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Journal of Molecular Structure: THEOCHEM 851 (2008) 84–91

THEO CHEM

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A total conformational analysis of diastereomeric esters and calculation of their conformational shielding models

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Received 21 August 2007; received in revised form 12 October 2007; accepted 30 October 2007
Available online 17 November 2007

Abstract

A total conformational analysis of diastereomeric esters was performed and the conformational shielding models (CSM) of the esters necessary for the NMR spectroscopic stereochemical assignment of carboxylic acids or alcohols were calculated. The esters of (*R*)-2-butanol and both enantiomers of *O*-methylphenylacetic acid (MPA), 2-phenoxypropanoic, 2-(2-formylphenoxy)propanoic, 2-methoxy-3-phenyl-propanoic and 2-methoxy-2-methyl-3-phenylpropanoic acids were investigated. The calculation method used was DFT B3LYP/6-31+G* (at the highest level in the optimization cascade). The Boltzmann weighting of individual conformers, covering an energy range of 2 kcal/mol, was used to evaluate the ring current effects of the aromatic group on the basis of a classical Pople point-dipole model describing anisotropy. The results afforded a CSM for the pairs of diastereomeric esters. The calculated CSM coincides with an empirical CSM of MPA and 2-phenoxycarboxylic acid esters and is in accordance with the experimental stereochemical results obtained for 2-methoxy-3-phenylpropanoic acid esters. The low values observed for the differential shieldings ($\Delta\delta^{RS}$) of 2-methoxy-2-methyl-3-phenylpropanoic acid esters were confirmed by their complex conformational equilibrium.

Keywords: Conformational analysis; NMR shielding calculations; Chiral derivatizing agent; DFT calculations

1. Introduction

The absolute configuration of secondary alcohols can be determined by NMR spectroscopy of the diastereomeric esters derived from an alcohol and an aromatic α-chiral carboxylic acid – a chiral derivatizing agent (CDA) [1–5]. An alcohol of unknown configuration is esterified with the pure enantiomers of a CDA. The differential shielding effects ($\Delta\delta^{RS}$ or $\Delta\delta^{SR}$) observed in the NMR spectra of the diastereomers give information about the spatial position of the aromatic ring in relation to the alcohol part of the ester [5]. Knowing the CSM of the diastereomeric CDA esters, the absolute configuration of the sec-alcohol can be derived.

Several α-chiral carboxylic acids have been developed for use as CDAs, such as methoxytrifluoromethylphenylacetic acid (MTPA) [6], *O*-methylphenylacetic acid (MPA) [7,8], mandelic acid [9,10], 2-phenoxy-carboxylic acids [11,12], etc. The empirical CSMs for the diastereomeric esters of these CDAs have been derived (Fig. 1).

The above CSMs are characterized by a synperiplanar arrangement of: (1) the carbinyl hydrogen, (2) the oxygen atom of the carbonyl group and (3) either the CF3 group (MTPA esters) the MeO group (MPA esters), or an H atom (2-phenoxypropanoic acid esters). The mutual spatial orientation of the first two structural elements can be taken as constant, to a good approximation (a violation "costs" more than 2 kcal/mol). The orientation of the third group

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doi:10.1016/j.theochem.2007.10.045

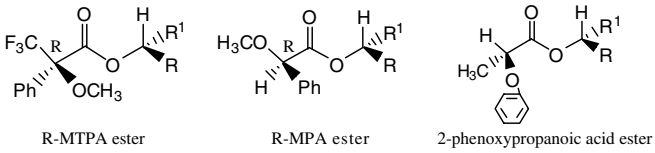


Fig. 1. The empirical conformational shielding models of secondary alcohol esters of MTPA, MPA and 2-phenoxypropanoic acid.

is a critical constituent of the CSM. It is defined by the characteristic dihedral angle D about the bond connecting the C_1 and C_2 atom of the CDA in the ester. The D value corresponding to the CSM for a substituent attached to a C_2 atom can be 0°, 120° and 240°. In practice, the weighted average value of D ($D^{average}$) over all conformers could be used. In a few cases information about the "mean conformation" can be obtained experimentally, but empirical CSMs are usually used. The empirical CSMs define the shielding region of an aromatic ring, but the deshielding region must be also taken into account [13]. As reported [14–16], theoretical calculations allow a more adequate analysis of the structure of CDA esters, as well as revealing the physical nature of the influence of the ring current of an aromatic ring. Until now, modelling and aromatic shielding calculations have been performed to improve the reliability of the empirical CSM [13,16].

The absolute configuration of novel α-chiral carboxylic acids could be determined by derivatization with a sec-alcoholic CDA followed by NMR of the resulting esters [14,17]. In this case the theoretically found CSM could allow the preliminary absolute configurational assignment of enantiomers.

