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TETRAHEDRON: *ASYMMETRY*

Conformational study of α-arylethylamides of (−)-camphanic acid

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Abstract

The absolute conformation and configuration of diastereomeric amides (**4A,B–6A,B**) of (1*S*,3*R*)-camphanic acid (lactone of 1-hydroxy-2,2,3-trimethylcyclopentan-1,3-dicarboxylic acid, (−)-camphanic acid **9**) with α-arylethylamines **1–3** are deduced from ^{1}H NMR data and MM2 calculations. The α-arylethyl group in diastereomers **A** and **B** adopt nearly opposite absolute conformations, stabilized by hydrogen bonding in the *syn*-oriented O–C(1)–C(6)–N–H unit, and repulsive interaction between the 1′C–Me group and the amide C=O group. The absolute configuration (1′*S*) is assigned to the **4A–6A** diastereomers, and the (1′*R*)-configuration to the **4B–6B** diastereomers; this assignment is confirmed by the preparation of **4A** and **5A** from enantiomerically pure (1′*S*)-α-arylethylamines **1** and **2**, respectively. These results also enabled the assignment of pro-*R* (H_R) and pro-*S* (H_S) protons in the benzyl derivative **7**.

1. Introduction

(1*S*,3*R*)-Camphanic acid (lactone of 1-hydroxy-2,2,3-trimethylcyclopentan-1,3-dicarboxylic acid, **9**) is repeatedly used as a chiral auxiliary for the separation of racemates,[1–3] in the preparation of chiral ligands for organometallic catalysts,[4–6] and in structural studies.[2,7,8] Amides of camphanic acid are prepared for the separation of racemic, cyclic *sec* amines.[9] An unusual fragmentation process, observed during the course of their cleavage by strong nucleophiles,[9] can be circumvented by using NaH/CS_2 under mild conditions, a method recently used in the preparation of thiocamphanic acid from amides.[10] Another particular application of camphanic acid is Gerlach's method for the determination of the enantiomeric excess of α-deuterated primary alcohols.[11]

Within an ongoing project for the preparation of new chiral modifiers for heterogeneous catalysis, we encountered the problem of effective resolution and configurational and conformational characterization of diastereomeric camphanic acid amides obtained from racemic α-arylethylamines **1–3**. Because of

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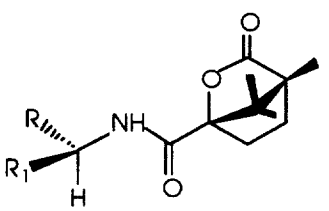
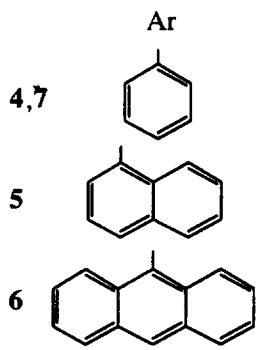
their high π-electron surface density combined with strong steric perturbations by the camphanoyl unit, pure diastereomeric amides **4A,B–6A,B**, and their corresponding amines, are expected to be effective surface modifiers in heterogeneous catalysis. Herewith we report on conformational properties of chromatographically separated amides, as studied by NMR and computational methods, which allow straightforward assignment of the absolute configuration at the stereogenic center of α-arylethylamino units. This is the first report on the use of the anisotropic effect of the aromatic ring in racemic compounds to be resolved, on the specific groups in the chiral auxiliary, as a tool for determination of absolute configuration in the former. All so-far reported examples of the determination of absolute configuration are based on the anisotropy of aromatic rings within the chiral auxiliary, such as O-methyl mandelic acid derivatives,[12] arylmethoxy acetic acid derivatives,[13] O-aryllactic acid derivatives,[14] and diazacyclophosphamides derived from L- and D-prolylphenylamine.[15]

2. Results and discussion

Starting from racemic α-arylethylamines **1–3** diastereomeric pairs **4A,B–6A,B** were prepared by standard procedures. Effective separation of diastereomers was performed by chromatography on silica gel, whereby diastereomers **6A** and **6B** exhibited large differences in R_f values (ΔR_f ca. 0.2) in a single solvent like dichloromethane. To separate diastereomers **4A,B** and **5A,B** binary solvent mixtures served the purpose (see Experimental).



