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Determination of relative configuration of symmetrical bis-Tröger's base derivatives

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ABSTRACT

Determination of the molecular covalent structure based on spectral analyses is almost routine; however, estimation of stereostructure is still challenging, particularly in case of symmetrical molecules. In this study, various spectral (NMR, IR and Raman) markers revealing relative configuration (syn and anti) of bis-Tröger's base diastereoisomers are identified. Differences in diastereoisomers ^{1}H chemical shifts seem to be most useful, as they can be interpreted by computations. Vibrational spectra of syn and anti diastereoisomers exhibited systematic differences, too. The relative configuration can be also predicted based on retention on silica, and unambiguously confirmed via chromatographic analysis on a chiral stationary phase.

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1. Introduction

The beginning of 21st century has brought more new dimensionality for famous Tröger's base (TB) derivatives [1], especially with the discovery of bisTB derivatives [2,3], which could be suitable building blocks of artificial receptors. BisTB derivatives can be seen as two Tröger's bases, which share one aromatic part, thus syn or anti diastereoisomers can be formed (Fig. 1). In the case of symmetrical bisTB derivatives, a crucial issue is how to recognize unambiguously syn and anti diastereoisomers without need of single-crystal X-ray diffraction.

In this study, on a series of twelve bisTB diastereoisomers (Chart 1), we investigate the reliability of some previously suggested empirical relations between relative configuration of bisTB and ^{1}H NMR, IR and Raman spectra, and support them with quantum chemical calculations. Furthermore, we also show some new, non-spectral (chromatographic) approaches.

2. Experimental methods

2.1. Materials

All solvents and chemicals were purchased from Sigma–Aldrich and used without additional purification. The preparations of studied compounds were described in our previous works: *syn*/*anti*-**1a** [4,5], *syn*/*anti*-**1b** [5], *syn*/*anti*-**1c** [5], *syn*/*anti*-**2a** [6,7], *syn*/*anti*-**2b** [6,7], *syn*/*anti*-**2c** [8], **3a** [4], **3b** [9], **3c** [9]. The structures of both *syn*-**1a** and *anti*-**1a** were already proofed via single-crystal X-ray diffraction [4], and can be obtained from the Cambridge Crystallographic Data Centre (CCDC 297485 *syn*-**1a** and CCDC 297484 for *anti*-**1a**).

2.2. Nuclear magnetic resonance

NMR spectra were recorded on 300 MHz NMR spectrometer Mercury Plus (Varian) and referenced to tetramethylsilane; chemical shifts are given in ppm and interaction constants in Hz. Chemical shifts of hydrogen atoms of methanodiazocine rings were determined by a spectral simulation [10]. All signals were assigned based on a combination of the common ^{1}H, ^{13}C, g-COSY, g-HSQC, g-HMBC and NOESY1D NMR spectra.

2.3. Vibrational spectroscopy

Infrared spectra (4000–600 cm^{-1}) were measured on Nicolet Nexus 670 FTIR spectrometer (Thermo Electron, USA) equipped with a single bounce ATR accessory MIRacle. Powdered samples were placed directly on the ZnSe crystal, dissolved in a few drops of $CDCl_3$, and left for several minutes until the solvent evaporated. Hence, a thin dry film well adhering to the ATR crystal was prepared. Afterwards 64 scans were accumulated per spectrum at 2-cm^{-1} resolution. Two repetitive measurements were performed for every sample. The same parameters were used to collect spectra of the solutions and of the solvent except for the cell compartment, where a metallic cap was used to prevent evaporation of the solvent. The averaged spectra were calculated and the spectrum of