The following factors concerning the design of the computational approach were considered important.

(A) Extensive sampling of as large a fraction of the accessible conformational space as possible [18–22].
(B) The choice of the high level of computation. DFT and a hybrid B3LYP [23] functional have reproduced the geometry of different compounds in very good agreement with experimental NMR and IR results [24,25]. The DFT B3LYP method with a 6-31+G* basis set has allowed a prediction of the Z vs. E-isomer ratio of 1-acetyl-2-methylhydrazine [26] and also enabled a reliable prediction of the yield of products of the Fries reaction of resorcinol and orcinol monobenzoate [27].
(C) Using procedures that take into account as many different low energy conformers as possible. The Boltzmann-averaging of the calculated 3JCC coupling constants for the conformers of 2,4-dimethylhex-5-en-1-ol resulted in good agreement between theory and experiment [28]. Based on the conformational analysis of 13-tridecano-13-lactones the computed circular dichroism spectra were obtained with good precision by summing up the spectra of individual conformers according to their Boltzmann weights [29].

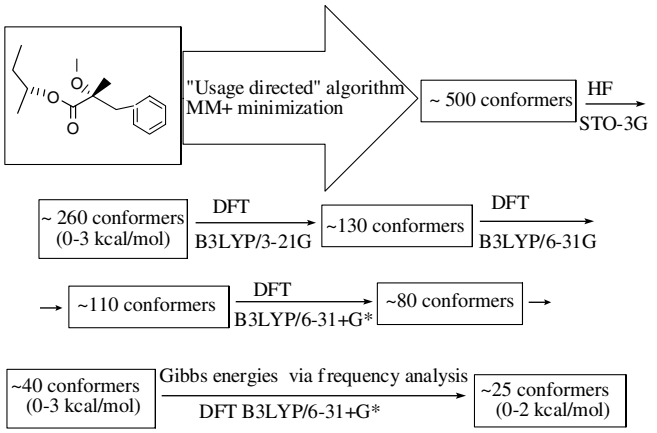


Fig. 2. The flow chart for the conformational analysis of esters using the example of (*R*)-2-methoxy-2-methyl-3-phenylpropanoic acid (*R*)-2-butanol ester.

As a central premise the authors consider the theoretical CSMs to be a reliable alternative to empirical ones. The main objective of this work was to strengthen the total conformational analysis procedure proposed (Fig. 2) by testing it on the calculation of NMR differential shielding effects of α-chiral carboxylic acid esters.

2. Theoretical approach

A total conformational analysis of esters was performed. The conformational search was conducted by using the Hyperchem 7.0 program [30] employing the MM+ force field. The search module allows acceptance of unique conformers while duplicates and higher energy conformers (above 6 kcal/mol in this study) are discarded. All dihedral angles significant for the conformational search were taken into account. The usage-directed approach for the conformational search [31] was used. The conformers obtained were optimized sequentially (Fig. 2) by using the Gaussian 98 program [32]. The initial level was the Hartree–Fock method with an STO-3G basis set. The resulting low-level ab initio calculated conformers were further optimized with the DFT method using a hybrid B3LYP exchange-correlation functional [23] and a 3-21G basis set (i.e. B3LYP/3-21G). The output was used as an input for the B3LYP/6-31G method. The optimization was finalized at the DFT/B3LYP level with a 6-31+G* basis set. Every optimization step was followed by a geometrical comparison of conformers with the aim of extracting the unique structures. A frequency analysis was performed at the final level to verify that the conformers correspond to local minima on the potential energy surface (PES) (all positive Hessian eigenvalues). The calculated frequencies were also used to calculate Gibbs free energies (with the temperature corrected to 300 K) allowing the conformers to be ranked in terms of energy.

To quantify the intramolecular (de)shielding effects arising from the aromatic ring current, the classical point-dipole model of Pople [33] was used:

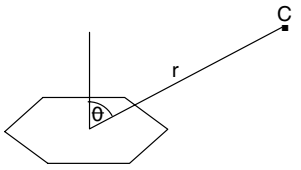


Fig. 3. A graphical presentation of parameters (Θ and r) for the Pople point-dipole model.

$$\sigma_{r\Theta} = r^{-3}(1 - 3\cos^2\theta) \quad (1)$$

In Eq. (1) and Fig. 3, r is the distance [Å] of a specified atom of interest from the ring center and Θ is the angle between the r vector and the sixfold symmetry axis of the benzene ring. The point-dipole model allows calculation of the sign (i.e. shielding or deshielding) and intensity of the ring current influence of an aromatic group on an atom of a diastereomer. Proceeding from these results the average value over an ensemble of conformers were also calculated. A negative value of the $\sigma_{r\Theta}$ parameter indicates a shielding effect, i.e. the atom observed lies in the shielding cone of the benzene ring.

