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High-performance liquid chromatographic enantiomeric resolution in the ten-vertex carborane series
Comparison of acetyl- and native β-cyclodextrin bonded chiral stationary phases

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Abstract

The HPLC resolution on native and acetyl β-cyclodextrin columns is reported for thirteen enantiomeric pairs of racemates, members of two series of positional isomers in the ten-vertex carborane family, the exo-9-L-*arachno*-5,6-$C_2B_8H_{12}$ (L=NH_3, primary or secondary amino group) or exo-6-L-*arachno*-5,10-$C_2B_8H_{12}$ (L=secondary or tertiary amino group). The study of influence of the structural factors on retention, selectivity and resolution of individual compounds is described on both chiral stationary phases (CSPs). The deep differences in enantio-selectivities has been observed for native and acetyl β-cyclodextrin CSPs. Circular dichroism (CD) spectra of exo-9-*t*-$BuNH_2$-*arachno*-5,6-$C_2B_8H_{12}$ and exo-6-Et_3N-*arachno*-5,10-$C_2B_8H_{12}$, members of each series are presented. The CD results indicate the different enantiodiscrimination mechanism on the two CSPs under study. © 1998 Elsevier Science B.V.

Keywords: Chiral stationary phases, LC; Enantiomer separation; Cyclodextrin-based stationary phases; Caraboranes; Ten vertex carboranes

1. Introduction

Native [1–8] or functionalized [1,9–13] covalently bonded β-cyclodextrin (β-CD) chiral stationary phases (CSPs) have proved to exhibit an exceptional performance in the optical isomer resolution of organic chiral compounds.

Many differences can be found between chiral cluster boranes and chiral organic compounds containing cyclic moieties, usually resolved on native β-CD. However, recent studies in this laboratory have proved that the chemically bonded native β-CD CSPs could be used as excellent supports for the enantioseparation of a wide range of chiral eleven-vertex carborane or eleven- and twelve-vertex metallaborane enantiomers [14–19]. The intercalation mechanism on β-CD CSPs was found ideal for space structures of these carborane and metallaborane moieties. For the above mentioned series of cage boron species, most compounds studied could be separated, at least with partial resolution. On the other hand, surprisingly, native β-CD CSPs failed in enantioseparation of the previously tested 5-X-6,9-$(Me_2S)_2B_{10}H_{11}$ or 5-X-6,9-$C_2B_8H_{13}$ [20] com-

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pounds from ten-vertex borane and carborane derivative series. Strong retention of such compounds evidences strong intercalation complex formation. However, bottom position of the substituent is likely to be unfavorable for enantioselective interaction with the hydroxyls at the rim of the CD cavity.

Recently, the synthetic route to two classes of new ten-vertex isomeric compounds with the formulae exo-9-L-*arachno*-5,6-$C_2B_8H_{12}$ (A) or exo-6-L-*arachno*-5,10-$C_2B_8H_{12}$ (B) has been found, based on reaction of the 5,6-$C_2B_8H_{12}$ with amines [21]. These two isomers differing in the positions of the skeletal carbon atoms have amino substituent in the upper skeletal position. One or both positional isomers originate in this reaction depending upon the nature of amine; see Fig. 1. Generally, reaction with tertiary amines led to species (A), reaction with ammonia or primary amines gave isomers (B) while secondary amines provided mixture of two isomers (A+B) in various ratios. Both isomeric series of these interesting compounds are pro-chiral and their surprisingly high stability toward a hydrolysis allowed a study of their separation in aqueous methanol or acetonitrile mobile phases conventionally used for separation on native β-CD materials.

Despite the native β-CD CSPs were useful for few members of this carborane family, most of the compounds of this type remained unresolved using this support. However, a partial success encouraged us to perform a search for other CD-based CSPs that should exhibit better enantioselectivity. Finally, we succeeded in enantioseparation of most remaining chiral compounds from above series using acetyl-β-CD material, based on derivatization of the previously used directly bonded native β-CD support. The first success in the separation of ten-vertex carborane derivatives has been already mentioned in a review article [19], but no details about chromatographic procedures and structure–selectivity considerations were given.

The aim of this article is to describe chromatographic details of the successful separation of 13 chiral ten-vertex carbaborane derivatives into enantiomers using native and acetyl-β-CD materials. The experimental data were obtained on a wide range of compounds differing in their structures. This material allowed for a deeper study of the structural aspect's influence on enantiodiscrimination on the native and acetyl-β CD materials.