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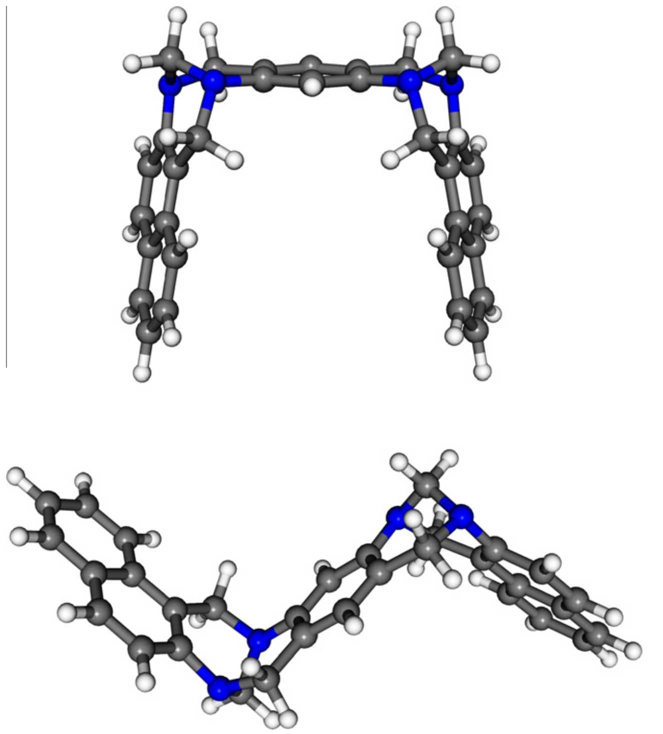

Fig. 1. Optimized structures of diastereoisomers *syn*-bisTB **1a** (upper) and *anti*-bisTB **1a** (lower).

the solvent was subtracted from spectra of solutions. The regions of the most intense absorption bands of the solvent (915–874 and 750–690 cm^{-1}) were blanked.

Raman spectra (4000–100 cm^{-1}) were recorded on Bruker FT Raman system (FT-NIR spectrometer Equinox 55/s plus FT Raman module FRA 106/S, Germany). The excitation source was Nd:YAG laser (Coherent, 1064 nm, laser power 150 mW). The samples were examined in glass vials both in the solid state as powdered samples and in $CDCl_3$ solution. The scattered light was collected in back-scattering geometry. 512 and 1024 separate interferograms per spectrum at 2-cm^{-1} resolution were accumulated four times and twelve times for solid samples and $CDCl_3$ solutions, respectively. The data for the solvent ($CDCl_3$) were measured in the same way as for the solutions. The averaged spectra and standard deviation records were calculated. The averaged spectrum of the solvent was subtracted from the spectra of solutions and the regions of the most intense bands of the solvent (2320–2165, 680–620, 375–350 and 271–247 cm^{-1}) were blanked.

2.4. Chromatography

The HPLC analyses were performed with LC 5000 HPLC system (INGOS, Czech Republic) on a chiral column CYCLOBOND I 2000 SN (250 × 4.6 mm, Supelco, USA) using dual detection (polarimeter detector CHIRALYSER and UV detector at 245 nm). The mixture of acetonitrile and acetic acid (8:2) with 0.1% of triethylamine (pH 4.2) was used for isocratic elution (0.75 mL/min).

The TLC analyses were performed on 10-cm TLC aluminum sheets Silica gel 60 F_{254} (Merk, Germany).

2.5. Computations

The Gaussian program [11] was used for the quantum mechanical calculations of equilibrium geometries, energies, and spectroscopic molecular properties. By default, the B3LYP [12] functional and 6–31G** Pople type basis set were used. After full optimization

