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Enantioselective hydrogenation of furancarboxylic acids: a spectroscopic and theoretical study

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Abstract

FTIR and NMR spectroscopy and ab initio calculations were applied to understand the nature of enantioselection in the hydrogenation of the heteroaromatic ring in furan- and benzofurancarboxylic acids over cinchonidine-modified Pd. Most probably, cinchonidine adsorbs on Pd, via its quinoline moiety, approximately parallel to the surface, and the protonated quinuclidine N atom and the OH function of the alkaloid form a cyclic complex with the deprotonated acid dimer (2:1 acid:cinchonidine). The acid dimer adsorbs via the electron-rich furan ring and the carboxylate groups close to parallel to the Pd surface; the furan O atom points toward the OH function of cinchonidine. In this position, hydrogen uptake from the Pd surface results in the (*S*)-enantiomer as the major product. Another cyclic complex (1:1) involving cinchonidine and only one acid molecule is also feasible in solution, but this rigid structure is thermodynamically less favored, and it may be difficult to fulfill the geometric constraints imposed by adsorption on the metal surface.

Keywords: Furancarboxylic acids; Benzofurancarboxylic acid; Asymmetric; Hydrogenation; Cinchonidine; Pd/Al_2O_3; NMR; IR; Ab initio calculations

1. Introduction

Chirally modified Pd has long been considered to be inferior to the Ni–tartaric acid and Pt–cinchonidine (CD) catalyst systems due to the medium enantioselectivities achieved in the hydrogenation of C=C bonds in various α,β-unsaturated ketones [1–4], α,β-unsaturated carboxylic acids [5–12], and esters [13] and the even lower *ee*s characteristic of the saturation of C=N bonds in imines [14,15] and oximes [16]. Migration of the C=C bond, leading to a loss of enantioselectivity, represents a further limitation on the application of chirally modified Pd [9,17,18]. However, the recent successful hydrogenation of the semiaromatic 2-pyrone derivatives has demonstrated that cinchona-modified Pd can afford over 90% *ee* [19–21].

Another recent extension of the application range of CD–modified Pd is the hydrogenation of the heteroaromatic ring in furan- and benzofurancarboxylic acids (Scheme 1) [22]. The enantioselectivities were moderate in this demanding transformation; still, the reaction represents one of the very few examples in which a heterogeneous catalyst performs better than the homogeneous chiral complex counterpart [23]. Further improvement of the enantioselectivity of Pd might be facilitated by clarifying the nature of CD–furancarboxylic acid interaction that is the topic of the present paper.

Three interaction models have been proposed for a similar reaction, the hydrogenation of α,β-unsaturated carboxylic acids over CD–modified Pd. The good enantioselectivity achieved in the hydrogenation of (*E*)-2,3-diphenyl-2-propenoic acid has been attributed to a 1:1 type interaction: the acid is bound to CD via two hydrogen bonds involving the protonated quinuclidine N and the OH group of cinchonidine (Fig. 1, left) [24]. This model fits well to the observed solvent effect [10]; the best selectivities were obtained in strongly polar protic solvent mixtures where dimerization of the carboxylic acid is disfavored. In contrast, in the hydrogenation of aliphatic α,β-unsaturated carboxylic acids

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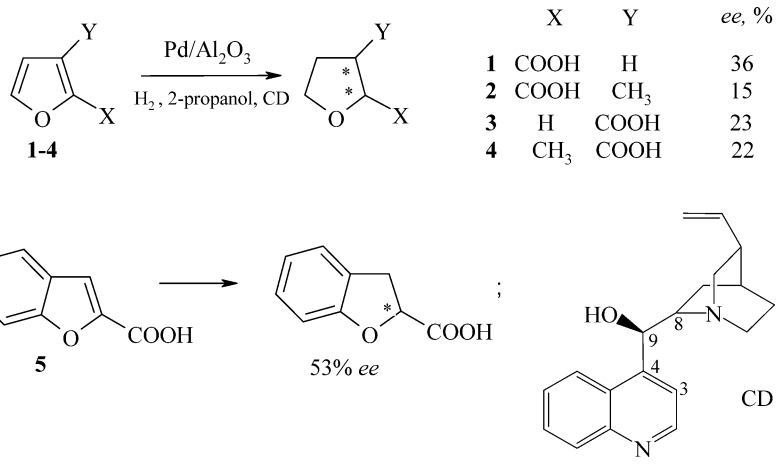

Scheme 1. Hydrogenation of furan- and benzofurancarboxylic acids over cinchonidine (CD)–modified Pd.

