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Enantioselective Recognition of Amino Acids by Enantiomerically Pure Calix[4]arene Carboxylic Acid or Their Diastereomerically Pure *N*–(1–Phenyl)ethyl Amides

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The interaction of inherently chiral calix[4]arene carboxilic acids and their amides with amino acids in the organic phase has been studied using electron spectroscopy. It was found that the chiral calix[4]arenes are able of enantioselective recognition of L- and D-forms of amino acids. Stability constants of the calixarene – amino acid supramolecular complexes were determined and mechanism of the host-guest interaction was examined by molecular modeling method.

Keywords: Chiral calix[4]arenes, enantioselective recognition, electron spectroscopy, DFT.

Энантиоселективное распознавание аминокислот энантиомерно чистыми каликс[4]аренкарбоновыми кислотами или их диастереомерно чистыми *N*–(1–фенил)этиламидами

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Методом электронной спектроскопии было изучено взаимодействие внутренне хиральных каликс[4] аренкарбоновых кислот и амидов на их основе с аминокислотами в органической фазе. Выявлено, что оптически активные каликс[4]арены способны к энантиоселективному распознаванию L- и D-валина. Были установлены константы устойчивости образующихся супрамолекулярных комплексов каликсарен – аминокислота. Методом молекулярного моделирования был изучен механизм образования комплексов "гость"-"хозяин".

Ключевые слова: Хиральные каликс[4]арены, энантиоселективное распознавание, электронная спектроскопия, DFT.

Introduction

The design and synthesis of chiral supramolecular receptors capable of enantioselective recognition of amino acids is the challenge in supramolecular chemistry, biology, medicine and pharmacology.[1-4] Now the separation of amino acids and their derivatives is an actual problem of their necessity in the manufacture of various proteins demanded for maintenance of life processes.[5-7] It is well known that most natural amino acids are α-amino acids in the *L*-configuration and all naturally occurring proteins from all living organisms consist of *L*-amino acids.[5-7] Most bacterial and fungal cell walls are formed by peptides and their derivatives containing *D*-amino acids,[5-7] therefore *D*-amino acids can be used as chiral markers for the detection of the microbial contamination.

Calix[4]arenes, which have the unique macrocyclic cape-shaped structure, are widely used as specific receptors for recognition, binding in supramolecular complexes and separation of anions, cations or neutral molecules similar in their properties.[8-10] In this area, the inherently chiral calix[4]-arenes, the optical activity of which is due to the asymmetric position of achiral substituents on the macrocyclic platform are of greatest importance.[11,12] Receptors based on these compounds can recognize and bind optical antipodes of chiral "guest" molecules. Inherently chiral calixarenes may also be used as organic catalysts or ligands in the metal complex catalysis for asymmetric synthesis, as enantioselective sensors, chiral stationary phases for column chromatography, chiral shift reagents for NMR spectroscopy.

Optically active inherently chiral calix[4]arenes containing hydroxyl, alkyl and aromatic fragments as well as chiral amide group are prospective molecular building blocks for the synthesis of chiral receptors further applied for enantioselective recognition of some amino acids. Due to macrocyclic structure containing different coordination centers, these calix[4]arenes can bind substrates via their cationic, anionic and neutral binding sites.

In this work, we describe the ability of enantiomerically pure inherently chiral calixarene carboxylic acids **1**, **2** or their diastereomerically pure *N*-phenylethylamides **3-4** to enantioselective recognition of some amino acids.

Experimental

Carboxycalixarene **1** was synthesised by hydrolysis of the corresponding amide.[13] Calixarenes **2-5** were synthesised as described elsewhere.[14]

Determination of Stability Constant and Stoichiometry of the Complex by UV Titration

The UV measurements were performed with "Shimadzu UV-3600" instrument. The $1 \cdot 10^{-3}$ M solution of amino acids (*L*-valine, *D*-valine, *D*,*L*-valine, *L*-leucine, *D*,*L*-leucine, *L*-lysine, *D*,*L*-lysine, *L*-alanine, *D*,*L*-alanine) (0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 μL) in methanol was added to 1 mL of the solution of receptor **1-5** ($3 \cdot 10^{-6}$ M) in methanol and finally diluted to 3 mL with methanol. The UV spectra of the solutions obtained were then recorded. The stability constant and stoichiometry of complexes were calculated as described elsewhere.[15] Three independent experiments were carried out for each series. Student's *t*-test was applied in statistical data processing.