	R	R_1
4A, 5A, 6A	Ar	CH_3
4B, 5B, 6B	CH_3	Ar
7	Ar	H



The most striking feature of the ^1H NMR spectra of diastereomeric pairs **4A,B–6A,B** represents a uniform and significant difference in the chemical shifts of the three methyl groups in the camphanic unit, and nearly superimposable peaks of diastereotopic C′1–Me groups in the α-arylethylamine unit of two diastereomers (Table 1). In diastereomeric mixtures **4A,B–6A,B**, singlets for Me-8, Me-9 and Me-10 appear as two signals in ca. 1:1 ratio; on chromatographic separation only three singlets remain. The assignment of Me-8 to Me-10 is based upon our recent NMR spectroscopic study of camphanic acid **9** and its complexes.[7] The correlation of ^1H and ^{13}C signals for diastereotopic α-arylethylamides with the reference amides **7**, **8** and parent acid **9** is evident from Table 1.

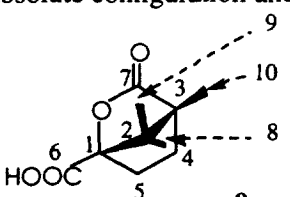
Taking prochiral benzylamide **7** as the standard for evaluation of the ^1H NMR shifts, $\Delta\delta$ in Table 1, one can see that the three methyl groups of the camphanate unit in diastereomers **4B–6B** exhibit shifts to higher field, and those in **4A–6A** to lower field relative to **7**. A noticeable and opposite influence of α-arylethyl units on magnetic nonequivalence of Me-8, Me-9 and Me-10 signals in the camphanic unit, all distant from the aromatic ring, indicated different stable conformers for diastereomeric series **A** and **B**. A tentative explanation can be offered from the inspection of models, which reveal that *syn*-oriented O–C(1)–C(6)–N–H units minimize repulsive interactions, ensure hydrogen bonding, and maximize σ–π interactions within the nearly coplanar, *anti*-related lactone group and amide carbonyl groups. This strong

Table 1
Signals of the methyl groups in ^1H and ^{13}C NMR spectra of diastereomeric pairs **4A,B–6A,B**, and of **7–9** in deuterochloroform

Comp.	(1'C)-config.	^1H-NMR of Me groups; δ, ppm				^{13}H-NMR of Me groups; δ, ppm		
		Me-9	Me-10	Me-8	Me-1'	Me-9	Me-10	Me-8
4A	(1'*S*)	0.96	1.12	1.13	1.51	16.26	9.44	16.57
Δδ(**4A-7**)[a]		+0.05	+0.02	0.00				
4B	(1'*R*)	0.80	1.06	1.09	1.51	16.20	9.41	16.45
Δδ(**4B-7**)		-0.11	-0.04	-0.04				
$\Delta\delta^{RS}$(**4B-4A**)		-0.16	-0.06	-0.04				
5A	(1'*S*)	0.98	1.10	1.16	1.67	16.26	9.42	16.57
Δδ(**5A-7**)		+0.07	0.00	+0.03				
5B	(1'*R*)	0.72	1.06	1.10	1.68	16.26	9.41	16.57
Δδ(**5B-7**)		-0.19	-0.04	-0.03				
$\Delta\delta^{RS}$(**5B-5A**)		-0.16	-0.04	-0.06				
6A	(1'*S*)	1.12	1.14	1.17	1.97	16.44	9.44	16.55
Δδ(**6A-7**)		+0.21	+0.04	+0.04				
6B	(1'*R*)	0.74	0.91	1.03	1.96	16.06	9.36	16.29
Δδ(**6B-7**)		-0.17	-0.19	-0.10				
$\Delta\delta^{RS}$(**6B-6A**)		-0.38	-0.23	-0.14				
7	--	0.91	1.10	1.13		16.31	9.42	16.51
8	--	1.00	1.12	1.19		16.42	9.36	16.56
9	--	1.02	1.11	1.14		16.91	9.93	16.96

a Positive Δδ values mean a downfield shift, negative an upfield shift relative to **7**.

hydrogen bonding is clearly observed in the ^1H NMR spectrum of **7**, where diastereotopic protons of the ($1'CH_2$) group from two well separated quartets are centered at 4.43 ppm, and at 4.53 ppm, respectively. On N–H(D) exchange, they collapse into an AB system of two doublets. Inspection of models, confirmed by calculations described hereafter, reveal that H_R gives the signal at higher field and H_S gives the signal at lower field. Although the difference between signals for diastereotopic benzylic protons in **7** is ca. 10 times smaller than observed by Gerlach on incorporation of benzylamine into cyclic thioamide,[16] it is still significant in the determination of absolute configuration and optical purity of α-$^2H_1$-benzylamines.