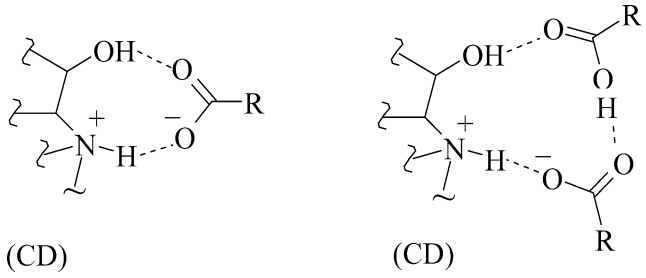

Fig. 1. Schematic illustration of the 1:1 and 2:1 type acid:cinchonidine (CD) interaction models developed for the enantioselective hydrogenation of α,β-unsaturated carboxylic acids.

the *ee* increased with decreasing solvent polarity—an indication of the importance of acid dimers and the cyclic 2:1 acid–CD complexes in enantioselection (Fig. 1, right) [6,25]. The relevance of 2:1 stoichiometry in the enantiodifferentiating step has been proven by catalytic hydrogenations in the presence of a strong organic base [25] and by spectroscopic studies (see below). A third mechanistic model assumed a single N–H–O type interaction between the protonated quinuclidine N of CD and the aliphatic alkenoic acid [7,26]. This early assumption, however, cannot interpret the loss of enantioselectivity after methylation of the OH function of CD [24,25].

Dimerization of carboxylic acids in apolar or weakly polar medium [27] and interaction of acid dimers with simple amines [28,29] is well documented in the literature. Interaction of carboxylic acids with CD, which may be considered as a 1,2-aminoalcohol, has been studied by NMR and IR spectroscopy as well as theoretical calculations [30,31]. The studies confirmed the existence of both 1:1 and 2:1 cyclic complexes in weakly polar medium, with a preference to 2:1 complexes at high acid:CD ratios due to thermodynamic reasons. Interestingly, stable half-cyclic structures were also found that can be considered as 1:1 cyclic complexes interacting with an additional acid molecule bound to either one of the carboxylate oxygen atoms via H-bonding. Formation of a cyclic complex between another 1,2-aminoalcohol type alkaloid, ephedrine, and a dicarboxylic acid has been evidenced by NMR spectroscopy [32].

The aim of the present spectroscopic and theoretical study is to clarify whether any of the mechanistic models presented in Fig. 1 can be applied also to the enantioselective hydrogenation of furancarboxylic acids over CD–modified Pd.

2. Experimental

Furan-2-carboxylic acid (**1**, Fluka, 98%), 3-methylfuran-2-carboxylic acid (**2**, Lancaster, 98%), furan-3-carboxylic acid (**3**, Aldrich, 99%), 2-methylfuran-3-carboxylic acid (**4**, Lancaster, 97%), benzofuran-2-carboxylic acid (**5**, Fluka, 98%), were purified by sublimation followed by recrystallization from hexane (**1**–**4**) or toluene (**5**). Cinchonidine (CD, Fluka, 98% alkaloid) and all other chemicals were used as received.

A 100-ml autoclave equipped with a 50-ml glass liner and a PTFE cover, and a magnetic stirrer (500 rpm) was used for hydrogenation. Hydrogen uptake and total pressure were controlled by computerized constant-volume constant-pressure equipment (Büchi BPC 9901). Catalyst pretreatment and the hydrogenation reactions were carried out at room temperature and 30 bar. At first, 40 mg 5 wt% Pd/Al_2O_3 catalyst (Engelhard 40692, Pd dispersion: 0.21 as determined by TEM) was prereduced with hydrogen for 5 min in 10-ml solvent. Then 0.45 mmol substrate and 68 µmol CD modifier were added (corresponding to a substrate/modifier molar ratio of 6.5) and the reaction started. Conversion and enantioselectivity were determined after derivatization using an HP 6890 gas chromatograph and a Chirasil-DEX CB (Chrompack 7502) capillary column for the hydrogenation products of **1**, **2**, **4**, **5** and a Cyclosilb (J&W 7419117) column for the hydrogenation products of **3**. Details of the method have been published elsewhere [22].