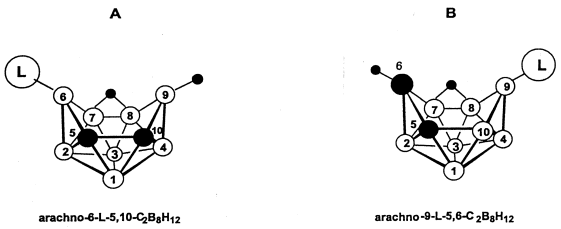

Fig. 1. Structures of the asymmetric carboranes of the exo-*arachno*-6-L-5,10-$C_2B_8H_{12}$ type (A) and exo-*arachno*-9-L-5,6-$C_2B_8H_{12}$ type (B). Terminal hydrogens are omitted for clarity.

2. Experimental

2.1. Synthesis of directly bonded acetyl-β-cyclodextrin stationary phase

A stainless steel HPLC column (125×4 mm I.D.) was slurry packed with β-cyclodextrin CSP having high cyclodextrin loading (carbon content 9%) [22]. The acetylation reaction was done in situ by following procedure: the column was washed by dry methanol (200 ml) and dry dichloromethane (200 ml) at flow-rate 1 ml/min. Acetanhydride (50 ml) was pumped through the column for 100 min. After 24 h, the column was washed using dichloromethane (200 ml), methanol (500 ml) and water (500 ml).

2.2. Columns

A stainless-steel HPLC column was slurry packed with β-cyclodextrin CSP having high cyclodextrin loading (carbon content 9%) (250×8 mm I.D.) [22] or the above directly bonded acetyl β-CD (125×4 mm I.D.) column was used. The commercially available column CYCLOBOND I (Astec, Whippany, NY) was also used. The void volumes of β-cyclodextrin columns were determined according to the literature method [23].

2.3. Apparatus

The chromatographic equipment consisted of a Merck-Hitachi HPLC system: L 6200 Intelligent Pump, a D-6000 interface, Rheodyne Model 7125

Table 1
Chromatographic data for optimum enantiomeric separation of two isomeric series of the L-*arachno*-$C_2B_8H_{12}$ compounds on directly bonded β-CD CSPs in aqueous methanolic mobile phases

Compound	No.	[a]k_1'	α	R_s	Column	% MeOH
6-Et_3N-5,10-$C_2B_8H_{12}$	1	2.58	1.12	1.35	A	100
6-Isoquinoline-5,10-$C_2B_8H_{12}$	2	4.55	1.07	1	A	100
6-HMTA-5,10-$C_2B_8H_{12}$[a]	3	9.89	1.1	1.2	A	95
9-Piperidine-5,6-$C_2B_8H_{12}$	4	6.63	1.24	0.95	B	50

[a]k_1'=Capacity factor of the first-eluting enantiomers.
HMTA=hexamethylenetetraamine; Column: A=directly bonded native β-CD column (250×8 mm) with high β-CD loading; flow-rate, 0.8 ml/min, B=CYCLOBOND I, β-CD column (250×4.6 mm); flow-rate, 0.8 ml/min.

sampling valve (Cotati, CA, US) with 10 or 200 μl loops and a L-7450 diode array detector with HSM 2.0 HPLC manager (Merck-Hitachi).

2.4. Chemicals, sample preparation and detection

Deionized water was used for the preparation of aqueous-organic mobile phases. All other chemicals were of an analytical grade (Lachema Brno, Czech Republic). Methanol was distilled before use. Eluents were filtered through a 0.45 μm filter and shortly degassed under vacuum.

All deltahedral borane compounds (1–14, Tables 1 and 2) were prepared in the Boron Chemistry Group of the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, according to an already published procedure [21] or by closely related methods. Synthesis of all compounds will be a subject of a separate full paper.

Special care was paid to ensure the purity of the individual proto-chiral positional isomers used in this study. The purity of all species was checked by ^1H (at 500 MHz) and ^{11}B (at 160 MHz) NMR and mass spectroscopy.

Samples were prepared just before the injection as methanolic solutions of concentrations 1.0 mg/ml. All samples were filtered through a 0.45 μm Teflon microfilter (Tessek, Czech Republic).