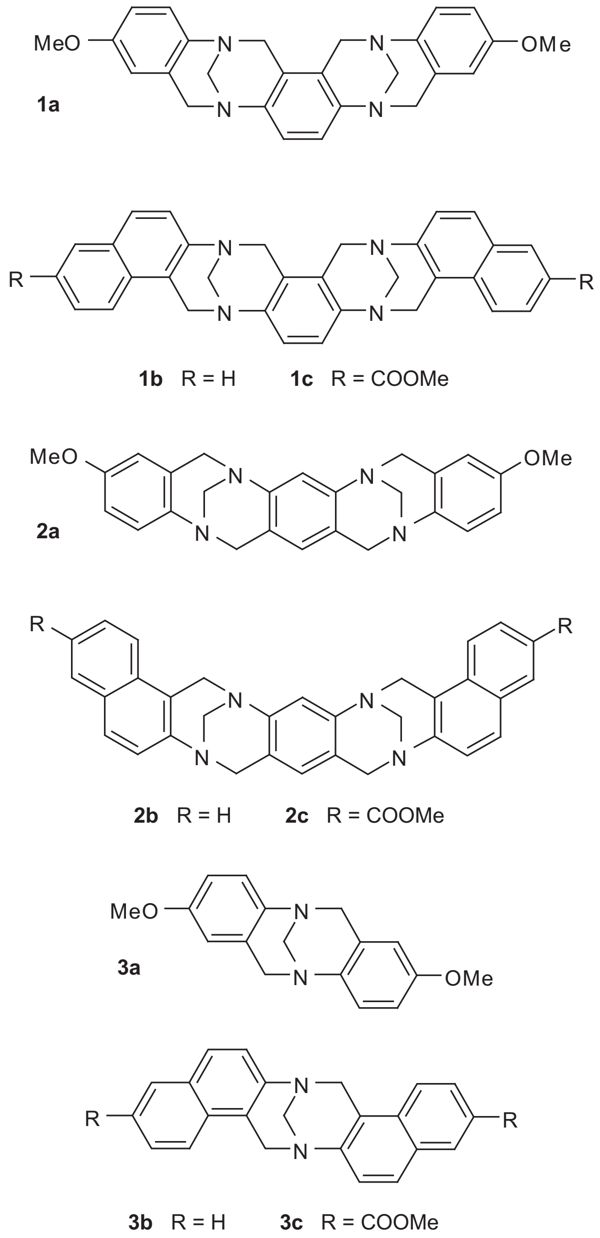

Chart 1. Studied compounds.

by the energy-minimization the harmonic force field was calculated for fully relaxed geometries, and infrared and Raman spectra generated with our own programs. The calculated intensities were convoluted with Lorentzian bands with a bandwidth (full width at half height) of 10 cm^{-1}. The Grimme dispersion energy correction [13] was used for some trial computation; however, it did not bring significant changes in the obtained spectra. Similarly, NMR spectral parameters were calculated by Gaussian, using the default GIAO method, using the EPR-II and IGLO-III basis sets for the shielding and 6-31G** for the geometry, with the B3LYP, M06L and VSXC functionals.

3. Results and discussion

3.1. Configuration assignment based on ^{1}H NMR spectra

Unambiguous determination of the relative configuration of bisTB diastereoisomers via NMR is possible only in the case of

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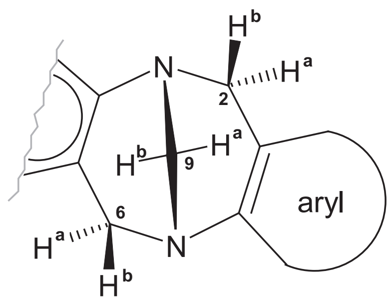
unsymmetrical derivatives. The otherwise usual approach based on weak allylic $^4J_{HH}$ interaction constants and NOE measurements [14,15] fails due to the equivalency of hydrogen atoms in the case of symmetrical bisTB diastereoisomers [16].

Fortunately, the chemical shifts of syn and anti diastereoisomers of bisTB derivatives differ significantly, thus an empirical relationship between chemical shifts and stereostructure was suggested [17]. The absolute value of the difference between the chemical shifts of the methylene group hydrogen atoms H2 ($\Delta\delta_{H2} = |\delta_{H2a} - \delta_{H2b}|$) and H6 ($\Delta\delta_{H6} = |\delta_{H6a} - \delta_{H6b}|$) is larger for syn diastereoisomers than for anti diastereoisomers, i.e., $\Delta\Delta\delta_{H2} = \Delta\delta^{syn}_{H2} - \Delta\delta^{anti}_{H2} > 0$ and $\Delta\Delta\delta_{H6} = \Delta\delta^{syn}_{H6} - \Delta\delta^{anti}_{H6}$, and smaller in the case of hydrogen atoms H9 ($\Delta\delta_{H9} = |\delta_{H9a} - \delta_{H9b}|$), i.e., $\Delta\Delta\delta_{H9} = \Delta\delta^{syn}_{H9} - \Delta\delta^{anti}_{H9} < 0$. Although, we showed previously that the differences depend strongly on the used solvent [4], this rule is valid in $CDCl_3$ for all known bisTB derivatives, as well as for bisTB derivatives **1** and **2** of this study (Table 1). Since the chemical shifts of H9a and H9b hydrogen atoms are similar, the difference is clearly apparent via the strength of the roofing effect (Fig. 2). It is worthy to note, a similar approach was published recently to determine relative configuration of methyl groups of a 1,3-dimethylpropane fragment based on chemical shifts differences of hydrogen atoms of the central CH_2 group [18].