In the hydrogenation of **1** the (*S*)-enantiomer formed in excess, as confirmed by using commercially available (*R*)-(+)-tetrahydrofuran-2-carboxylic acid. On the basis of anal-

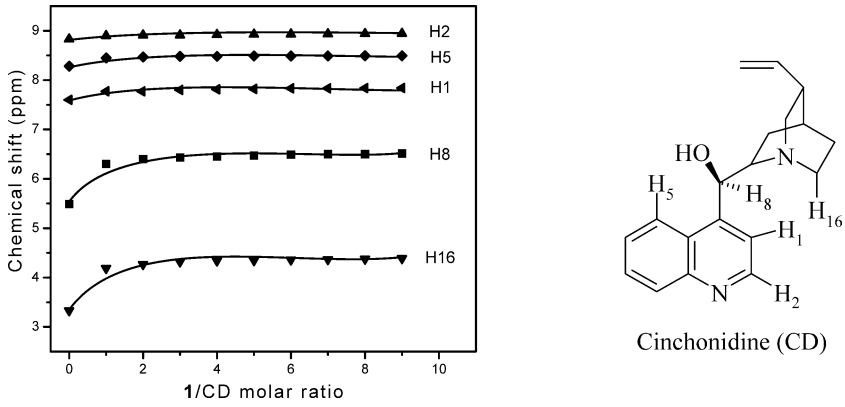

Fig. 2. Chemical shifts of some representative NMR signals during titration of CD with **1** in acetone; 2.0 mg CD, 1 ml acetone-d_6.

ogous separation of the products we assumed that also in the hydrogenation of **3** and **5** the (*S*)-enantiomer was the major product [22]. In the hydrogenation of **2** and **4** the *cis* diastereomers were dominant (close to 100% *de*); in these reactions the major enantiomers were not identified.

NMR spectra were recorded on a Bruker Avance 500 MHz. A solution of 2 g/L CD in acetone-d_6 was titrated with different amounts of **1**.

IR spectra were recorded on a Bruker Vector 33 spectrometer at a resolution of 2 cm^{-1} by coaddition of 25 scans using a variable path-length cell equipped with KBr windows. Compounds **1**–**5** were analyzed in toluene, CH_2Cl_2, and 2-propanol at a concentration of 0.01 M. Besides, mixtures of **1** and CD at molar ratios varying from 0.25 to 10 were analyzed in CH_2Cl_2 at a constant acid concentration of 0.01 M. The neat solvent served as the reference for the absorbance spectra. For comparison, in the catalytic hydrogenation reactions the concentration of **1** was 0.045 M and the **1**/CD molar ratio 6.5.

Intermolecular interactions between **1** and cinchonidine were studied by quantum chemical calculations using Gaussian98 [33]. The B3LYP [34] density-functional hybrid method was used together with a 6-31G* basis set. For geometry optimization all intra- and intermolecular degrees of freedom were completely relaxed. Several structures were chosen as initial geometries in optimization runs. CD was assumed to be in its Open-(3) conformation, which is the most stable when CD is protonated at the quinuclidine N (see Ref. [35] and references therein).

3. Results and discussion

3.1. NMR study of acid–modifier interactions

The acid–base type interaction between the chiral modifier and the substrate in solution was investigated by titration of CD with furan-2-carboxylic acid (**1**) in acetone-d_6. Most of the hydrogen signals of CD were shifted when the acid was added. This shift is mainly due to protonation of the quinuclidine N of CD and the resulting rotation around the C4–C9 and C9–C8 bonds (Scheme 1) [35]. Fig. 2 shows the shifts of some representative aromatic and nonaromatic proton signals of CD. The shift of the nonaromatic H8 and H16 signals by 0.9 and 1 ppm, respectively, indicates protonation of the quinuclidine N atom ($pK_a = 10.0$ [36]). Its complete protonation requires approximately three equivalents of **1** ($pK_a = 4.0$ [37]). In contrast, protonation of the quinoline N ($pK_a = 4.9$ [38]) is barely detectable even above a **1**/CD molar ratio of 10, as illustrated by the insignificant (0.2 ppm) shift of the signals of the aromatic H1, H2, and H5. For comparison, one equivalent of a considerably stronger acid, trifluoroacetic acid ($pK_a = 0.52$ [38]), resulted in a similar shift of the H8 signal, while protonation of the less basic quinoline N started with addition of the second equivalent [21].