Details of Calculations

All structures were fully optimized without symmetry constraints using the TURBOMOLE program suit (version 6.4).[16,17] The corrected on electron dispersion effects Grimme's B97-D DFT functional[18,19] was used in combination with the TZVP basis sets (the TZV basis sets of triple-zeta quality suggested by Ahlrichs *et al.*[20] augmented by adding one *p*-function set for hydrogen and one *d*-function set for all other atoms). The Resolution of the Identity (RI) option was used for a higher performance.[21] The vibration frequencies were calculated numerically. The absence of imaginary frequencies proved the structures to correspond to true local minima. The relative energies (ΔE and ΔG) were calculated

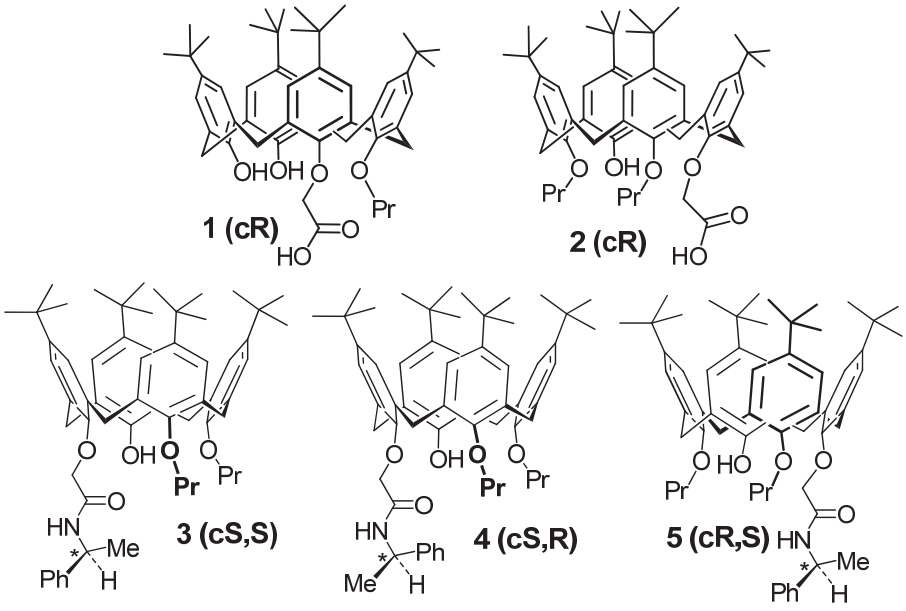

Figure 1. The structure of calix[4]arenes **1**–**5**.

adding zero-point energy (*ZPE*) corrections and thermal corrections to Gibbs free energy (*TCGFE*), respectively, to total energy values. All the thermodynamic parameters were derived under standard conditions (temperature 298.15 K, pressure 0.1 MPa) using the freeh routine as chemical potential. By default, *ZPE*- and *TCGFE* -correction values were scaled by 0.9914. The solvent effects (methanol) were taken into account using the COSMO procedure.[22,23] The calculated structures were presented graphically using the VMD program.[24]

Results and Discussion

It is well known that the structure of the receptor should contain different fragments able to the multi-point interactions for the enantioselective recognition of amino acids.[1] Therefore the enantioselective recognition of amino acids containing alkyl substitutes is rather difficult. To solve this problem, the inherently chiral enantiomerically pure calix[4]arene carboxylic acids **1**, **2** and diasteriomerically pure calix[4]arene amides **3**, **4**, **5** were selected (Figure 1).[13,14]

The following amino acids: *L*-valine, *D*-valine, *D,L*-valine, *L*-leucine, *D,L*-leucine, *L*-lysine, *D,L*-lysine, *L*-alanine, *D,L*-alanine were taken as substrates (Figure 2).

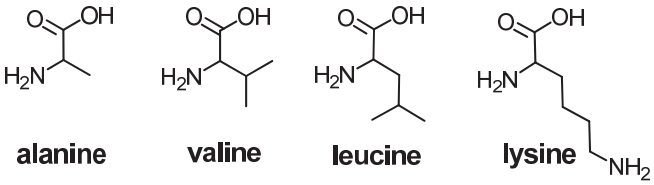

Figure 2. The structures of amino acids.

The UV spectroscopy is an universal tool for studying complexation properties of calix[4]arene derivatives. The changes in the absorbance spectrum of calix[4]arenes after addition of the amino acids indicate the formation their complexes with the substrates. The study of the interaction of calix[4]arenes **1-5** with amino acids by UV spectroscopy in methanol showed significant absorbance changes in some cases. Thus, the interaction of calix[4]arenes **1-5** with racemic amino acids led to hyperchromic effect (Figure 3). In the case of optically active amino acids, the interaction of