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In spite of the expected high conformational mobility (free rotation) of the α-arylethylamino unit in both diastereomeric series **A** and **B**, two distinctly different spatial regions are available to the aromatic ring. In diastereomers **4B–6B** the aromatic ring can approach more closely the methyl groups of the camphanic unit than in diastereomers **4A–6A**. This conformational arrangement places methyl groups in diastereomers **4B–6B**, in particular Me-8 and Me-9, within the anisotropic cone of the aromatic ring,[17]

and explains their regular higher shift in diastereomeric series **A** than in the series **B**, Table 1. Taking into account this relationship, and the fact that the Me groups on (C′-1) in both series are approximately in the same electronic surroundings, distant from the electron-rich amide C=O group, it is easy to determine from the models that the α-arylethyl unit in the **A** series possesses the (1′*S*) configuration and in the **B** series the (1′*R*) configuration. Surprisingly, the high conformational stability of camphanic amides **4–6** is reflected by minimal changes of the ^{1}H NMR spectrum of **4B** on heating in $CDCl_3$ from 20°C to 55°C; only the signals for Me-8, Me-9, and Me-10 were shifted downfield by 0.001, 0.005, and 0.013 ppm, respectively.

It is interesting to note that Latypov et al.[13] observed for (+)-bornylamides of α-arylmethoxyacetic acid the lack of any strong conformational preference about the NH–CO bond because of the high mobility about CO–C_α bond. This is reflected in much smaller $\Delta\delta^{RS}$ values for the Me-8, Me-9 and Me-10 groups in the (+)-bornyl unit, than for the same groups in (−)-camphanic acid, which comprises a similar bicyclic system. In the average $\Delta\delta^{RS}$ the values in the former are 2–5 times lower than we observed for the signals of the analogous methyl groups in **4A,B–6A,B**, where conformational mobility seems rather restricted (Table 1). To confirm the above considerations, and to obtain more exact data on the conformational population, we performed MM2 calculations for **4A**, **4B** and reference amide **7**. The results are summarized in Fig. 1. According to MM2 calculations, **4A** and **4B** adopt two energy minima conformations, characterized by nearly opposite values for torsional angles ≤5′ ,1′, 2′, 3′; for **4A** it is −82°, and for **4B** it is +83°. For the achiral benzylic unit in **7**, three shallow energy minima are found, characterized by torsional angles of ca. +80° (**7a**), −80° (**7b**) and +160° (**7c**). The most stable conformer **7b** (MMX 33.34 kcal/mol), ca. 0.7 and 0.9 kcal/mol more stable than **7a** and **7c**, respectively, possess H_R in the shielding region of the amide carbonyl group, and H_S distant from this group.

Thus, the results of MM2 calculations confirm qualitative conformational analysis based on the NMR data and inspection of the models. For both diastereomers **4A** and **4B** C1′–Me is placed nearly *trans* to the amide C=O group and *cis* to the hydrogen bonded proton. This spatial arrangement moves the phenyl group in **4a** away from the methyl groups in the bicyclic unit, while in **4b**, phenyl is found close to this unit. This explains the stronger shielding of Me groups of the bicyclic system in **4B** than in **4A**. Consequently, the absolute configuration at C1′ in **4A** should be (1*S*), and in **4B** (1*R*). The assignment was simply confirmed by independent preparation of **4A** and **5A** from the commercially valuable (1*S*)-α-arylethylamines **1** and **2**, respectively. The extension of this configurational assignment to **6A** is straightforward.