Interaction of the weaker acid acetic acid ($pK_a = 4.75$ [38]) with CD is similar to that of **1**: it protonates CD only at the quinuclidine N and the acid/CD molar ratio necessary for the complete protonation is around 20 [35,39]. In contrast, it has been suggested recently that protonation of the quinuclidine N of CD would be incomplete in acetic acid, and trifluoroacetic acid would not be sufficiently strong for double protonation of CD [40].

A further point to be discussed is the effect of solvent on the reactant–modifier interaction. We have reported earlier [22] that in the hydrogenation of **1** the *ee*s were in the range 31–42% in all weakly polar or apolar solvents, including 2-propanol, 3-pentanone, THF, and toluene. Toluene could not be applied for the NMR analysis due to the very low solubility of CD in the absence of reactant. In order to prove that acetone used here for the NMR analysis is suitable also for the enantioselective hydrogenation reactions, we repeated the hydrogenation of **1** in acetone. The *ee* was 33% at 18% conversion (after 3 h under standard conditions, 20 ml solvent), which is similar to the value achieved in 3-pentanone (39% *ee* at 19% conversion).

3.2. The role of acid–acid interactions (dimerization)

Dimerization of furan- and benzofurancarboxylic acids was investigated in toluene and CH_2Cl_2 at an acid concen-

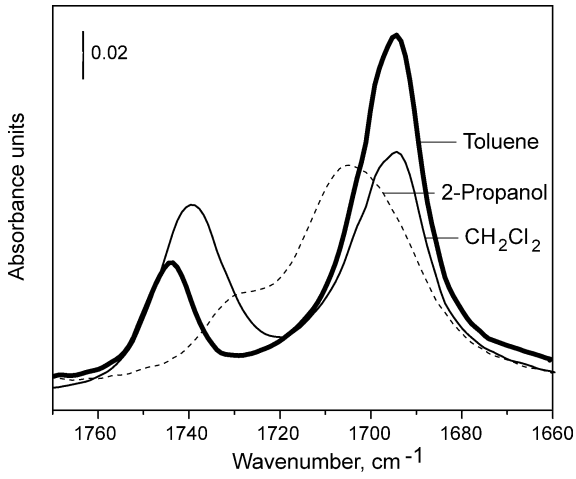

Fig. 3. Effect of solvent on the dimerization of furan-3-carboxylic acid (**3**). The concentration of **3** was 0.01 M in all cases.

Table 1
Role of dimerization of furancarboxylic acids **1**–**5** in the enantioselection

Substrate	pK_a	Ratio of the signals associated with dimer and monomer[a]		ee[b] (%)
		Toluene $E_T^N = 0.099$	CH_2Cl_2 $E_T^N = 0.309$	Toluene
1	4.03	2.7	1.1	31
2	3.45	6.9	1.6	14
3	3.16	2.8	1.3	33
4	4.37	4.7	1.6	17
5	2.90	–[c]	1.1	–[c]

[a] Substrate concentration: 0.01 M.
[b] Conditions: 0.45 mmol substrate, 10 ml solvent, 40 mg 5% Pd/Al_2O_3, substrate:CD molar ratio 6.5.
[c] Not determined due to low solubility of **5**.

tration of 0.01 M. It was attempted to use 2-propanol, a good solvent of the enantioselective hydrogenation of furancarboxylic acids, but overlapping of the two bands corresponding to the dimer and to the monomer hydrogen bonded to the solvent prevented quantitative analysis (Fig. 3).

In toluene and CH_2Cl_2 the dimer/monomer ratios were determined from the heights of the C=O signals corresponding to the dimer (at around 1696 cm^{-1}) and the monomer (at around 1740 cm^{-1}). Fig. 3 and Table 1 show that the dimer/monomer ratio is remarkably higher in the weakly polar toluene, as expected [41]. Furthermore, there is a qualitatively good negative correlation between enantioselectivity achieved in toluene and the extent of dimerization in both solvents, suggesting that extensive dimerization diminishes the *ee*.

In contrast to this structural effect, in the hydrogenation of **1**–**5** the enantioselectivity either increased by using less polar solvents where dimerization is more extensive, or there was no clear correlation between *ee* and the empirical solvent parameter E_T^N [42]. Hence, no unambiguous correlation is seen between the extent of dimerization of the substrate in solution and the enantioselectivity achieved on the Pd surface.