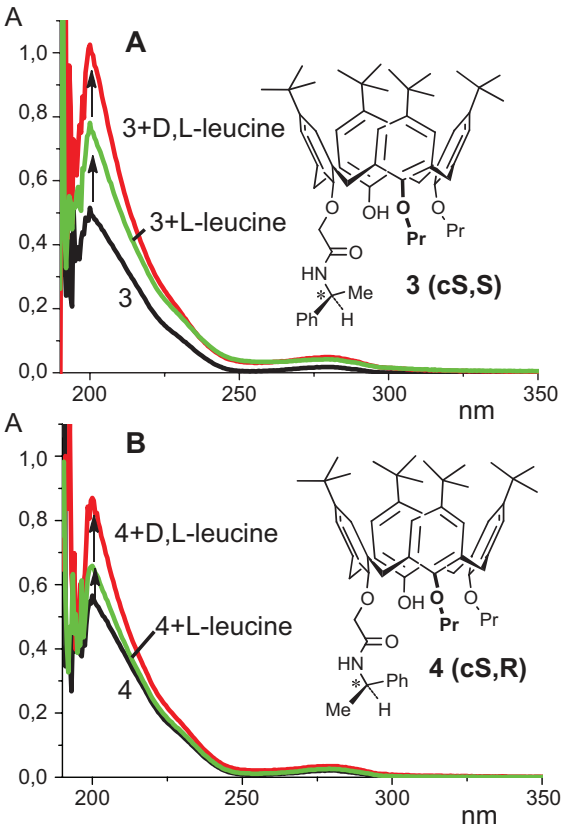

Figure 3. UV spectra of *p-tert*-butylcalix[4]arenes (A) **3** and (B) **4** ($c = 1 \cdot 10^{-6}$ M) after the addition of *L*-leucine and *D,L*-leucine ($c = 1.7 \cdot 10^{-6}$ M) in methanol.

the macrocycles with the substrates also resulted in increased absorption intensity at 190-300 nm (Figure 3). Spectroscopic results showed that significant spectral changes were observed due to the effective interaction between calix[4]-arenes **1-5** and the substrates.

To quantify the molecular recognition of amino acid by calix[4]arenes, the stability constants and the stoichiometry of the complex "calixarene – amino acid" formed in the organic phase were established (Table 1).

It was shown that the interaction of inherently chiral calix[4]arenes **1-5** with the substrates led to formation of the 1:1 and 2:1 complexes.

Table 1. Logarithms of the stability constants (log*K*) of the 1:1 (or 2:1) host-guest complexes of calixarene **1-5** with amino acids.

Amino acids	Calix[4]arenes				
	1 (cR)	**2** (cR)	**3** (cS, S)	**4** (cS, R)	**5** (cR, S)
L-Alanine	4.70±0.26	4.72±0.25	4.10±0.17	4.72±0.19	2.35±0.11*
D, L-Alanine	4.93±0.29	4.09±0.26	4.08±0.18	4.79±0.18	4.07±0.31
L–Valine	2.79±0.11*	5.00±0.33	4.54±0.14	5.13±0.28	4.73±0.30
D-Valine	4.01±0.29	4.51±0.19	5.37±0.10	4.47±0.15	5.33±0.15
D, L–Valine	5.08±0.20	4.72±0.24	4.63±0.21	4.27±0.19	4.40±0.14
L–Leucine	4.89±0.29	3.26±0.16*	3.59±0.25	3.16±0.20	5.21±0.17
D, L–Leucine	5.12±0.21	4.33±0.14	5.26±0.25	5.08±0.31	4.92±0.15
L–Lysine	4.83±0.20	3.24±0.16*	3.97±0.09	3.95±0.11	4.56±0.16
D, L–Lysine	5.48±0.11	4.96±0.14	4.33±0.17	4.27±0.30	5.27±0.19

* – stoichiometry of the host-guest complexes 2:1

Optically pure calix[4]arene carboxylic acids **1** and **2** with inherent chirality effectively interacted with amino acids, the logarithms of the stability constants changed from 3 to 5. In the case of the compounds **1** and **2**, the calix[4] arene **1** less effectively interacted with optically pure amino acids than with racemic mixture of amino acids. The transition from the compound **1** to the macrocycle **2** by decreasing number of binding sites in the structure of macrocycle showed the efficiency of interaction lesser by an order of magnitude. In the case of the compound **2**, the logarithms of the stability constants did not change by transition from optically pure amino acids to racemic mixture of amino acids. It is interesting to note, that during the interaction of the compound **2** with "bigger" amino acids *L*-leucine and *L*-lysine, the stoichiometry was changed. One molecule of the substrate interacted with two molecules of the macrocycle **2**. Calix[4]arene **1** only with *L*-valine formed 2:1 complex, although the interaction of macrocycle **1** with *D*- and *D,L*-valine led to formation of the 1:1 complexes. The transition from the compound **1** to the macrocycle **2** showed that during the interaction of the calix[4]arenes **1** and **2** with *L*-valine, the stoichiometry and, hence, efficiency of interaction were changed.