To support this empirical rule we tried to find a computational model, which would predict the NMR shift differences, $\Delta\Delta\delta_H$. NMR isotropic shielding values obtained by DFT calculations [11] were used, wherein we tested several combinations of basis sets (EPR-II and IGLO-III for shielding, and 6-31G** for geometry), functionals (B3LYP, M06L and VSXC), size of the integration grid [19] and addition of the CPCM solvent correction [20]. No computational level gave signs of $\Delta\Delta\delta_H$ matching the experimental ones for all compounds at all hydrogen atoms chemical shifts (H2, H6 and H9). The most reliable was calculation of $\Delta\Delta\delta_{H2}$, the correct sign of which was obtained by most of the calculations. The best results were obtained by M06L/6-31G** (geometry) + M06L/IGLO-III (shielding), and B3LYP/6-31G** (geometry) + B3LYP/IGLO-III (shielding) method combinations, which both gave a wrong sign of $\Delta\Delta\delta_H$ only for one value (the continuum solvent model was omitted in both cases [21]). A full match of signs and the smallest deviation from experimental values was obtained when the $\Delta\Delta\delta_H$ values of the these calculations were averaged (Table 1).

An obvious disadvantage of this approach is the need of both diastereoisomers, since a direct comparison of calculated δ_H or $\Delta\delta_H$ values with experimental values is not reliable (see supplementary material). On the other hand, all studied compounds fulfill relation $\Delta\delta^{syn}_{H9} < 0.04$ ppm $< \Delta\delta^{anti}_{H9}$.

Table 1
Experimental and calculated values of $\Delta\Delta\delta_H$ [ppm].



		$\Delta\Delta\delta_{H2}$	$\Delta\Delta\delta_{H6}$	$\Delta\Delta\delta_{H9}$
1a	exp.	0.037	0.070	−0.044
	calcd.	0.030	0.025	−0.088
2a	exp.	0.128	0.090	−0.025
	calcd.	0.130	0.090	−0.016
1b	exp.	0.073	0.089	−0.088
	calcd.	0.075	0.021	−0.086
2b	exp.	0.240	0.120	−0.09
	calcd.	0.166	0.136	−0.100
1c	exp.	0.077	0.087	−0.077
	calcd.	0.045	0.040	−0.066
2c	exp.	0.219	0.129	−0.041
	calcd.	0.132	0.131	−0.062

3.2. Configuration assignment based on infrared and Raman spectra

We have found previously [4] that *syn*-**1a** and *anti*-**1a** can be distinguished based on a comparison of infrared and Raman spectra, wherein a syn diastereoisomer exhibits smaller differences between its infrared and Raman spectra than the corresponding anti diastereoisomer. To demonstrate the relation reliably we sought the closest corresponding peak positions in the corresponding Raman and IR spectra creating pairs of IR/Raman peak positions for all compounds **1**–**3**. For each pairs we calculated the absolute value of the wavenumber difference, summed these differences, and divided them by the number of pairs, to obtain an average difference for a particular compound either in solid state or in solution. As it is demonstrated in Table 2 the differences between infrared and Raman spectra are in all cases smaller for syn diastereoisomers; however, there is no critical value which would serve as a syn or anti indicator, thus both diastereoisomers have to be compared in each any individual case.