Comparing the data in Table 1 reveals that the acid strength characterized by the pK_a values of the substrates [38] does not play an important role in the extent of dimerization and in the enantioselection.

3.3. IR study of acid–modifier interactions

Next, the substrate–modifier interaction was analyzed by IR, using **1** as a model for furancarboxylic acids. The **1**/CD molar ratio was varied in the range 0.25–10, while the concentration of **1** was kept constant. For these experiments CH_2Cl_2 was chosen as a solvent due to the limited solubility of the CD–**1** salt in toluene. Some control experiments were carried out in toluene at a high **1**/CD ratio, where the solubility of CD was sufficiently high. The spectra showed the same type of interactions in toluene and CH_2Cl_2. 2-Propanol could not be used for these measurements due to complicating interactions with the solvent.

A very broad band in the range approximately from 3000 to 2000 cm^{-1} was observed for **1**–CD mixtures (not shown). Such broad absorption bands are associated with proton polarization [43]. In our case the appearance of this band indicates the formation of $N–H^+\cdots O^-$ type hydrogen bonds between **1** and CD and thus supports protonation of CD observed by NMR.

Additional information on the interaction between CD and **1** can be extracted from the behavior of the free (not hydrogen-bonded) OH group of CD. The intensity of the ν(OH) signals around 3600 cm^{-1} decreases remarkably with increasing **1**/CD ratio in the range 0.25–10 (Fig. 4A). This is a clear indication that upon protonation of CD by **1**, the OH group of CD is also involved in the reactant–modifier interaction via hydrogen bonding.

The ν(OH) signal in the spectrum of **1** is located in the high-frequency range at 3500 cm^{-1} and it belongs to the monomer acid (Fig. 4A). In the titration experiments this signal disappears at low **1**/CD ratios and appears again above 2 molar ratios (Fig. 4B). The absence of the acid monomer at or below a **1**/CD molar ratio of 2 indicates that in this range all acid molecules are involved in interactions with CD or another acid molecule.

There are three features in the IR spectra that disclose the existence of 1:1- and 2:1-type acid–CD complexes:

(i) The weak ν(OH) signal at 3400 cm^{-1} corresponds to CD involved in cyclic CD–acid complexes. This band is almost absent for mixtures at **1**/CD molar ratio below 1 and its intensity increases with increasing **1**/CD ratio in the range 1–2 (Fig. 4B). This is an indication that the band is associated with a 2:1 acid–CD complex. Above this molar ratio the decreasing amount of CD (at constant concentration of **1**) hinders the unambiguous detection.

(ii) The coexistence of two different carboxylate bands $\nu^s(COO^-)$ at 1390 and 1358 cm^{-1} (Fig. 4D). The two signals corresponding to the $\nu^{as}(COO^-)$ of monomer