Increasing the efficiency of interaction of compound **1** with *D,L*-valine in comparison with optically pure amino acids can be explained. By interaction the compound **1** with *L*-isomer, 2:1 complex is observed. *D*-Valine as well as racemic mixture of amino acids, complex with 1:1 stoichiometry formed. Hence, during the interaction of compound **1** with *D,L*-valine, the complex of macrocycle **1** with *D*-valine dominated. It should be noted, that pure amino acids and racemic mixture of amino acids were used with the same concentration. Consequently, in the case of *D,L*-valine, the amount of *D*-amino acid is less in comparison with pure isomer. As a result, the concentration of the complex: macrocycle **1** – *D*-valine will be also smaller due to the interaction with the racemic mixture of amino acids. Thus, the constant of interaction for the system [macrocycle **1** + *D*-valine + *L*-valine] will be bigger than for the system [macrocycle **1** + *D*-valine], that was experimentally confirmed.

The introduction of additional chiral site (phenylethylamide fragment) in the structure of macrocycles should significantly influence on the enantiomer discrimination properties of calix[4]arenes. The interaction of the macrocycles **3**-**5** with amino acids was studied using electron spectroscopy. It should be mentioned that the selected macrocycles **3** and **4** have the same calixarene platform (planar chirality) in cS-form but different symmetry of amide fragment (S or R). Compounds **3** and **5** have the same amide group in S-form but different chirality of calixarene platforms (cS or cR). Calix[4]arenes **4** and **5** are enantiomers.

The comparison of the interaction of the (cS, S)- and (cS, R)-calix[4]arenes **3** and **4** with *L*-amino acids showed similar changes in the efficiency of interaction with no respect of the type of calix[4]arene isomer. The efficiency of the interaction between (cS, S)- and (cS, R)-calix[4]arenes **3**, **4** and *L*-amino acids decreases in the range: *L*-valine > *L*-alanine > *L*-lysine > *L*-leucine (Table 1). The increase in the efficiency and selectivity of interaction with *L*- and *D*-valine, *L*-alanine depends on the size of the substrates. Thus, most efficient binding was observed for the "smallest" amino acids compared with the substrates studied. Only in the case of valine a full correspondence between the size of an amino acid and the binding site of calix[4]arenes was observed.

The opposite tendency was found for racemic amino acids their interacted with (cS, S)- and (cS, R)-calix[4]-arene **3** and **4**. For (cS, S)-calix[4]arene **3**, the efficiency of interaction decreases in the range: *D,L*-leucine > *D,L*-valine > *D,L*-lysine > *D,L*-alanine (Table 1). In the case of (cS, R) -calix[4]arene **4**, the logarithms of the stability constants decreased in the range: *D,L*-leucine > *D,L*-alanine > *D,L*-valine > *D,L*-lysine (Table 1). Thus, for racemic amino acids, most effective and selective interaction was observed for "bigger" amino acid, *i.e.* leucine, compared with other substrates studied. All the substrates considered except lysine belong to aliphatic amino acids. Lysine is positively charged in solution, but most selective and effective interaction was observed with *L*-and *D*-valine, *D,L*-leucine due to the formation of hydrophobic and hydrogen bonds with the receptors. Thus, the presence of additional binding sites in the structure of amino acid has negligible influence on the efficiency of interaction.

The comparison of the interaction of the macrocycles **3** and **5** with substrates showed that the change of inherent chirality of calix[4]arene **3** and **5** did not influence the efficiency of interaction with *L*- and *D,L*-lysine. However, the compound **5** less effectively interacted with *L*-, *D*-, *D,L*-valine and *D,L*- alanine than the compound **3**. The logarithms of the stability constants decreased by the order of magnitude. In the case of *L*-alanine the stoichiometry was changed. Two molecules of the macrocycle **5** interacted with one molecule of *L*-alanine. However, the comparison of the efficiency of interaction of the compounds **5** with *L*- and *D*-valine as in the case of the macrocycle **3**, showed that the compound **5** more effectively interacted with *D*-valine. The transition from the compound **3** to macrocycle **5** different in inherent chirality showed more efficient interaction with *D,L*-leucine than with *L*-leucine. However, in the case of *L*-leucine, the stability constants of macrocycles **3** and **5** with different inherent chirality greatly differed from each other in about 1.5 of magnitude. Although for the compounds **3** and **4** containing substitutes with different chirality, the maximum difference of stability constants was 0.9 of magnitude as it was shown for *D*-valine. Hence the differences of the stability constants in the case of calix[4]arenes **3** and **5** with *L*-leucine can be explained by the difference in inherent chirality of the macrocycles. In contrast to the macrocycle **3**, the opposite tendency was also observed for the interaction of the compound **5** with *L*-amino acids. The efficiency of interaction decreased in the range: *L*-leucine > *L*-lysine > *L*-valine. In the case of interaction of the macrocycle **5** with racemic amino acids other tendency was observed than with compound **3**. The efficiency of interaction decreased in the range *D,L*-lysine > *D,L*-leucine > *D,L*-valine > *D,L*-alanine.