All compounds (1–13, Tables 1 and 2) were detected at fixed wavelengths 225 and 254 nm.

2.5. Circular dichroism spectra

Eluent in the range of peaks of both enantiomers

Table 2
Chromatographic data for optimum enantiomeric separation of two isomeric series of the L-*arachno*-$C_2B_8H_{12}$ compounds on functionalized acetyl-directly bonded β-CD column (125×4 mm) in aqueous methanolic mobile phases

Compound	No.	50% MeOH			55% MeOH			65% MeOH		
		k_1'	α	R_s	k_1'	α	R_s	k_1'	α	R_s
6-Isoquin-5,10-$C_2B_8H_{12}$	2	–	–	–	10.4	1.20	1.40	8.47	1.21	1.30
6-HMTA-5,10-$C_2B_8H_{12}$	3	–	–	–	–	–	–	9.25	1.30	0.95[a]
9-Piper-5,6-$C_2B_8H_{12}$	4	13.63	1.45	1.18	6.64	1.31	2.1	3.62	1.17	1.27
9-H_3N-5,6-$C_2B_8H_{12}$	5	5.75	1.20	1.40	4.36	1.13	1.33	2.7	1.10	0.85
9-$MeNH_2$-5,6-$C_2B_8H_{12}$	6	6.16	1.23	1.18	4.60	1.19	0.95	2.79	1.10	0.85
9-$PrNH_2$-5,6-$C_2B_8H_{12}$	7	6.93	1.38	1.25	5.26	1.25	1.65	2.90	1.16	0.95
9-$BuNH_2$-5,6-$C_2B_8H_{12}$	8	12.55	1.28	1.10	6.64	1.21	1.38	3.50	1.14	0.85
9-t-$BuNH_2$-5,6-$C_2B_8H_{12}$	9	7.62	2.36	3.27	5.20	2.28	5.32	2.98	1.81	2.85
6-Et_2NH-5,10-$C_2B_8H_{12}$	10	10.58	1.28	1.30	6.85	1.21	1.36	3.53	1.15	0.88
9-Et_2NH-5,6-$C_2B_8H_{12}$	11	8.88	1.61	2.09	5.87	1.51	1.95	2.88	1.36	1.62
6-Bu_2NH-5,10-$C_2B_8H_{12}$	12	10.50	1.13	0.70	6.47	1.09	0.65	2.99	1.0	NR
9-Bu_2NH-5,6-$C_2B_8H_{12}$	13	9.32	1.24	1.05	5.99	1.21	1.10	3.96	1.09	0.60

[a] Better values: k'=4.11, α=1.30 and R_s=1.21 were obtained in 70% MeOH.
NR=not resolved; flow-rate=0.4 ml/min.

was collected from 20 successive injections and the solvent evaporated off immediately in vacuum at low temperature. The samples were dissolved in 2 ml methanol just before the measurements.

CD spectra were recorded on an Auto Dichrographe Mark V equipment (Jobin Yvon, France). The instrument is driven by a microcomputer (Silex, France) loaded with our own software. The measurements were performed in quartz cells with the optical path length 1 or 0.1 cm. The spectra are computer averages over 2–3 instrument scans and the intensities are presented for 6-Et_3N-5,10-$C_2B_8H_{12}$ (1) in $\Delta\varepsilon$, for 9-tBuNH2-5,6-$C_2B_8H_{12}$ (9) in arbitrary units, respectively.

3. Results and discussion

The schematic structure of all compounds under study is shown in Fig. 1. The retention data, selectivities (α) and resolution values (R_s) for these ten-vertex carbaborane compounds are summarized in Tables 1 and 2. Only data for successful enantiomeric separations are listed in these tables.

3.1. Native β-CD columns

From the results summarized in the Table 1 can be seen, that two native β-CD CSPs (directly bonded β-CD and CYCLOBOND I) columns tested have been efficient only for compounds with 6-triethylamine, 6-hexamethylene tetraamine and 6-isoquinoline (Fig. 2) (1–3), members of structural type (A). All these compounds have bulky, tertiary amine substituent in position 6 and the rare, thermodynamically unfavorable, bottom positions of carbon atoms (5, 10). Enantiomers of only one member of the second type (B) could be resolved, in the case of compound substituted by piperidine (4), but only if CYCLOBOND I column was used. Noteworthy is very strong retention of all species on directly bonded native β-CD support, much higher than for all previously reported series of the eleven-vertex carborane derivatives [14] and the increasing trend in the resolution with increasing methanol content. The best selectivity and resolution values were obtained for 6-Et_3N-5,10-$C_2B_8H_{12}$ (1) substituted compound, which could be resolved on the directly bonded