The point-dipole approximation has been shown to give results which are qualitatively comparable with results obtained using mathematically more advanced Haigh-Mallion and Johnson-Bovey methods for assessing ring current effects [34].

3. Results

The total conformational analysis of esters (**1**)–(**10**) (Fig. 4) afforded geometries and energies (and the Boltzmann populations) of the preferred conformers. The calculation of the ring current influence of the aromatic ring has yielded (de)shielding values for the C_1 and C_3 atoms of the sec-butanol fragment of the ester conformers (Figs. 5 and 6; Supplementary information (SI): Tables 1–5). The weighted average (de)shielding values for the diastereomers were also calculated (Table 1). The latter results enabled the construction of theoretical CSM for each pair of diastereomers (Fig. 4). The deviation of the dihedral angle D (Fig. 4) from the theoretical CSM was calculated for single ester conformers (SI: Tables 1–5 and Figs. 1, 2) and the D^{average} was calculated over the conformers for each ester studied (Table 1; SI: Figs. 1 and 2).

4. Discussion

A survey of MPA esters as well as of the esters of α-phenoxyalkanoic acids (of known CSM) was undertaken. In addition to the investigation involving theoretical calculations, synthetic and NMR studies of 2-methoxy-3-phenylpropanoic acid [35] esters (**7**), (**8**) as well as 2-methoxy-2-methyl-3-phenylpropanoic acid esters (**9**), (**10**) were performed. Neither of the latter two carboxylic acids has previously been used in the role of a CDA and no CSM has been reported for their esters. The enantiomers of both