The comparison of the interaction of the two enantiomers – macrocycles **4** and **5** with amino acids showed that the combined effect of two chiral elements (inherent chirality and the chirality of the substituents) can change the stability constants by the two orders of magnitude as it was found in the case of *L*-leucine.

It should be mentioned that the study of the interaction of (cS, S)- and (cS, R)-calix[4]arenes **3** and **4** with *L*-, *D*-, *D*,*L*-valine showed enantioselective recognition of the optical antipodes of the amino acid (Table 1). In the case of (cS, S)-calix[4]arene **3**, the interaction with *D*-valine was more efficient (log*K* = 5.37) than that with *L*- and *D*,*L*-valine. In contrast to macrocycle **3**, the interaction of the calix[4]arene **4** with *L*-valine was more efficient (log*K* = 5.13).

In order to put these data on the firmer ground, quantum chemical (DFT-D) calculations have been carried out for the adducts of **3** and **4** with *D*- and *L*-valine. The studied structures can adopt a large number of conformations resulted from different orientations of substituents at the upper and lower rims of the calixarene cavity and *i*-Pr group in valine. This influences insignificantly on the total energy values. The real structure is a result of the dynamic equilibrium between several most favorable conformational isomers. The geometry optimization within the gas phase approximation provides some insight about the structures. The Grimme's B97-D DFT functional[18,19] was used in combination with the TZVP "triple-zeta" basis sets from Ahlrichs group.[20] The approach is suitable for the correct reproducing electron dispersion effects. While the charge and polar interactions are of the most importance for the valine coordination, modeling the selectivity of the chiral hosts towards the *D*- or *L*-valine requires taking into account these, even less strong, dispersion interactions. In particular, geometry optimization results in the flattened cone conformation for the calixarene scaffold: the distances between C^{arom}-Bu^t carbon atoms are 5.30 and 9.50 Å for **3**, 5.25 and 9.47 Å for **4**. This is probably supported by favorable electron dispersion interactions between the bulky *t*-Bu substituents at the upper rim of the calixarene.

From the several located conformations, the two most favored ones have been chosen, (cS, S)-host/*D*-valine and (cS, R)-host/*L*-valine. In the latter structure (Figure 4,B), π,π-stacking interaction occurs between the Ph ring of the substituent at the lower rim of the host and the aromatic ring of the calixarene. For the former structure, (Figure 4,A) the phenyl substituent does not participate in any interaction. Instead of the favorable π,π-stacking the interaction is essentially compensated by increased number of states of freedom, which in turn provides a larger negative contribution of the entropy-containing term. The amino acids exist as zwitterions in methanol,[5] and the same structure is resulted from the quantum chemical calculations for *D*(*L*)-valine in the adducts with calixarenes. In the optimized structures (Figure 4), the NH_3^+ group of amino acid forms two hydrogen bonds with two of four oxygen atoms at the lower rim of the calixarene ($NH^1\cdots OH$ 1.737 Å for A and 1.657 Å for B; $NH^2\cdots OPr$ 1.926 Å for A and 1.909 Å for B) and one intramolecular hydrogen bond with the carboxylic oxygen ($NH^3\cdots O^-$-C=O 1.939 Å for A and 2.064 Å for B). Additionally, the carboxylic group of amino acid forms hydrogen bonding with the NH group of the amide moiety and the intramolecular O-H···O bonding is kept in the macrocycle. The located conformations of (cS, S)-host/*L*-valine and (cS, R)-host/*D*-valine (for example, structures C and D in Figure 5) possess higher total energies and are less favored. Noteworthy, even the weak C=O···HC-N hydrogen bonds in the chiral substituent at the lover rim probably contribute to the total energies of the favorable structures A and B.