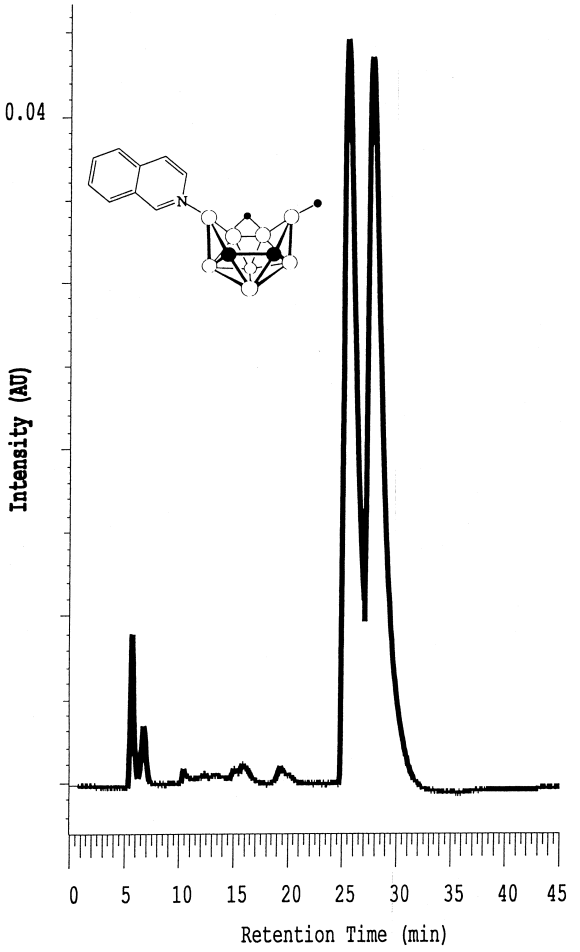

Fig. 2. Separation of the enantiomers of the *arachno*-6-isoquinolino-5,10-$C_2B_8H_{12}$ on native CD column. Chromatographic conditions: column: native-directly bonded-β-cyclodextrin (250× 8 mm I.D.); mobile phase: 100% methanol, flow-rate: 0.8 ml/min; injection: 10 μl of the solution of 1 (approx. concentration 1 mg/ml), detection: UV DAD fixed wavelength 254 nm.

β-CD with reasonable R_s values with advantage in pure aqueous methanol. The semi-preparative scale separation (see Fig. 3) afforded about 15 mg of pure enantiomers, and the CD spectra of both enantiomers were measured (see Fig. 4a). Replacement of methanol by aqueous acetonitrile (70–85%) led to appreciable decrease of the resolution. All other compounds under study, including 6-Et_2NH-5,10-$C_2B_8H_{12}$ and 6-Bu_3N-5,6-$C_2B_8H_{12}$ (not summarized in the tables) remained unresolved on this type of CSP. Sometimes a peak broadening was observed.