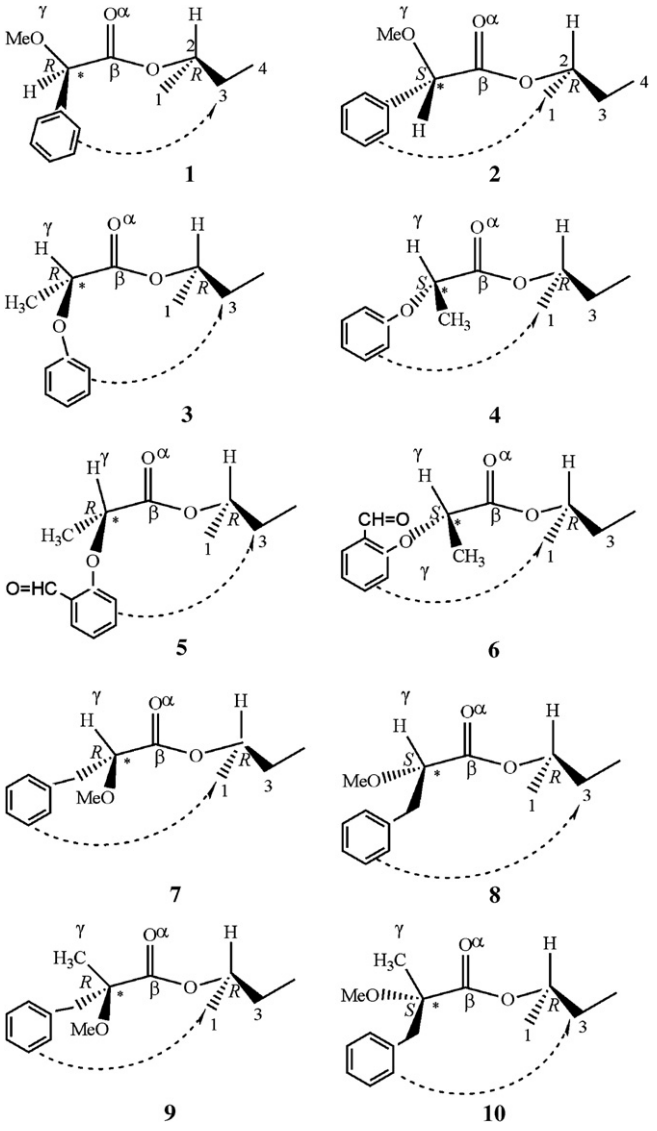


Fig. 4. The perspective structures of the theoretical conformational shielding models for the diastereomeric esters of (*R*)-2-butanol with α-chiral carboxylic acids: **1**, **2**: *O*-methylphenylacetic acid (MPA) $\Delta\delta^{(RR\text{-}SR)}(C_1) > 0$; $\Delta\delta^{(RR\text{-}SR)}(C_3) < 0$. **3**, **4**: 2-phenoxypropanoic acid $\Delta\delta^{(RR\text{-}SR)}(C_1) > 0$; $\Delta\delta^{(RR\text{-}SR)}(C_3) < 0$. **5**, **6**: 2-(2-formylphenoxy)propanoic acid $\Delta\delta^{(RR\text{-}SR)}(C_1) > 0$; $\Delta\delta^{(RR\text{-}SR)}(C_3) < 0$. **7**, **8**: 2-methoxy-3-phenylpropanoic acid $\Delta\delta^{(RR\text{-}SR)}(C_1) < 0$; $\Delta\delta^{(RR\text{-}SR)}(C_3) > 0$. **9**, **10**: 2-methoxy-2-methyl-3-phenylpropanoic acid $\Delta\delta^{(RR\text{-}SR)}(C_1) < 0$; $\Delta\delta^{(RR\text{-}SR)}(C_3) > 0$. [1]The dashed curves indicate a relative shielding influence (a higher shielding or lower deshielding) of the ring current of the aromatic moiety on the C_1 or C_3 atom of the 2-butanol carbon chain in the ester. [2]The dihedral angle D (see also Newman projections in SI Fig. 2) is defined by the following atoms: O(α)–C(β)–C(*)–H,O,C(*) which are the carbonyl oxygen atom (α), the carbonyl carbon atom (β), the chiral center (*) of CDA and the atom (γ) synperiplanar ($D = 0$) with O(α) in the CSM of the ester, respectively.

the latter carboxylic acids were identified – their correspondence to the ester diastereomers was determined (Fig. 4) by using NMR and high performance liquid chromatography (HPLC) of the esters followed by polarimetric measurements and a chiral HPLC resolution of the corresponding acid enantiomers gained upon hydrolysis of the esters. For both acids the (*S*)-(+)-enantiomer appeared to be the