Also in this case we tried to support the empirical rule by a comparison of experimental vibrational spectra and calculated ones. Although the calculated IR and Raman intensity profiles reasonably well agree with the experimental spectra, clearly distinguishable and reproducible stereochemistry markers in the spectra of studied compounds are quite rare. The Raman scattering spectroscopy allowing to measure low-frequency vibrations seems to be slightly more sensitive to the syn–anti isomerism than the mid-IR spectrometry, especially within the 200–400 cm^{-1} (delocalized deformation modes in the aliphatic part) and 800–1000 cm^{-1} (involving the C–C and C–N stretching modes) wavenumber regions (see supplementary material).

3.3. Configuration assignment based on retention on silica

Another empirical method we found is based on a silica TLC analysis ($CHCl_3$:CH_3OH, 95:5). The R_f values of all presented compounds decrease in the order: common TB > *anti*-bisTB > *syn*-bisTB (Table 3). An explanation based on the known fact that silica strongly binds amines could be proposed. Considering that the common TB derivatives **3** have only two nitrogen atoms they should be less retarded on a silica stationary phase than the four-nitrogen-atoms bisTB derivatives **1** and **2**. The difference between *anti*-bisTB and *syn*-bisTB derivatives could be related to the probability of simultaneous binding of nitrogen atoms. The syn diastereoisomers, in contrary to the anti diastereoisomers, have all nitrogen atoms on the same side of molecule, thus syn diastereoisomers are expected to be more retarded on silica. This approach has the same limitation as the previous ones (*vide supra*), i.e., the requirement of both diastereoisomers (the similarity between R_f values of corresponding **1** and **2** derivatives can be helpful).

3.4. Configuration assignment based on chiral separations

Finally, an unambiguous determination of the configuration of symmetrical bisTB derivatives is based on a chiral resolution. We

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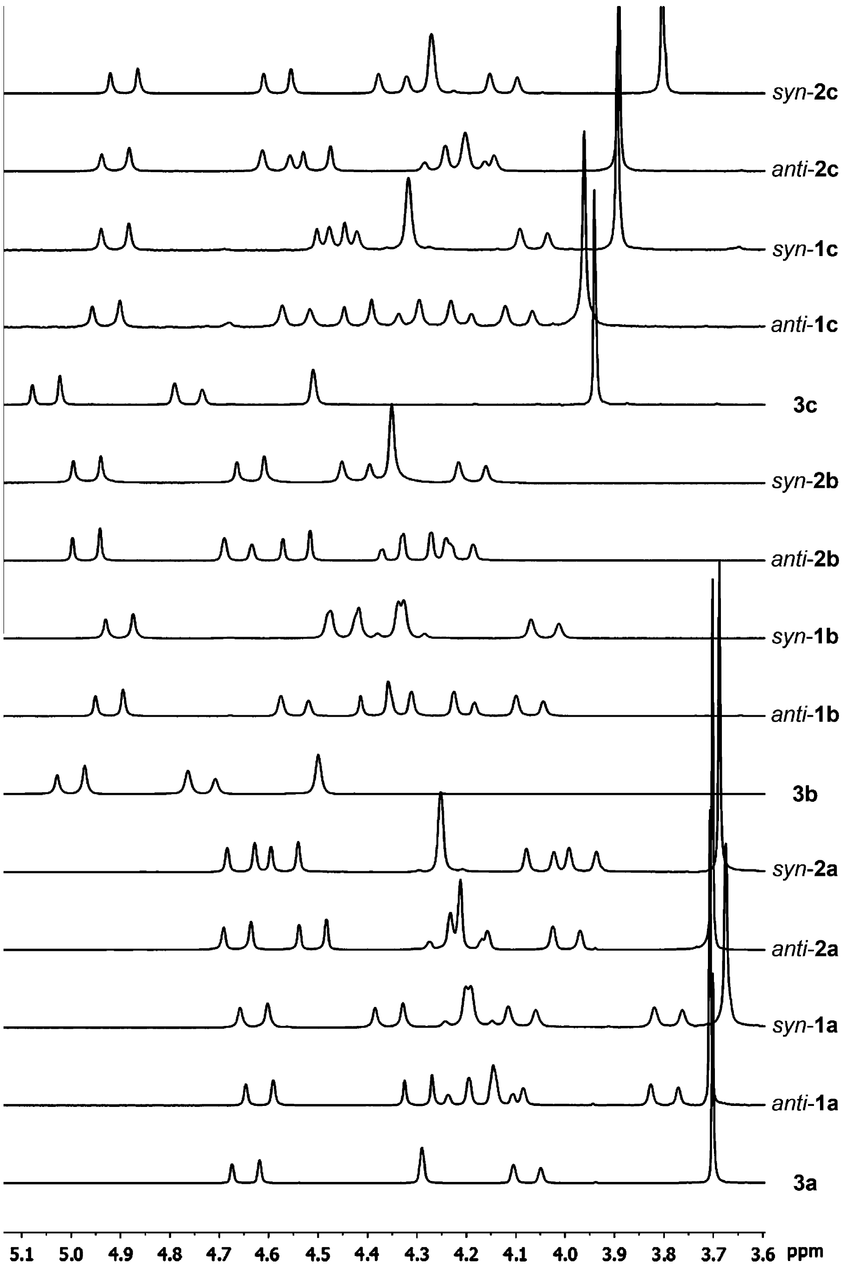