In conclusion, we have demonstrated that α-arylethylamides of camphanic acid, **4A,B–6A,B**, potential chiral modifiers in heterogeneous catalysis, possess well defined conformations, which can be deduced by a combined study of ^{1}H NMR spectra and MM2 calculations. These data also allow the assignment of absolute configuration at (C1′) in both diastereomeric series.

3. Experimental

IR: Perkin–Elmer 297 spectrometer for KBr pellets. ^{1}H and ^{13}C NMR: Varian Gemini XL 300 spectrometer for $CDCl_3$ solutions, δ in ppm relative to TMS as internal reference, and *J* in hertz. HPLC: HP 1050 chromatograph with Eurosphere C18 RP column; separation was monitored by an HP 1050 UV detector set up at 254 nm and connected to HP 3396A integrator. Mp: electrothermal apparatus, not corrected. Optical rotations: Optical Activity AA-10 automatic polarimeter in a 1 dm cell; c in g/100 ml.

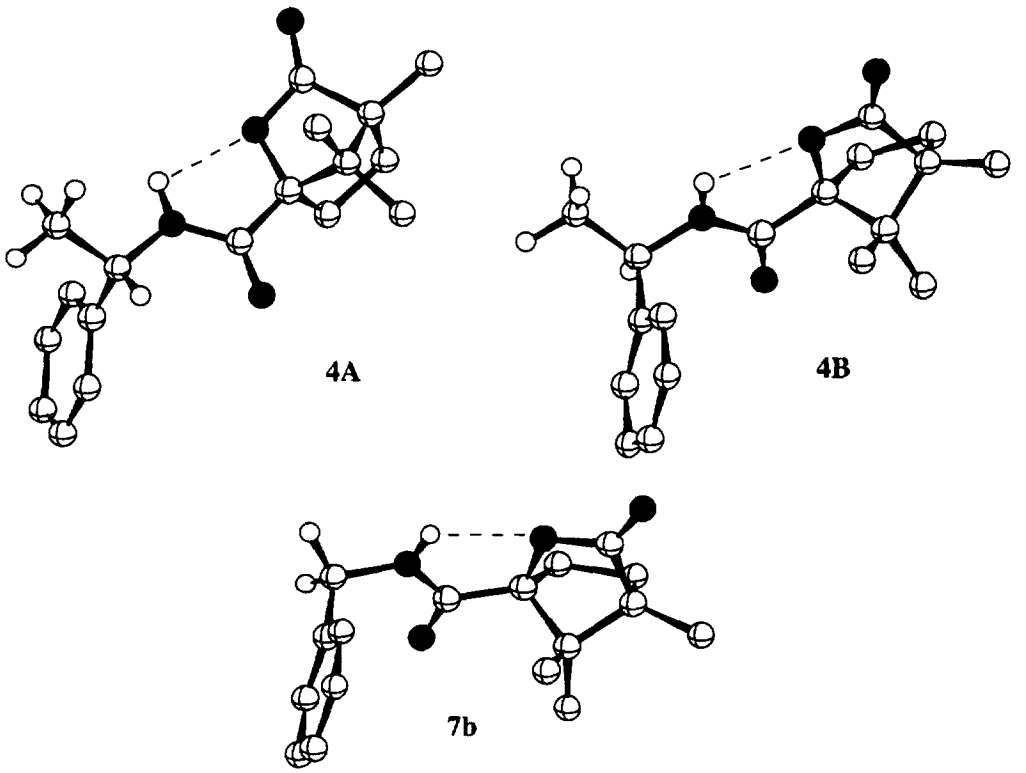

Fig. 1. Force field calculated stable conformers of **4A**, **4B** and **7b**

3.1. Acylation of α-arylethylamines. General procedure

Camphanic acid, thionylchloride, and a drop of DMF were heated for 6 h, then the thionylchloride was evaporated to dryness. Evaporation was repeated after addition of toluene, then the solid residue was dissolved in dichloromethane (5 ml). α-Arylethylamine, and triethylamine (100 mg, 1.0 mmol) were then added. After 18 h stirring at ambient temperature, the reaction solution was washed first with 0.5 M aq. bicarbonate, then dil. hydrochloric acid. The organic phase was dried (Na_2SO_4), the solvent evaporated and the diastereomeric product mixture separated by chromatography.