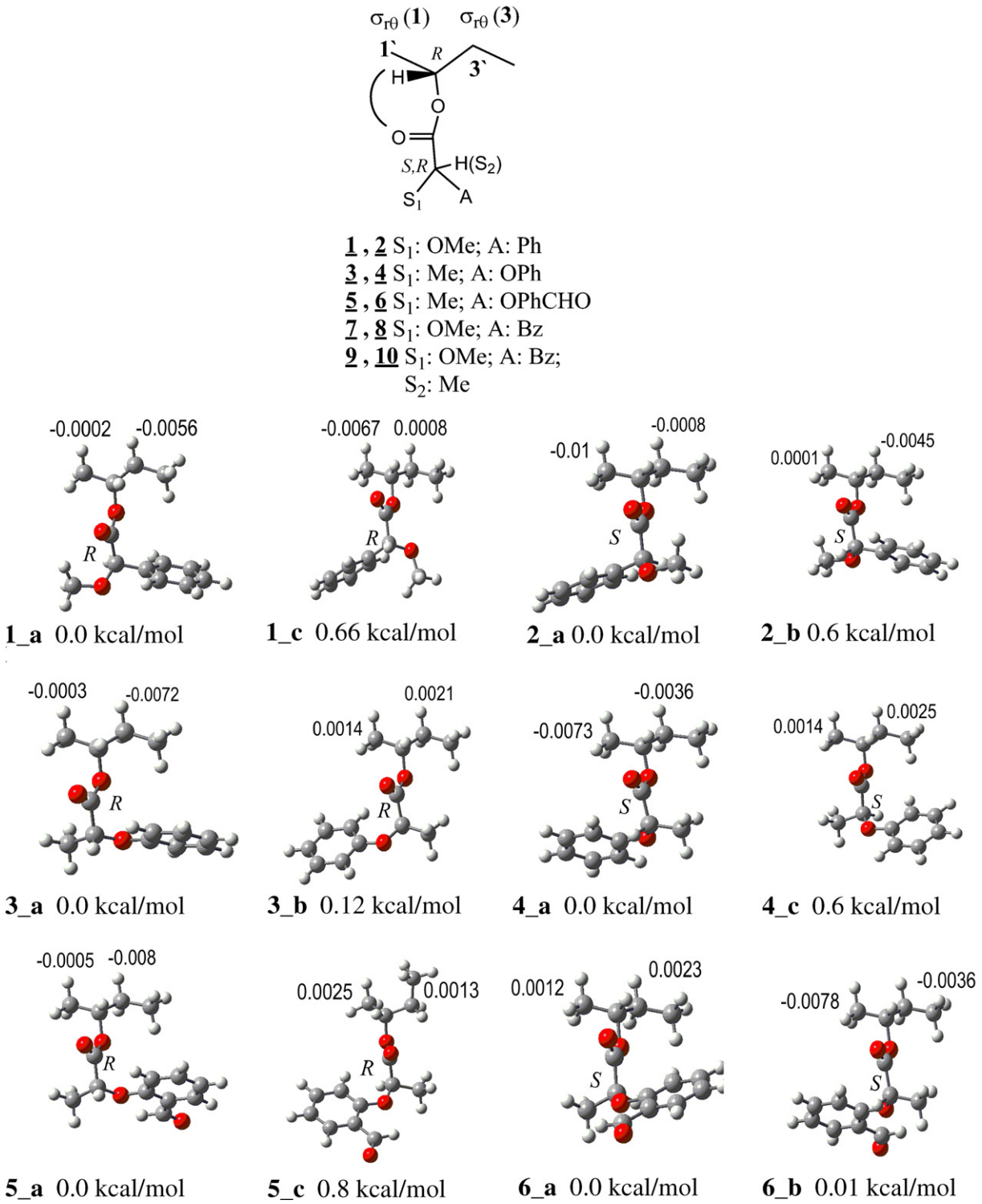


Fig. 5. The low-energy conformers of diastereomeric esters **1**–**6** (Fig. 4). The conformers resulted from the optimization process using DFT calculations at the B3LYP 6-31+G* level of theory; the ring current effects ($\sigma_{r\theta}$) for the C_1 and C_3 atoms of the alcohol are included. The numbering of conformers corresponds to that used in SI: Tables 1–3.

faster moving one when analyzed by the HPLC using a Daicel Chiralcel ODH column [36].

For the CDA esters of simple structure (MPA, mandelic acid esters, etc.), the empirical CSM and the D^{lowest} and $D^{average}$ have been considered to coincide to a satisfactory approximation. The geometry of a CSM has been expressed by the dihedral angle D only [10]. However, D^{lowest} may actually differ drastically from the valid CSM as well as from $D^{average}$ over the conformers. The latter parameter takes into account also the Boltzmann energy