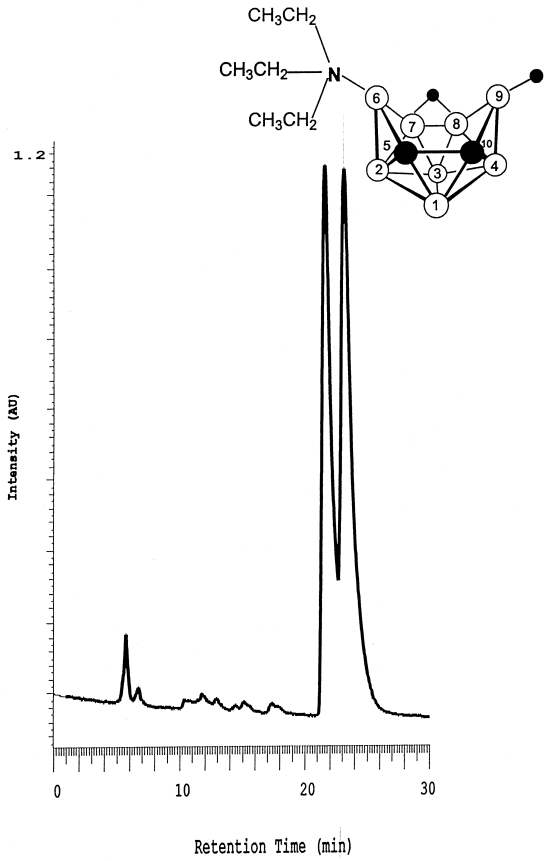

Fig. 3. Preparative separation of the enantiomers of the *arachno*-6-Et_3N-5,10-$C_2B_8H_{12}$ on native CD column. Chromatographic conditions: column, native directly bonded β-cyclodextrin (250×8 mm I.D.); mobile phase: 100% methanol, flow-rate: 0.8 ml/min; injection: 100 μl of the solution of 1 (concentration 10 mg/ml), detection: UV DAD fixed wavelength 254 nm.

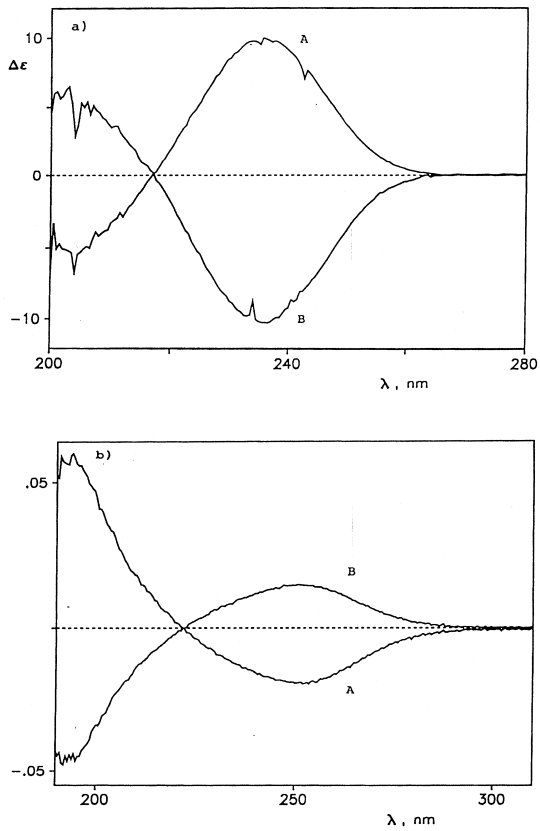

Fig. 4. CD spectra of the enantiomers of compounds 1 (a) and 9 (b). Curves A and B represent those of the first and second eluting enantiomers.

3.2. Acetyl-β-CD column

In contrast, the new directly bonded acetyl-β-CD support allowed for an enantioseparation of most of chiral compounds (see Table 2) under study. Taking into account that only short 12.5 cm column was used, the R_s values of most of these species are exceptionally good. Examples of separations are given in Figs. 5 and 6.

A remarkable decrease of retention was observed on acetyl-β-CD in comparison with the parent underivatized directly bonded β-CD support. The dependence of k' and R_s values on organic modifier content indicate behavior of carboranes on these CSPs, observed already on the native supports for eleven-vertex carboranes [14]. Increasing the organic modifier content in the mobile phase (studied in the range 50–65%), k' values decrease monotonously. The optimum R_s value for most of the compounds lies at approximately 55% of methanol. Down to this concentration, peak tailing usually appears due to poor mass transfer and, also due to unfavorable strong interactions of amino moieties with remaining CD-hydroxy, or silanol groups at the support surface. Increasing the methanol concentration, the resolution decreases due to a competition of the organic modifier with solutes in the intercalation process. For details see Table 2, which summarizes the retention data for three mobile phase compositions.

The appreciably high R_s values for 9-*t*-Bu-NH_2-$C_2B_8H_{12}$ (9) allowed for semi-preparative separation

