thin, colorless needles; yield: 320 mg (86%), m.p. 98−101°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3495 cm^{-1} (m, *tert*. OH, associated), 3366 (s, *sec*. OH, associated), 1700 (s), 1495 (m), 1448 (m), 1213 (s), 1063 (m), 895 (m), 753 (s), 746 (s), 699 (s), 611 (s).

(*R*)-**1** · *BrCH$_2$CO$_2$H:* According to procedure B, a colorless, amorphous product (350 mg, 82%) was isolated, m.p. 95−96°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3516 cm^{-1} (m, *tert*. OH, weakly associated), 3348 (m, *sec*. OH, associated), 1680 (s), 1449 (s), 1185 (m), 1172 (m), 1062 (m), 1014 (m), 896 (m), 754 (s), 743 (s), 699 (s), 613 (s).

(*R*)-**1** · *ICH$_2$CO$_2$H:* According to procedure A, a colorless, amorphous product (390 mg, 82%) was obtained, m.p. 102.5−104°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3513 cm^{-1} (m, *tert*. OH, weakly associated), 3337 (m, *sec*. OH, associated), 1674 (s), 1449 (m), 1284 (m), 1263 (m), 1171 (m), 1062 (m), 1012 (m), 897 (w), 752 (m), 744 (s), 699 (s), 613 (m).

(*R*)-**1** · *Cl$_2$CHCO$_2$H:* Procedure B gave 330 mg (79%) of a colorless, amorphous product, m.p. 91−92°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3526 cm^{-1} (m, *tert*. OH, weakly associated), 3411 (m, *sec*. OH, associated), 1709 (s), 1449 (s), 1194 (m), 1062 (m), 1015 (m), 754 (m), 741 (s), 699 (s), 613 (s).

(*R*)-**1** · *CH$_3$CH$_2$CO$_2$H* (Procedure A): The product crystallized in colorless needles; yield: 350 mg (96%), m.p. 112.5−114°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3497 cm^{-1} (m, *tert*. OH, weakly associated), 3307 (m, *sec*. OH, associated), 3300 (m), 2984 (m), 1686 (s), 1668 (s), 1450 (s), 1173 (s), 1062 (s), 1019 (s), 896 (s), 755 (s), 744 (s), 699 (s), 613 (s).

(*R*)-**1** · *rac-CH$_3$CH(Cl)CO$_2$H:* According to procedure A, (*R*)-**1** (290.3 mg, 1.0 mmol) and *rac*-CH$_3$CH(Cl)CO$_2$H (217.0 mg, 2.0 mmol) were combined to afford 370 mg (93%) of a colorless, amorphous product, m.p. 98.5−99.5°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3504 cm^{-1} (m, *tert*. OH, weakly associated), 3404 (m, *sec*. OH, associated), 1699 (m), 1449 (m), 1204 (m), 1172 (m), 1061 (m), 1019 (m), 896 (m), 754 (m), 741 (s), 699 (s), 613 (m).

(*R*)-**1** · *rac-CH$_3$CH(Br)CO$_2$H:* According to procedure B, (*R*)-**1** (290.3 mg, 1.0 mmol) and *rac*-CH$_3$CH(Br)CO$_2$H (306.0 mg, 2.0 mmol) were stirred in cyclohexane to afford a colorless, amorphous product; yield: 400 mg (90%), m.p. 86−87°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3491 cm^{-1} (m, *tert*. OH, weakly associated), 3387 (m, *sec*. OH, associated), 1676 (s), 1449 (s), 1174 (s), 1061 (s), 1018 (m), 897 (m), 753 (s), 740 (s), 699 (s), 613 (s).

(*R*)-**1** · *PhCH=CHCO$_2$H* (Procedure A): Crystallization gave 390 mg (89%) of thin, colorless needles, m.p. 115−116.5°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3457 cm^{-1} (m, *tert*. OH, associated), 3292 (m, *sec*. OH, associated), 1693 (s), 1672 (s), 1628 (s), 1449 (s), 1284 (s), 1204 (m), 972 (m), 748 (s), 741 (s), 696 (s), 674 (m), 612 (m).

(*S*)-**1** · *CH$_3$NHCHO* (Procedure A): Crystallization yielded 310 mg (89%) of colorless needles, m.p. 89−90°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = 3403 cm^{-1} (s, *tert*. OH, associated), 3360 (s, *sec*. OH, associated), 1664 (s), 1536 (m), 1493 (m), 1449 (m), 1391 (m), 1172 (m), 1047 (m), 756 (s), 746 (s), 699 (s), 618 (m).

(*S*)-**1** · *(CH$_3$)$_2$NCHO:* According to procedure A, a colorless, amorphous product (320 mg, 88%) was obtained, m.p. 86−88°C; molar host/guest ratio = 1:1. − IR (KBr): $\tilde{\nu}$ = ca. 3400 cm^{-1} (shoulder, *tert*. OH, associated), 3370 (m, *sec*. OH, associated), 1658 (s), 1495 (m), 1448 (m), 1169 (w), 1062 (m), 751 (m), 701 (s), 697 (s), 613 (m).

Crystal-Structure Analyses: The crystals were grown as described above. All X-ray diffraction experiments were performed at room temp. using a four-circle diffractometer (Siemens P3) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The intensities were collected in $\omega/2\Theta$ scan mode. No absorption correction was applied (0.078 mm^{-1}< μ < 0.085 mm^{-1}). The structures were solved by direct methods with SHELXTL-PLUS[17a] and refined by full-matrix least squares on F^2 using SHELXL-93[17b] or SHELXL-97[17c] [(*R*)-**1** only]. All non-H atoms were refined with anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100801. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44(0)1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

Crystal Structure Data of (*R*)-**1** · CH$_3$CO$_2$H: C$_{22}$H$_{22}$O$_4$, mol. mass: 350.4 crystal dimensions: 0.20 × 0.40 × 1.00 mm, crystal system: monoclinic, space group: $P2_1$ (no. 4), Z = 2, unit cell: a = 5.857(1), b = 18.043(4), c = 9.048(2) Å, β = 101.19(2)°, V = 938.0(3) Å^3, $\rho_{calcd.}$ = 1.241 mg mm^{-3}. Number of reflections measured: 2430 ($2\Theta_{max}$ = 55°); 2237 unique reflections, of which 1791 with $I > 2\sigma(I)$ were used for the structure solution. All H atoms were refined freely with isotropic U. The refinement finally converged at $R1$ = 0.0374, $wR2$ = 0.2128, 322 parameters. Residual electron density: −0.154 < $\Delta\rho$ < 0.145 e Å^{-3}.

Crystal Structure Data of (*S*)-**1** · CH$_3$NHCHO: C$_{22}$H$_{23}$NO$_3$, mol. mass: 349.4 crystal dimensions: 0.35 × 0.60 × 0.80 mm, crystal system: monoclinic, space group: $P2_1$ (no. 4), Z = 2, unit cell: a = 5.895(2), b = 17.990(5), c = 9.168(2) Å, β = 105.02(2)°, V = 939.1(5) Å^3, $\rho_{calcd.}$ = 1.236 mg mm^{-3}. Number of reflections measured: 2545 ($2\Theta_{max}$ = 56°); 2342 unique reflections, of which 2039 with $I > 2\sigma(I)$ were used for the structure solution. All H atoms were refined freely with isotropic U. The refinement finally converged at $R1$ = 0.0310, $wR2$ = 0.0857, 328 parameters. Residual electron density: −0.130 < $\Delta\rho$ < 0.147 e Å^{-3}.

☆ Dedicated to Professor *Dietrich Mootz* on the occasion of his 65th birthday.

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