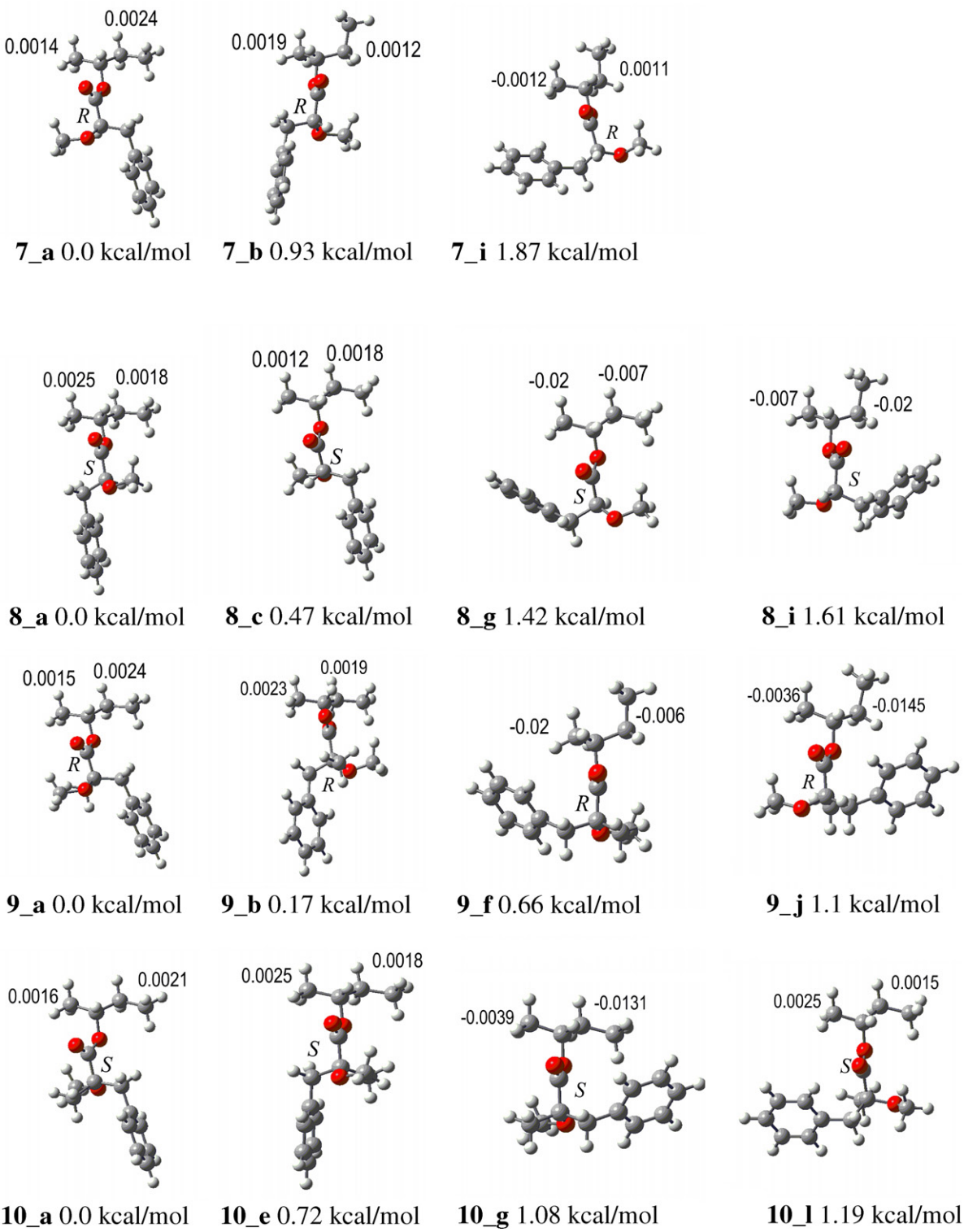


Fig. 6. The low-energy conformers of diastereomeric esters **7**–**10** (Fig. 4). The conformers resulted from the optimization process using DFT calculations at the B3LYP 6-31+G* level of theory; the ring current effects ($\sigma_{r\Theta}$) for the C_1 and C_3 atoms of the alcohol are included. The numbering of conformers corresponds to that used in SI: Tables 4 and 5.

distribution of conformers with variable *D*s. The calculation of (de)shielding values for atoms is, in turn, based on the geometries and energies of conformers and also takes into account the shielding properties of an aromatic group.

Geometry vs. shielding effects calculated for MPA esters: validation of the computational procedure. Our results (SI: Table 1 and Fig. 2) are in accordance with the simple conformational composition and the empirical CSM reported for the esters of MPA [13]. For the lowest

Table 1
A summary of the calculated dihedral angles and weighted average ring current (de)shielding effects found for diastereomeric esters **1**–**10**

Carboxylic acid (*R*)-2-butanol ester (No.)[a]	Dihedral angle D		Ring current effect ($\sigma_{r\Theta}$)	
	D^{lowest} [b]	D^{average} [b]	C_1[c]	C_3[c]
(1)	+19.6	−13.7	−0.0049	−0.0019
(2)	−20.4	+12.4	−0.0012	−0.0073
(3)	−23.0	+65.3	−0.0028	+0.007
(4)	+29.9	−37.5	−0.0013	−0.0042
(5)	−25.9	+78.8	−0.0021	+0.0008
(6)	−141.4	−85.2	+0.0001	−0.0017
(7)	+138.7	+82.5	+0.0018	+0.0014
(8)	−142	−102.6	+0.0005	+0.0007
(9)	+131.2	+43.7	−0.0004	−0.0015
(10)	+27.3	−8.8	−0.0001	+0.0443

[a] The numbering of compounds corresponds to that used in Fig. 4.
[b] The dihedral angles D^{lowest} and D^{average} (Fig. 4) characterize differences in torsional angles between the conformational shielding model ($D = 0$) and the angles found: (1) for the lowest energy conformer and (2) as the weighted average torsional angle over all optimized conformers.
[c] For the C_1 and C_3 atoms of the 2-butanol in esters (Fig. 4).

energy conformers of the diastereomers (**1**) and (**2**) the C═O and the (C_α)-OMe groups are in a synperiplanar position (Fig. 5; **1_a**, **2_a**). The energy of the conformers with these groups in an antiperiplanar position is 0.6 kcal/mol higher for both esters (i.e. **1_c**, **2_b**). The overall synperiplanarity of these groups is also reflected by a low deviation of the D^{average} for esters (**1**) and (**2**) from the CSM (−13.7° and +12.4°, respectively; SI: Figs. 1 and 2).