Fig. 2. ^{1}H NMR spectra of the studied compounds at 300 MHz (the region of H2, H6 and H9 hydrogen atoms signals).

employed HPLC analysis using column with a chiral stationary phase. Diastereoisomers *anti*-**1** and *anti*-**2** having C_2 symmetry are racemic mixtures of enantiomers, while diastereoisomers *syn*-**1** and *syn*-**2**, having plane symmetry C_S, are mesoforms. Thus, only anti diastereoisomers can be resolved on a chiral column into two peaks of an intensity ratio 1:1. As an example, we present the chiral separation of **2b** (an equimolar mixture of *anti*-**2b** and *syn*-**2b**) on Cyclobond I 2000 SN column with simultaneous UV and polarimeter detections. As expected, three peaks in the integral ratio 2:1:1 (the extinction coefficients of *anti*-**2b** and *syn*-**2b** are almost identical [8]) were observed at the UV detector, while only two gave responses of opposite signs at the polarimeter detector (Fig. 3). Therefore these peaks can be assigned to *syn*-**2b**, (−)-*anti*-**2b** and (+)-*anti*-**2b**. It should be emphasized that this approach is unambiguous only for the case when the chiral resolution is reached; the assignment of anti configuration is then doubtless. However, when no chiral separation is observed then diastereoiso-

Table 2
The average differences between peak positions of infrared and Raman band pairs (cm^{-1}).

	Symmetry	In solid	In $CDCl_3$
Syn-**1a**	C_S	2.1	1.9
Anti-**1a**	C_2	2.9	3.1
Syn-**2a**	C_S	1.4	1.7
Anti-**2a**	C_2	2.5	2.7
3a	C_2	1.4	1.1
Syn-**1b**	C_S	1.4	1.3
Anti-**1b**	C_2	2.6	2.7
Syn-**2b**	C_S	1.6	1.5
Anti-**2b**	C_2	2.4	2.5
3b	C_2	1.6	1.1
Syn-**1c**	C_S	2.2	2.2
Anti-**1c**	C_2	2.6	3.0
Syn-**2c**	C_S	1.1	1.4
Anti-**2c**	C_2	2.0	2.1
3c	C_2	1.6	1.3

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Table 3
The R_f values on silica.

	syn-	*anti-*	**3**
1a	0.27	0.46	0.57[a]
2a	0.21	0.48	
1b	0.31	0.76	0.83[b]
2b	0.30	0.79	
1c	0.36	0.74	0.86[c]
2c	0.34	0.77	

[a] **3a**.
[b] **3b**.
[c] **3c**.