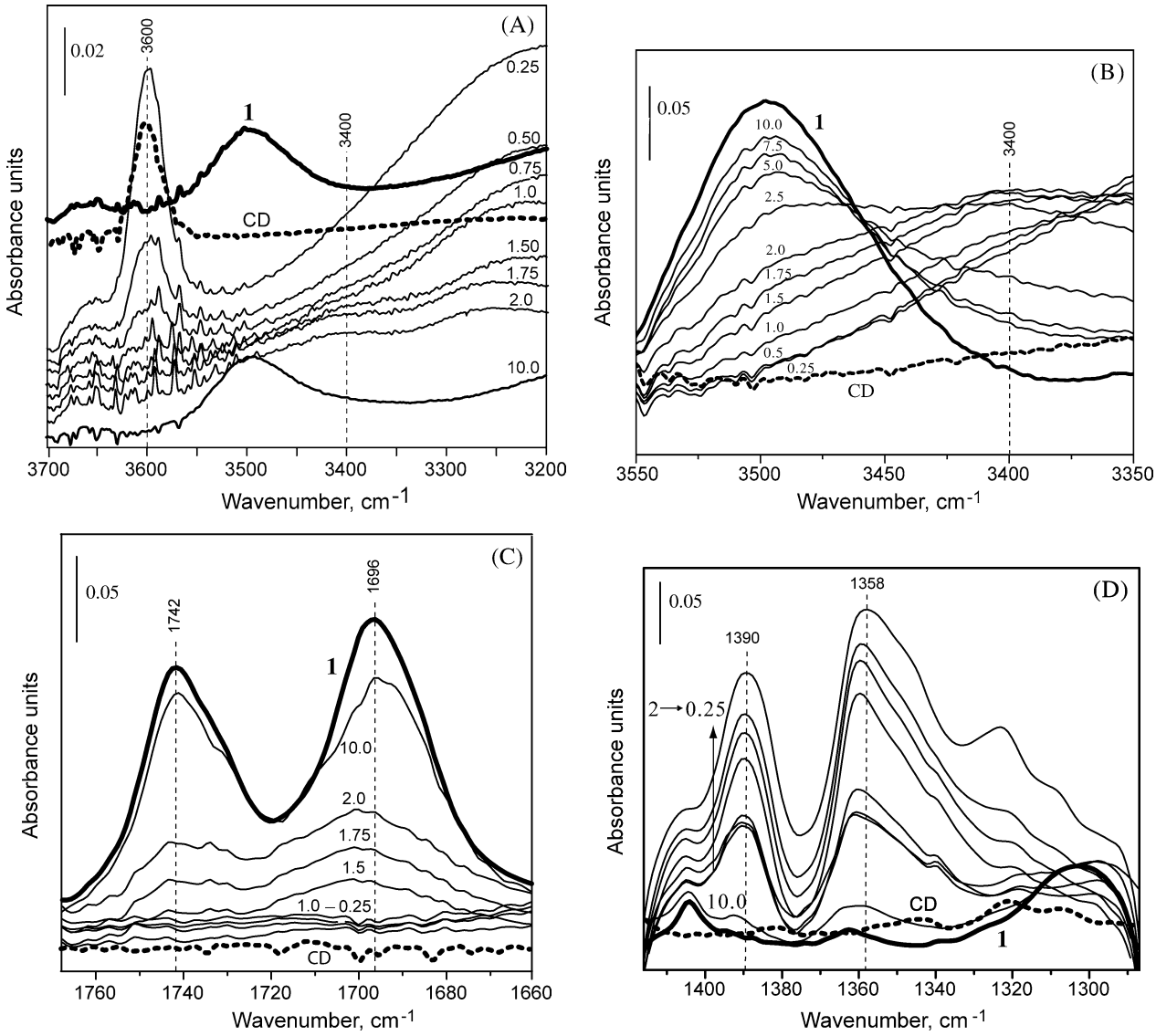

Fig. 4. IR spectra of **1** and **1**:CD mixtures at 0.25, 0.5, 0.75, 1, 1.5, 1.75, and 2 molar ratio in CH_2Cl_2. The concentration of **1** was 0.01 M in all cases. The spectrum of CD alone was measured for a 0.01 mM concentration. (**A**), (**B**) ν(OH) region, (**C**) ν(C=O) region, (**D**) $\nu^S(COO^-)$ region. Spectrum **1** in panel (**A**) is slightly offset for clarity. The sharp bands above 3500 cm^{-1} arise due to incomplete compensation of water vapor. The arrow indicates the development of the signal upon decreasing **1**:CD ratio.

and dimer appear in the same region as that of the quinoline ring vibrations of cinchonidine (1593 and 1571 cm^{-1}, not shown), so it is difficult to use these bands for structural analysis.

(iii) The coexistence of two different carbonyl bands at around 1742 cm^{-1} (corresponding to the non-hydrogen-bonded carbonyl group in the free **1** molecules) and 1696 cm^{-1} (corresponding to the hydrogen-bonded carbonyl group in the acid dimer and in the 2:1 acid–CD complex) (Fig. 4C). Closer inspection of the bands at 1696 cm^{-1} at different **1**/CD ratios reveals that this band cannot be attributed only to dimerization of **1**. Its broadening indicates that other species should also contribute to the overall intensity. The carbonyl band is slightly shifted towards higher frequencies at low **1**/CD ratios due to a change in the relative abundance of the species contributing to this band.

For high **1**/CD molar ratios, corresponding to the experimental conditions used in enantioselective hydrogenation, interaction between the O atom of the furan ring and CD cannot be observed. The corresponding ν(C–O) band appears at around 1300 cm^{-1} and it is very weak. The interaction is less probable due to the fact that the weakly basic furan O atom has a poor ability to form hydrogen bonds (furan: dipole moment 0.66 Debye) [44].