Overall, for all optimized structures, the calculated Δ*E* values for reaction (1) are slightly negative (Table 2), but are shifted into a positive area by taking into account the entropy contribution (going to Δ*G* magnitudes).

$$\text{host} + D(L)\text{-valine} \rightarrow \text{adduct} + \Delta E\ (\Delta G) \qquad (1)$$

While DFT calculations not always provide proper reaction energies for forming macrocyclic adducts in

Table 2. Total energy values (*E*, Hartree), zero-point energy correction values (*ZPE*, Hartree), thermal correction to Gibbs free energy values (*TCGFE*, Hartree), corrected energy values (*E*+*ZPE* and *E*+*TCGFE*, Hartree), reaction (1) energies (Δ*E* and Δ*G*, kcal/mol) and the lowest vibrational frequencies (cm^{-1}) calculated for structures A-D at the RI-B97-D/TZVP level of theory in the gas phase and in methanol, using the COSMO routine at the RI-B97-D/TZVPP//RI-B97-D/TZVP level of theory (*in italic*).

Structure	*E*	*ZPE*	ν	*E*+*ZPE*	Δ*E*	*TCGFE*	*E*+ *TCGFE*	Δ*G*
A	–3166.181118	1.397962	7.3	–3164.783155	–8.51	1.267549	–3164.913568	4.46
	–3166.359410				–5.79 [a]		–3165.091860 [b]	*9.43* [b]
B	–3166.183839	1.398572	12.2	–3164.785267	–10.18	1.270554	–3164.913284	4.84
	–3166.363211				–7.80 [a]		–3165.092657 [b]	*9.62* [b]
C	–3166.180308	1.398883	11.1	–3164.781425	–7.42	1.270554	–3164.909754	6.85
	–3166.358499				–5.21 [a]		–3165.087945 [b]	*11.88* [b]
D	–3166.183318	1.399017	14.6	–3164.784301	–9.57	1.271796	–3164.911522	5.95
	–3166.362665				–7.46 [a]		–3165.090869 [b]	*10.74* [b]
3	–2763.895831	1.233810	10.5	–2762.662021	–	1.118176	–2762.777655	–
	–2764.045526				–		–2762.927350 [b]	–
4	–2763.895644	1.234174	5.6	–2762.661470	–	1.117658	–2762.777986	–
	–2764.046117				–		–2762.928459 [b]	–
D(*L*)-valine	–402.268149	0.160569	57.7	–402.107580	–	0.125130	–402.143018	–
	–402.304663				–		–402.179533 [b]	–

[a] Calculated from uncorrected COSMO total energies.

[b] Calculated using TCGFE corrections calculated at the RI-B97-D/TZVP (gas-phase) approximation level.