Geometry vs. CSM of 2-phenoxypropanoic and 2-(2-formylphenoxy)propanoic acid esters. The calculated CSMs (Table 1; Fig. 4) fully agree with the known empirical CSMs [11] for sec-alcohol esters of 2-phenoxyalkanoic acids; the C═O group and H atom attached to the C_2 atom of CDA in the ester are synperiplanar. Both D^{average} and D^{lowest} are regular with CSM for esters (**3**) and (**4**). In contrast to this, D^{lowest} calculated for the 2-(2-formylphenoxy)propanoic acid esters (**5**) and (**6**) indicate that on this level no reliable CSM can be found. This is because the aromatic substituent is positioned on the side of the ethyl group of sec-butanol in the lowest energy conformers of both diastereomers (Fig. 5; SI: Fig. 2). Somewhat unexpectedly, the synperiplanar and antiperiplanar conformers of lowest energy for ester (**6**) (i.e. **6_a** and **6_b**; Fig. 5) are very similar in energy. However, the corresponding shielding values show a regular behaviour with CSM (Fig. 5; Table 1). Hence for both diastereomers (**5**) and (**6**) the lowest energy synperiplanar as well as antiperiplanar conformers, although being geometrically "opposite", show qualitatively the same differential shielding within the molecule.

In summary, the empirical and calculated CSMs coincide. The CSM is also in accordance with the NMR results obtained for the diastereomeric esters of 2-(2-formylphenoxy)heptanoic acid [37].

Geometry vs. CSM for 2-methoxy-3-phenylpropanoic acid esters. The weighted average $\sigma_{r\Theta}$ values calculated for the C_1 and C_3 atoms of the sec-butanol fragment in esters (**7**) and (**8**) are positive (Table 1), i.e. this corresponds to a deshielding influence of the ring current magnetic field. Therefore, the CSM for esters (**7**) and (**8**) has been constructed according to an "apparent" differential shielding effect (i.e. by the lower value deshielding calculated for the C_1 or C_3 atom (Table 1; SI: Table 4)). The CSM found for esters (**7**) and (**8**) is not in accordance with either the calculated D^{average} or D^{lowest}. These values show the synperiplanarity of the ester carbonyl group with a (C_α)-OMe group, as found in MPA esters.

In the lowest energy conformers of (**7**) and (**8**) the plane of the aromatic ring is roughly parallel to the axis connecting the two chiral centers and the C atom of the carbonyl group. This takes place by a combined rotation around the C_α-CH_2 and CH_2-Ph. The conformers of esters (**7**) and (**8**) for which the actual shielding has been calculated, are 1.4 and 1.9 kcal/mol, respectively, higher in energy.

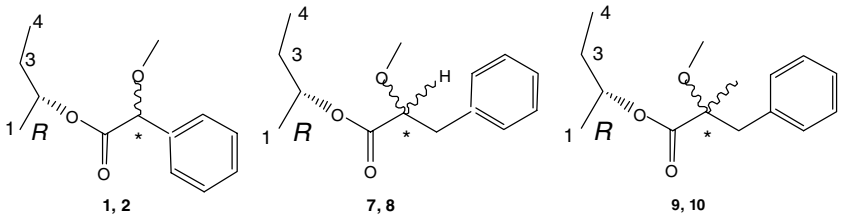
The experimental NMR $\Delta\delta^{RS}$ values found for esters (**7**) and (**8**) are comparable with the respective values found for MPA esters (Table 2). Evidently, 2-methoxy-3-phenylpropanoic acid could be used in the role of a CDA. In this case an alternative model, a conformational "deshielding" model is suggested, proceeding from the actual physical nature of the ring current influence (Fig. 7).

Geometry vs. CSM for 2-methoxy-2-methyl-3-phenylpropanoic acid esters. In case of esters (**9**) and (**10**) the NMR $\Delta\delta^{RS}$ values measured are far lower than those determined for esters (**7**) and (**8**) (Table 2). This is undesirable if the parent acid is to be used as a CDA. Observation of low $\Delta\delta^{RS}$ values could be explained by a complex conformational equilibrium and/or an unfavourable spatial position of the aromatic group within the lower energy ester conformers. These explanations were supported by the computational results. The minimum energy conformers **9_a** and **10_a** are similar to the corresponding conformers of esters (**7**) and (**8**) in the orientation of the phenyl group. The values of D^{average} are in accordance with CSM.

The conformers that are in accordance with the CSM are **9_f** and **10_g**. These conformers, respectively, 0.7 and 1.1 kcal/mol higher in energy, are of considerable abundance in the conformational equilibrium. Besides, the relatively low difference in energy between the lowest energy "deshielding" and "shielding" conformers of esters (**9**) and (**10**) compared to that of esters (**7**) and (**8**) (0.7–1.1 vs. 1.4–1.9 kcal/mol) seems to be a factor which also contributes to the mutual cancellation of the shielding and deshielding influence.

In conclusion, the relatively unrestricted rotation around the bond connecting C_α and C═O in the esters (**9**) and (**10**) (see also D values in SI: Table 5) may be the reason for the weak differential shielding effects measured by NMR.