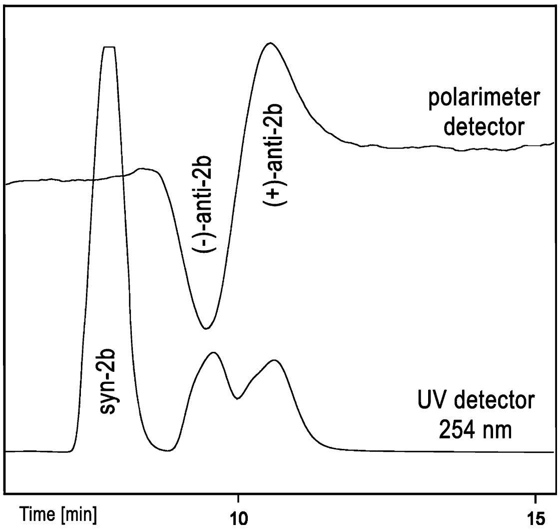

Fig. 3. The HPLC separation of **2b** on Cyclobond I 2000 SN column.

mer can be syn or anti, hence the possibility of unsuitable conditions to reach the resolution should be considered. Fortunately, the enantioseparation on the Whelk O1 column seems to be quite universal [22]. An analogous utilization of chiroptical properties was used recently to solve a similar structural problem of molecular tweezers [23].

4. Conclusion

We found that determination of the relative configuration of bisTB diastereoisomers based on NMR characteristics (the differences between $\Delta\delta_H^{syn}$ and $\Delta\delta_H^{anti}$) is reliable when measured in $CDCl_3$, as they can be verified by the quantum chemical calculation. Due to the significant roofing effect on signals of H9, the diastereoisomers can be recognized by naked eye. The alternate method based on the comparison of IR and Raman spectra can also be used. However, currently we did not find any sufficiently accurate support in the quantum chemical calculations; moreover, the analysis of fine spectral differences is laborious. In addition, we demonstrated that the relative configuration can also be estimated from the retardation factors of bisTB diastereoisomers obtained by TLC on silica.

In contrary to the previous methods, the separation on the chiral HPLC column is very straightforward, and does not require further analyses. It is probable that exploitation of chiral chemical shift reagents in the NMR analysis could be used as well [24]. Another method, which also does not require availability of both diastereoisomers, can be based on the ion mobility spectrometry, where the missing diastereoisomers can be prepared by ionization in an ion source [25].

Nevertheless, we believe that the combination of more methods makes determination of the relative configuration of bisTB diastereoisomers without need of single-crystal X-ray diffraction more reliable, and that the described approaches can be adapted easily for solving similar structural tasks.

Acknowledgments

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Appendix A. Supplementary material

The full assignments of ^1H and ^{13}C chemical shifts; the calculated chemical shifts values (δ_{H2}, δ_{H6}, δ_{H9}) and their detailed comparison with the experimental values; the experimental and calculated IR and Raman spectra. This material is available free of charge via the Internet. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.04.018.