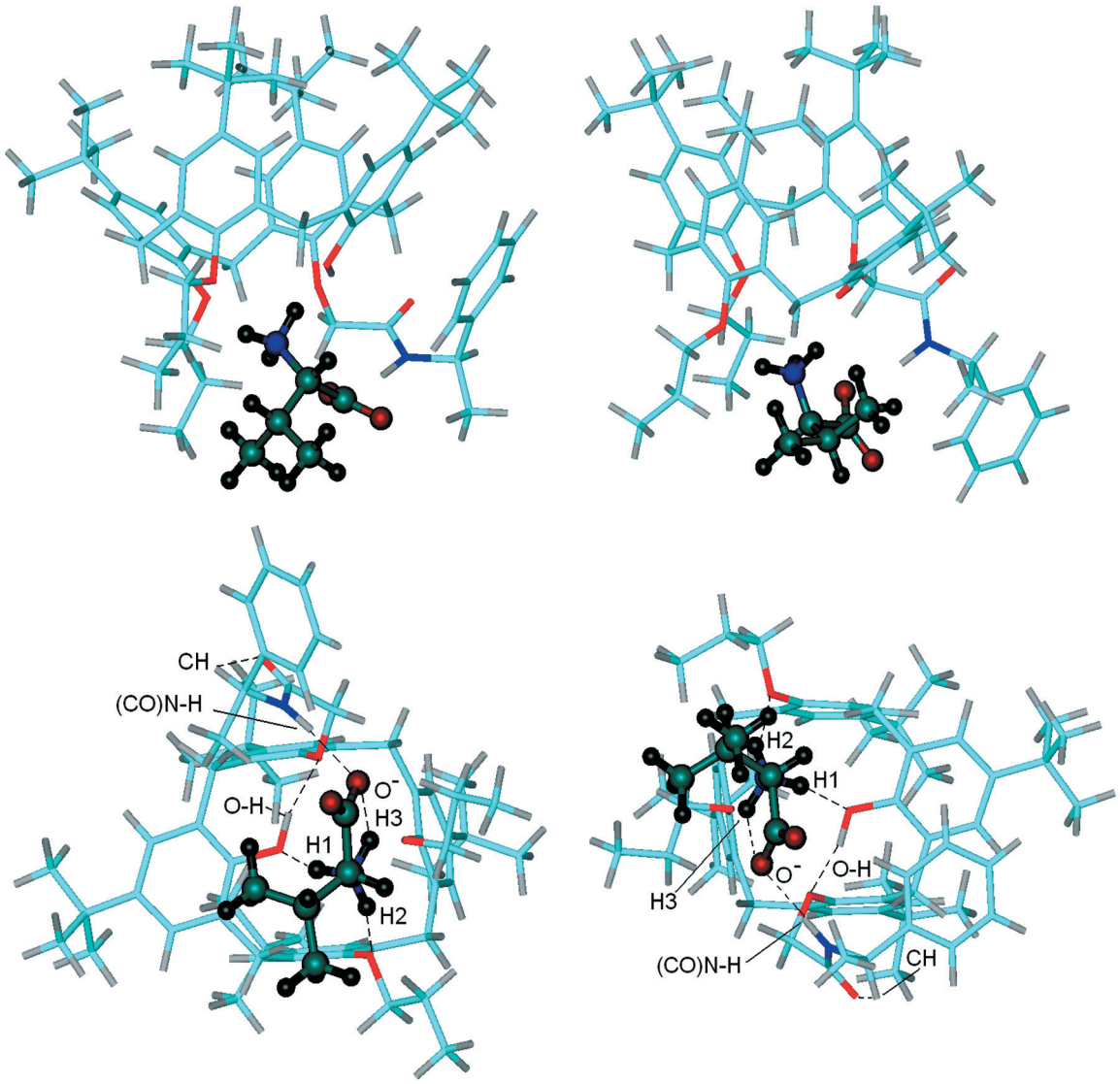

Figure 4. VMD plots of complexes: (A) **3** (cS, S)-*D*-valine, (B) **4** (cS, R)-*L*-valine: side view (top) and bottom view (bottom).

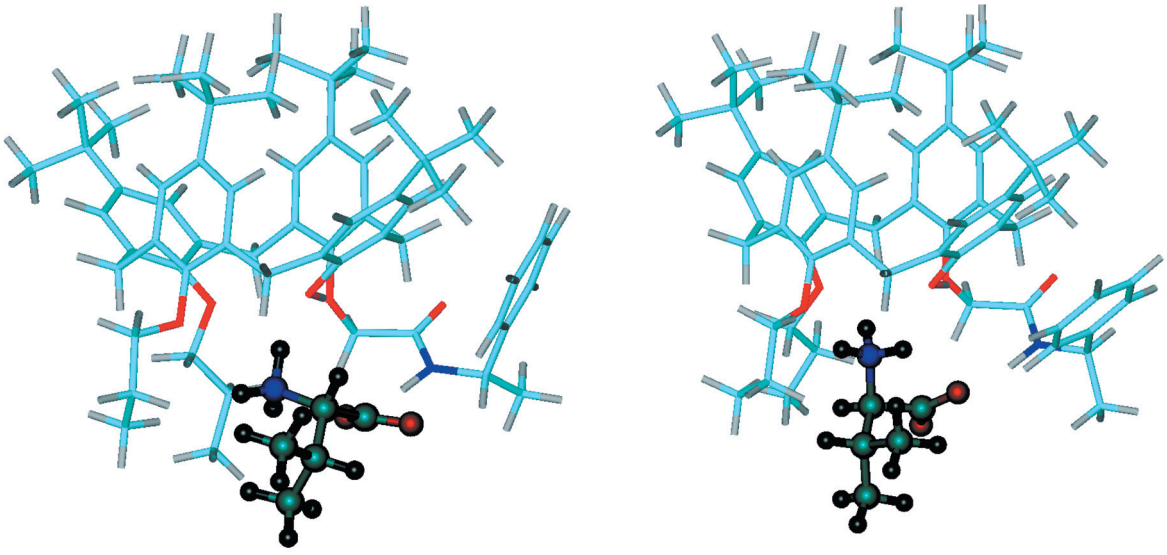

Figure 5. VMD plots of complexes: (C) **3** (cS, S)-*L*-valine (Δ*G* +2.4 kcal/mol relative to A), (D) **4** (cS, R)-*D*-valine (Δ*G* +1.1 kcal/mol relative to B).

solutions,[25] such result probably indicates rather low stability for the considered adducts. The similar results have been obtained by taking solvent effects (methanol) into account using the COSMO empirical routine and more polarized (TZVPP) basis sets by single-point energy calculations (see Table 2 in italic font).