3.4. Theoretical calculations

For understanding the interaction of CD with **1**, the conformation of CD itself is of importance. The various con-

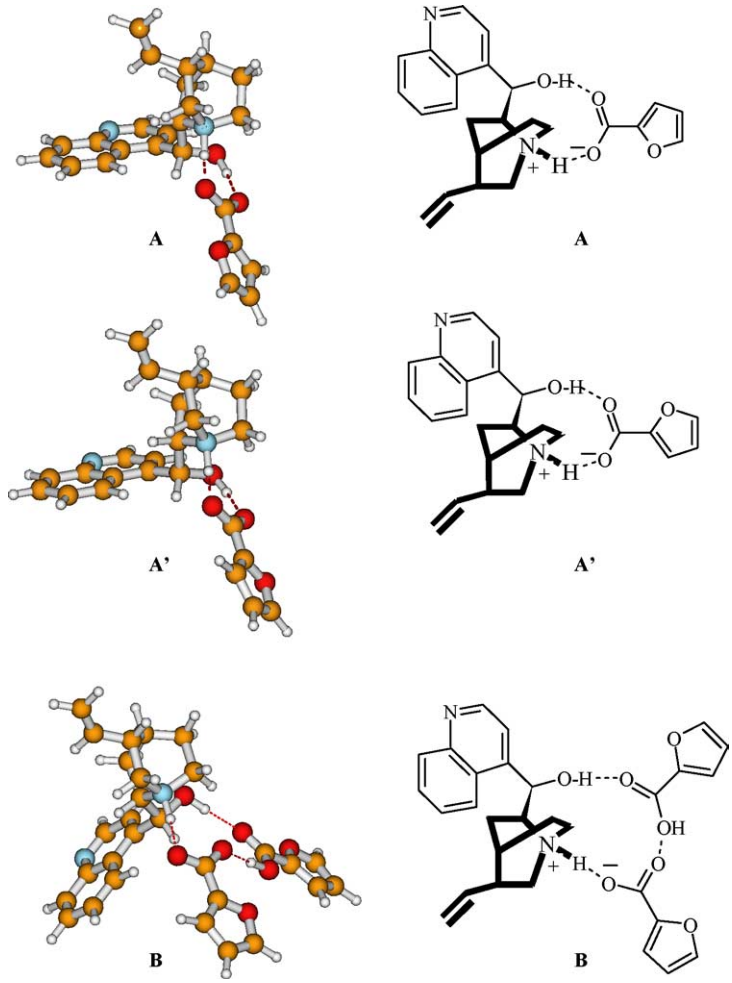

Fig. 5. Calculated structures of possible CD–**1** complexes (side views) and their conventional formulas (top views). The bold structure of the quinuclidine fragment indicates that this part of the modifier is above the Pd surface.

formers of CD have been classified according to their torsion angles C_3–C_4–C_9–C_8 and C_4–C_9–C_8–N (see Scheme 1) [45,46]. The solvent-dependent conformational behavior of unprotonated CD in solution has been investigated by NMR experiments and ab initio reaction field calculations [35,46, 47]. It has been shown that conformer Open(3) is the most stable. Protonation of the quinuclidine N further stabilizes Open(3).

As shown above, CD may interact with furancarboxylic acids via two H-bonds involving both the quinuclidine N atom and the OH function. To confirm the feasibility of the acid:CD 2:1 and 1:1 interaction models (Fig. 1) developed for the hydrogenation of α,β-unsaturated carboxylic acids, quantum chemical calculations were performed using the Open(3) conformation of CD (Fig. 5). In the following discussion of the models we use the common assumption that addition of hydrogen occurs from the palladium side. Therefore, depending on which enantioface the reactant is adsorbed during hydrogenation the chirality of the product will be (*R*) or (*S*).