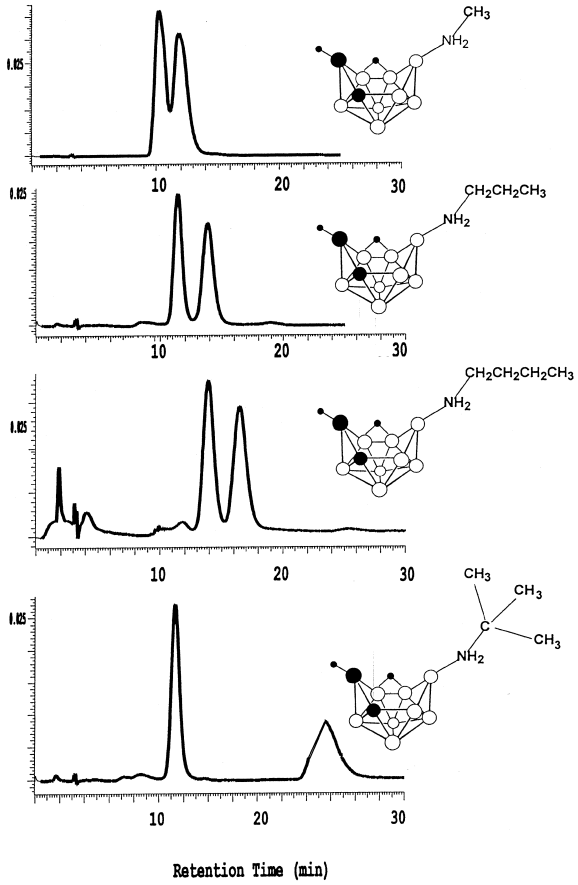

Fig. 5. Influence of nature of the primary amino ligand L in the structure of the *arachno*-9-L-5,6-$C_2B_8H_{12}$ on enantioselectivity on bonded-acetyl-β-cyclodextrin column. Chromatographic conditions: column: acetyl-directly bonded-β-cyclodextrin (125×4 mm I.D.); mobile phase: 55% methanol, flow-rate: 0.4 ml/min; detection: UV DAD, fixed wavelength 254 nm.

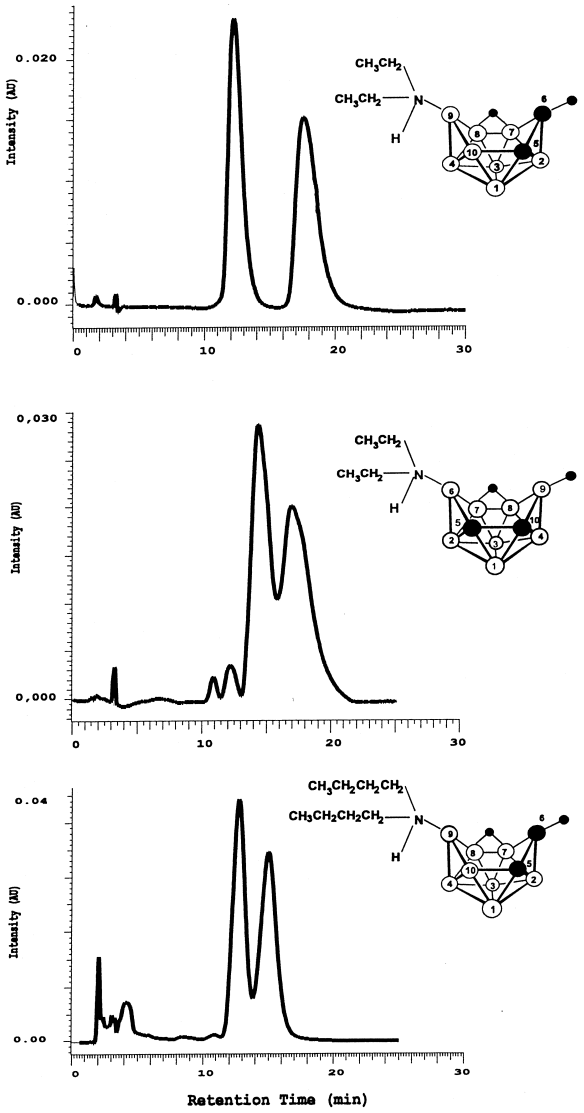

Fig. 6. Influence of the isomer structure and the size of alkyls on the secondary amino-group as ligand L in *arachno*-9-L-5,6-$C_2B_8H_{12}$ series on separation on bonded-acetyl-β-cyclodextrin column. Chromatographic conditions as in Fig. 5.

of the enantiomers even on the short analytical column. The amount of both pure enantiomers necessary for circular dichroism spectra measurement (see Fig. 4b) was obtained.