Conclusion

The interaction optically pure inherently chiral calix[4] arene carboxylic acid and their amides with the amino acids in organic phase has been studied using electron spectroscopy. It was found that the chiral calix[4]arenes are able to enantioselective recognition of *L*- and *D*-valine. (cS, S)-Calix[4]arene **3** effectively interacts with *D*-amino acid, while (cS, R)-macrocycle **4** with *L*-valine. Highly effective binding for the "smallest" amino acids, *i.e.* *L*-valine and *L*-alanine, in the range of the substrates considered by (cS, S)- and (cS, R)-calix[4]arenes was observed. However, in the case of racemic amino acids, most effective interaction was found for "bigger" leucine. The presence of additional binding sites in the structure of amino acids did not affect the efficiency of interaction. It has been shown that the change of inherent chirality of calix[4]arenes significantly influence on the efficiency of interaction with amino acids. During the interaction of the two inherently chiral macrocycles **3** and **5**, the significant change in the efficiency of interaction with *L*-leucine was shown. The difference in the logarithms of the stability constants was 1.53 of magnitude. The introduction of additional binding sites in the structure of macrocycles significantly increases efficiency of interaction with substrates.

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References

1. Lehn J.M. *Supramolecular Chemistry: Concepts and Perspective*. Weinheim: Wiley-VCH, **1995**. 271 p.
2. Schneider H.J., Yatsimirsky A. *Principles and Methods in Supramolecular Chemistry.* Chichester: Wiley, **2000**. 151 p.
3. Schalley C. *Analytical Methods in Supramolecular Chemistry*. Weinheim: Wiley-VCH, **2007**. 484 p.
4. Peczuh M.W., Hamilton, A.D. *Chem. Rev.* **2000**, *100*, 2479-2494.
5. Nelson D.L., Cox M.M. *Lehninger*, *Principles of Biochemistry* 3rd Ed. Worth Publishing: New York, **2000**. 1255 p.
6. Miller S.L. *Science* **1953**, *117*, 528-559.
7. Miller S.L., Urey H.C. *Science* **1959**, *130*, 245-251.
8. Gutsche C.D. *Calixarenes: An Introduction*. Cambridge: RSCPublishing, **2008**.276 p.
9. Vicens J., Harrowfield J. *Calixarene in the Nanoworld.* Dordrecht: Springer, **2007**. 395 p.
10. Asfari Z., Böhmer V., Harrowfield J., Vicens J. *Calixarenes 2001*. Dordrecht: Kluwer Academic Publisher, **2001**. 684 p.
11. Li S.-Y., Xu Y.-W., Liu J.-M., Su C.-Y. *Int. J. Mol. Sci.* **2011**, *12*, 429-455.
12. Zheng Y.-S., Luo J. *J. Inc. Phen.* **2011**, *71*, 35-56.
13. Karpus A.O., Yesypenko O.A., Andronov L.P., Boyko V.I., Voitenko Z.V., Chernega A.N., Kalchenko V.I. *J. Incl. Phenom. Macrocycl. Chem.* **2012**. DOI 10.1007/s10847–012–0231–8.
14. Karpus A.O., Yesypenko O.A., Andronov L.P., Boyko V.I., Garasevich S.G., Voitenko Z.V., Chernega A.N., Kalchenko V.I. *Tetrahedron: Asymmetry* **2012**, *23*, 1243-1250.
15. Yushkova E.A., Stoikov I.I., Zhukov A. Yu., Puplampu J.B., Rizvanov I. Kh., Antipin I.S., Konovalov A.I. *RSC Adv.* **2012**, *2*, 3906-3919.
16. Ahlrichs R., Bär M., Häser M., Horn H., Kölmel C. *Chem. Phys. Lett.* **1989**, *162*, 165-169.
17. TURBOMOLE ver. 6.4 (2012), a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since **2007**; http://www.turbomole.com.
18. Grimme S. *J.Comput. Chem.* **2006**, *27*, 1787-1799.
19. Grimme S., Antony J., Schwabe T., Mück-Lichtenfeld C. *Org. Biomol. Chem.* **2007**, *5*, 741-758.
20. Schäfer A., Huber C., Ahlrichs R. *J. Chem. Phys.* **1994**, *100*, 5829-5835.
21. Klamt A., Schüürmann G. *J. Chem. Soc. Perkin Trans. 2* **1993**, 799-805.
22. Schäfer A., Klamt A., Sattel D., Lohrenz J.C. W., Eckert F. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2187-2193.
23. Eichkorn K., Treutler O., Öhm H., Häser, M., Ahlrichs R. *Chem. Phys. Lett.* **1995**, *240*, 283-290.
24. VMD for Windows-32, ver. 1.9 (2011), NIH Center for Macromolecular Modeling & Bioinformatics, University of Illinois, Illinois, USA; http://www.ks.uiuc.edu.
25. Rozhenko A.B., Schoeller W.W., Letzel M.C., Decker B., Mattay J. *New J. Chem.* **2013**, *37*, 356-365.

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