In the 1:1 acid–CD complex the protonated quinuclidine nitrogen and the hydroxyl group of CD bind to the carboxylate group of the deprotonated acid. Figs. 5A and 5A′ illustrate the 1:1 interaction between substrate and modifier, considering the two ways of adsorption of **1** on the metal surface. The calculations indicated an energy difference between the two optimized structures of only 0.29 kcal/mol. This difference corresponds approximately to the energy difference between the two conformations of the free acid molecule, which was calculated to be 0.35 kcal/mol in favor of the conformer that has the OH group in *cis* position to the furan O atom. The binding energy with respect to the separated neutral molecules (CD and **1**) was 18.7 kcal/mol for complex A. The energy difference between the two complexes A and A′ (0.29 kcal/mol) is smaller than the estimated accuracy of the calculations. A possible interpretation is that the two arrangements A and A′ coexist on the Pd surface and the moderate *ee*s achieved in this reaction (around 30%) are due to the small energy difference between the two adsorption modes of **1**. Another feasible explanation is that the calculations not involving interactions with the Pd surface cannot reliably differentiate between the two structures.

Calculations were also performed for the 2:1 complex that would afford the (*S*) enantiomer (Fig. 5B), in agree-

ment with the results of the catalytic reactions. In the three-membered complex the alkenoic acid dimer protonates the quinuclidine N of CD and the dimer is bound via the carbonyl group of the second acid molecule to the OH function of CD. The binding energy with respect to the separated neutral molecules was calculated to be 35.8 kcal/mol, a remarkably higher value than that characteristic of the 1:1 complex.

More reliable calculations involving interactions of substrate and chiral modifier with the Pd surface are yet too demanding. Still, analysis of the optimized structures A and B in Fig. 5 gives useful hints concerning the feasibility of 1:1 (A) and 2:1 (B) type interactions on the metal surface. Complex A is very rigid as the two O atoms that interact with CD are separated by only one C atom, which leads to a considerable "ring stress." Adsorption of this complex requires special surface cites; it cannot adsorb on an approximately flat surface without breaking the weaker H-bond (O–H–O connectivity). Complex B is structurally rather flexible and its adsorption on the metal surface appears less demanding. Hence, we assume that when the furancarboxylic acid is present in excess to CD (typical reaction conditions) both 1:1 and 2:1 complexes exist in solution but interaction of the acid dimer with CD strongly adsorbed on the Pd surface will determine the enantioselectivity.

4. Conclusions

Enantioselective hydrogenation of furan- and benzofurancarboxylic acids **1**–**5** is a new extension of the application range of cinchona–modified palladium [22]. On the basis of FTIR and NMR spectroscopic investigations and ab initio calculations the following major conclusions can be drawn concerning the mechanism of enantiodifferentiation:

(i) The carboxylic acid substrates are present as a mixture of monomer and dimer in solution. The monomer/dimer ratio varies with the solvent and the structure of the substrate; no unambiguous correlation could be established between the monomer/dimer ratio in solution and the enantioselection on the Pd surface.

(ii) In the substrate–modifier interactions both the basic quinuclidine N atom and the OH function of CD are involved. The weakly basic quinoline N atom is important in the adsorption of the alkaloid on the Pd surface [48] but no interaction with the furancarboxylic acid could be detected.

(iii) Two types of cyclic complexes are formed between the carboxylic acid substrate and the 1,2-aminoalcohol type alkaloid. In the 1:1 complex the protonated alkaloid and the deprotonated acid form a nine-membered ring, as depicted in Fig. 1. In the 2:1 complex an acid dimer interacts with the alkaloid to form an extended cyclic structure. In solution the two complexes coexist.

(iv) Thermodynamic considerations favor the formation of 2:1 acid:CD complex (Fig. 5B) at high acid:CD ratios that correspond to the reaction conditions. The same conclusion can be drawn when adsorption of this flexible complex and hydrogen uptake from "below," from the surface of polydisperse Pd particles are considered. It is expected that adsorption of the rigid 1:1 complex (Fig. 5A) requires special surface sites due to the considerable "ring stress;" adsorption on an approximately flat Pd surface is hindered.

The suggested mechanistic model B in Fig. 5 is analogous to the empirical model developed for the enantioselective hydrogenation of aliphatic α,β-unsaturated carboxylic acids [6,25]. Major limitation of both proposals is that there is no explanation yet for the adsorption mode of the unsaturated carboxylic acids over the Pd surface in such a geometry that results in the experimentally observed major enantiomer. Considering the state of art in a broader view, the present model of the hydrogenation of furancarboxylic acids seems to be rather sophisticated compared to some other reactions in heterogeneous enantioselective catalysis where even the basic elements of substrate–modifier interactions are debated due to absence of convincing experimental evidence.

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