References

[1] The first description (a) J. Tröger, J. Prakt. Chem. 36 (1887) 225;
The correct structure suggestion (b) M.A. Spielman, J. Am. Chem. Soc. 57 (1935) 583;
(c) The most recent reviews (a) S. Sergeyev, Helv. Chim. Acta 92 (2009) 415; (b) B. Dolenský, J. Elguero, V. Král, C. Pardo, M. Valík, Adv. Heterocycl. Chem. 93 (2007) 1.
[2] C. Pardo, E. Sesmilo, E. Gutierrez-Puebla, A. Monge, J. Elguero, A. Fruchier, J. Org. Chem. 66 (2001) 1607.
[3] M. Valík, B. Dolenský, H. Petříčková, V. Král, Collect. Czech Chem. Commun. 67 (2002) 609.
[4] B. Dolenský, M. Valík, P. Matějka, E. Herdtweck, V. Král, Collect. Czech Chem. Commun. 71 (2006) 1278. Erratum: the chemical shifts of H^{8b} were switched, i.e., it should be 4.02 ppm for 4a and 4.05 ppm for 4b.
[5] M. Havlík, V. Král, R. Kaplánek, B. Dolenský, Org. Lett. 10 (2008) 4767.
[6] M. Havlík, V. Král, B. Dolenský, Org. Lett. 8 (2006) 4867.
[7] M. Havlík, V. Král, B. Dolenský, Collect. Czech Chem. Commun. 72 (2007) 392.
[8] M. Havlík, V. Parchaňský, P. Bouř, V. Král, B. Dolenský, Collect. Czech Chem. Commun. 74 (2009) 1091.
[9] A. Tatar, J. Čejka, V. Král, B. Dolenský, Org. Lett. 12 (2010) 1872.
[10] MestReC, version 4.9.9.6, Mestrelab Research, Santiago de Compostela, Spain, www.mestrelab.com, 2011.
[11] Gaussian 03, Revision C.02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M.Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
[12] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[13] (a) S. Grimme, J. Comput. Chem. 27 (2006) 1787;
(b) V. Parchaňský, P. Matějka, B. Dolenský, M. Havlík, P. Bouř, J. Mol. Struct. 934 (2009) 117.
[14] A. Hansson, T. Wixe, K.-E. Bergquist, K. Wärnmark, Org. Lett. 7 (2005) 2019.
[15] (a) J. Cudero, P. Jiménez, C. Marcos, C. Pardo, M. Ramos, J. Elguero, A. Fruchier, Mag. Reson. Chem. 34 (1996) 318;
(b) C. Pardo, M. Ramos, A. Fruchier, J. Elguero, Mag. Reson. Chem. 34 (1996) 708;
(c) J. Elguero, A. Fruchier, T. Mas, C. Pardo, Mag. Reson. Chem. 43 (2005) 665.
[16] Although, there are NMR techniques which enable measurement of ^1H-^1H NOE between "equivalent" hydrogens (^1H–^{13}C to ^1H–^{12}C), it would be hardly

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applied in the case of bisTB derivatives, since the solubility of bisTB derivatives is very low and useful hydrogens are separated in distance more than 0.45 nm; see (a) J. Kawabata, E. Fukushi, J. Mizutani, J. Am. Chem. Soc. 114 (1992) 1115; (b) R. Wagner, S. Berger, Mag. Res. Chem. 35 (1997) 199;
Another possibility is measurement of residual dipolar couplings; see (c) C.M. Thiele, Eur. J. Org. Chem. (2008) 5673.
[17] (a) T. Mas, C. Pardo, F. Salort, J. Elguero, M.R. Torres, Eur. J. Org. Chem. (2004) 1097;
Also applied to trisTB derivatives (b) J. Artacho, P. Nilsson, K.-E. Bergquist, O.F. Wendt, K. Wärnmark, Chem. Eur. J. 12 (2006) 2692.
[18] Y. Schmidt, B. Breit, Org. Lett. 12 (2010) 2218.
[19] S.E. Wheeler, K.N. Houk, J. Chem. Theory Comput. 6 (2010) 395.
[20] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 24 (2003) 669.
[21] C-PCM solvent model may be missing some interactions important for NMR M. Dračínský, P. Bouř, J. Chem. Theory Comput. 6 (2010) 288.
[22] S. Sergeyev, S. Stas, A. Remacle, C.M.L. Vande Velde, B. Dolenský, M. Havlík, V. Král, J. Čejka, Tetrahedron: Asymm. 20 (2009) 1918.
[23] G. Fukuhara, S. Madenci, J. Polkowska, F. Bastkowski, F.-G. Klärner, Y. Origane, M. Kaneda, T. Mori, T. Wada, Y. Inoue, Chem. Eur. J. 13 (2007) 2473.
[24] (a) G. Uccello-Barretta, F. Balzano, P. Salvadori, Curr. Pharm. Des. 12 (2006) 4023;
(b) J.M. Seco, E. Quinoa, R. Riguera, Chem. Rev. 104 (2004) 17;
(c) C. Michon, M.-H. Gonçalves-Farbos, J. Lacour, Chirality 21 (2009) 809.
[25] Á. Révész, D. Schröder, T.A. Rokob, M. Havlík, B. Dolenský, Angew. Chem. Int. Ed. 50 (2011) 2401.