3.3. Comparison of the native and the acetyl-β-CD CSPs

In a study described in the literature, exemplifying effect of the amine moiety structure on resolution on native β-CD, the increase in the resolution was observed in the order primary<secondary<tertiary amino groups attached on a metallocene framework [2]. Similarly, recently, the enhancement in resolution of nitrogen bridged metallaboranes has been observed, increasing substitution by alkyl groups at the bridge atom. Therefore, the resolution of compounds with bulky tertiary amino groups 1–3 on the native β-CD seems to fall within the above results.

In contrast, as can be seen from data in Table 2, on the acetyl-β-CD a different order in the mag-

nitude of the selectivity and R_s values was observed if the substituent was an aliphatic amino group. Increasing the number of substituents on amino nitrogen, the resolution apparently decreases on this material. The support provided generally good selectivity and resolution for compounds (5–13) with bare, primary and secondary amino groups. Probably enhanced hydrogen donor character of these amino groups is responsible for higher selectivity due to hydrogen bonding interaction with polar acetyl groups. The size and space requirements of the alkyl substituent were found to play an additional role, likely to be important for tight intercalation in the cavity. As can be clearly seen from the data for compounds with primary amino substituents (6–9) (see Table 2 and Fig. 5), as the size of alkyl groups increases, the selectivity and resolution increase up to an optimum value for *n*-propyl or *tert*-butyl for primary amino substituents, and then slightly decreases for *n*-butyl substituted compound 8. For compounds bearing secondary amino groups (10–13), where both A and B isomers were available, better R_s values were observed for isomeric series B (11, 13) with substituent in position 9 and carbon atoms in positions 5 and 6 of the skeleton. The resolution of the second isomer (10, 12) with substituent in position 6 and bottom positions of carbons 5 and 10 was poorer (for example see Table 2 and Fig. 6). The different position of the CH groups in the framework and, especially, the presence of a CH_2 group with endo proton of the enhanced acidity [24,25] in the structure of isomer B should be responsible for the observed differences.

No resolution was observed on this CSPs for compounds substituted by tertiary aliphatic amines, i.e., only peak broadening was observed for 6-Et_3N- or 6-Bu_3N-5,10-$C_2B_8H_{12}$ substituted derivatives from the series A. On the other hand, all three compounds with cyclic tertiary amines (2–4) were successfully resolved also on this material. In contrast, 9-isoquinoline-derivate isomeric to compound 2 was unresolved either on native or acetylated cyclodextrin supports. From the point of view of the structural factors seems interesting, that bulky hexamethylene tetraamine substituted species was resolved along with two planar aromatic amine derivatives. More rigid structures of all three compounds can better account for the resolution than lower steric requirements of planar aromatic amino substituents of compounds 2 and 4, in intercalation mechanism. Another possibility may exist, that the mechanism is different for these species, i.e., bulky amino moieties are intercalated preferably.

Comparing the above results on native and acetyl-β-CD, the selectivity of these CSPs for the resolution of ten-vertex chiral cage borane species bearing primary, secondary and tertiary amino groups is almost complementary. An exception exists for latter compounds with cyclic amino substituents, which were resolved on both supports.

3.4. Circular dichroism spectra

Circular dichroism (CD) spectra of the first and second eluted enantiomers of the compound 1 and 9 (Fig. 4a,b), exhibit very similar character, typical for carboranes without a chromophoric group [14]. Only a single Cotton effect was observed in short wavelength range with maximum about 250 nm. On the other hand, the direction of the Cotton curves for first eluting enantiomers is just opposite for species 1 (resolved on native CD), and corresponding enantiomer of 9 (resolved on acetyl-β-CD support). Hence, the enantiomer discrimination mechanism seems different on these two CSPs. This can explain the above discussed differences in enantioselectivities.

4. Conclusions

The acetyl-β-cyclodextrin CSPs have proved efficient for the resolution of enantiomers of a variety of ten-vertex carbaboranes, separation of which being impossible using underivatized β-CD CSPs. Almost complementary selectivity order was observed on these two supports along with some evidence for a different enantioseparation mechanism. In the above study, the acetyl-β-CD CSPs was found to be a new valuable tool for the separation of chiral cage carbaborane and metallaborane species, especially those bearing groups with hydrogen donor properties.

The practical application of these separation methods for preparative challenges has proved possible. The pure enantiomers could be isolated in amounts sufficient for subsequent studies of their physical

properties, e.g., CD spectra measurements and additionally, for the possible determinations of their absolute structures by X-ray diffraction analysis.

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