Table 2
The ^{1}H and ^{13}C NMR chemical shifts (δ_{TMS}, ppm) of the marked atoms[a] from the spectra measured for the diastereomeric (*R*)-2-butanol esters of 2-methoxyphenylacetic acid (**1**, **2**), 2-methoxy-3-phenylpropanoic acid (**7**, **8**) and 2-methoxy-2-methyl-3-phenylpropanoic acid (**9**, **10**)



Isomers	Atom	*RS**		*RR**		*RR**–*RS**	
		^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1, **2**	1	1.08	19.05	1.22	19.46	+0.14	+0.41
	3	1.61 (pro *R*)	28.64	1.44 (pro *R*)	28.57	−0.17	−0.07
	3	1.55 (pro *S*)		1.46 (pro *S*)		−0.09	
	4	0.86	9.53	0.64	9.21	−0.22	−0.32
7, **8**[b]	1	1.22	19.48	1.14	19.30	−0.08	−0.18
	3	1.57 (pro *R*)	28.64	1.60 (pro *R*)	28.73	+0.03	+0.09
	3	1.49 (pro *S*)		1.53 (pro *S*)		+0.04	
	4	0.85	9.62	0.89	9.65	+0.04	+0.03
9, **10**[c]	1	1.22	19.34	1.20	19.31	−0.02	−0.03
	3	1.64 (pro *R*)	28.69	1.64 (pro *R*)	28.73	0	+0.04
	3	1.55 (pro *S*)		1.55 (pro *S*)			
	4	0.88	9.66	0.91	9.67	+0.03	+0.01

[a] The numbering of atoms and compounds corresponds to that used in Fig. 4.
[b] The absolute configuration of the carboxylic acid enantiomers corresponding to ester diastereomers (**7**, **8**) has been reported [35] and further confirmed herein by calculations and NMR results.
[c] The absolute configuration of the carboxylic acid enantiomers corresponding to ester diastereomers is herein proposed by calculation results.

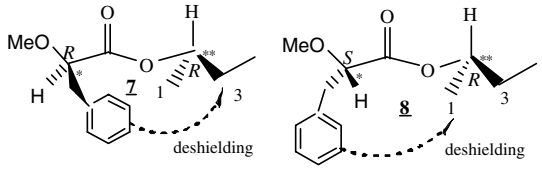


Fig. 7. A conformational "deshielding model" for the diastereomeric esters of 2-methoxy-3-phenylpropanoic acid.

5. Conclusions

1. A total conformational analysis of the esters of (*R*)-2-butanol with both the enantiomers of *O*-methylphenylacetic (MPA), 2-phenoxypropanoic, 2-(2-formylphenoxy)propanoic, 2-methoxy-3-phenylpropanoic and 2-methoxy-2-methyl-3-phenylpropanoic acids was carried out using the Hyperchem and Gaussian software. The geometries and energies of the conformers (within 0–2 kcal/mol) were used to calculate the (de)shielding effects. The Boltzmann weighting over the conformers of the ring current (de)shielding values ($\sigma_{r\Theta}$) afforded the averaged values which allowed the construction of CSM for the pairs of diastereomeric esters.
2. The calculated CSM confirms an empirical CSM for the esters of MPA and 2-phenoxycarboxylic acids and is in accordance with the experimental results obtained for 2-methoxy-3-phenylpropanoic acid esters. A CSM has been proposed for the (*R*)-2-butanol esters of 2-methoxy-2-methyl-3-phenylpropanoic acid.
3. The characteristic dihedral angles *D* found for the lowest energy conformers, as well as the weighted average torsional angles over the conformers, may drastically differ from that corresponding to the CSM ($D = 0$).
4. The conformers for which the deshielding effect is operative are energetically more preferable if an aromatic moiety is linked to the chiral center of the CDA via a methylene group.
5. The $\Delta\delta^{RS}$ values determined for 2-methoxy-3-phenylpropanoic acid esters are of the same magnitude as for classical MPA esters, so this carboxylic acid could thus serve as a potential CDA. However, a further experimental confirmation based on the investigation of a set of esters is desirable.
6. For 2-methoxy-2-methyl-3-phenylpropanoic acid esters the low differential shielding was observed and confirmed by complex conformational equilibrium according to theoretical calculations.

7. A general agreement with experimental results has provided a justification for the proposed calculation procedure. The highest level of theory used (i.e. B3LYP/6-31+G*) has allowed an efficient discrimination between the conformers substantially different in geometry, but with a negligible difference in energy (even less than 0.1–0.2 kcal/mol).

Acknowledgements

The authors thank the Estonian Science Foundation for financial support (Grants 4381, 4758, 6520, 6778, 7009).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2007.10.045.

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[36] Experimental results will be published separately.
[37] Our unpublished results.