Compounds **1**, **2** and **9** were purchased from Aldrich, compounds **3** and **8** were prepared according to known methods.[18,19]

3.2. (1S,3R)-N-[(1′S)- and -(1′R)-Phenylethyl]-1-carboxamido-1-hydroxy-2,2,3-trimethylcarboxylic acid lactone (4A and 4B)

Starting from 200.0 mg (1.0 mmol) of camphanic acid and 250.0 mg (2.0 mmol) of (±)-1-phenylethylamine was obtained 302 mg of crude **4A**,**B**. Separation was performed on a silica gel column (40 g) using cyclohexane:diisopropylether (1:1) as eluent. Obtained were 122 mg of **4A** and 126 mg of **4B** (total yield 82%), both with ≥97% purity according to ^{1}H NMR.

Data for compound **4A**: mp 84.9–86.6°C; $[\alpha]_D$=−44.4 (c 1.1, CH_2Cl_2); IR: 3360, 2960, 1790, 1670, 1530, 1450, 1170, 1060, 920, 700 cm^{-1}; ^{1}H NMR: 0.96 (s, 3H), 1.12 (s, 3H), 1.13 (s, 3H), 1.51 (d, 3H), 1.64–1.72 (m, 1H), 1.83–1.99 (m, 2H), 2.45–2.55 (m, 1H), 5.14–5.22 (m, 1H), 6.72 (d, NH), 7.27–7.38 (m, 5H); ^{13}C NMR: 9.4, 16.3, 16.5, 21.8, 28.8, 30.0, 48.4, 53.7, 55.1, 92.3, 126.0, 127.5, 128.7, 142.4,

166.0, 178.4. Anal. for $C_{18}H_{23}NO_3$ (301.386), calcd: C 71.73, H 7.69, N 4.65; found: C 71.79, H 7.46, N 4.68.

Data for compound **4B**: mp 111.2–113.0°C; $[\alpha]_D$=+25.1 (c 1.9, CH_2Cl_2); IR: 3380, 2970, 1790, 1670, 1680, 1530, 1450, 1170, 1060, 920, 700 cm^{-1}; ^1H NMR: 0.80 (s, 3H), 1.06 (s, 3H), 1.09 (s, 3H), 1.51 (d, 3H), 1.66–1.73 (m, 1H), 1.89–2.00 (m, 2H), 2.50–2.57 (m, 1H), 5.10–5.20 (m, 1H), 6.73 (d, NH), 7.24–7.36 (m, 5H); ^{13}C NMR: 9.4, 16.2, 16.5, 21.6, 28.9, 30.1, 48.4, 53.9, 55.1, 92.3, 126.0, 127.4, 128.6, 142.9, 166.1, 178.4. Anal. for $C_{18}H_{23}NO_3$ (301.386), calcd: C 71.73, H 7.69, N 4.65; found: C 71.80, H 7.59, N 4.50.

3.3. (1S,3R)-N-[(1′S)- and -(1′R)-Naphth-1′-yl-ethyl]-1-carboxamido-1-hydroxy-2,2,3-trimethylcarboxylic acid lactone (5A and 5B)

Starting from 1.00 g (5.0 mmol) of camphanic acid and 1.60 g (9.3 mmol) of (±)-1-naphthylethylamine* was obtained 1.70 g (97%) of **5A,B**, HPLC asssay 89%. Separation was performed on a silica gel column (130 g) using cyclohexane:diisopropylether (1:1) as eluent. Obtained were 766 mg of **5A** and 780 mg of **5B**, both with ≥99% HPLC purity.

Data for compound **5A**: mp 127.3–128.9°C; $[\alpha]_D$=+18.6 (c 1.8, CH_2Cl_2); IR: 3360, 2960, 1785, 1675, 1535, 1450, 1260, 1060, 920, 775 cm^{-1}; ^1H NMR: 0.98 (s, 3H), 1.10 (s, 3H), 1.16 (s, 3H), 1.68 (d, 3H), 1.77–1.97 (m, 3H), 2.47–2.57 (m, 1H), 5.96–6.01 (m, 1H), 6.74 (d, NH), 7.43–8.07 (m, 7H); ^{13}C NMR: 9.4, 16.3, 16.6, 20.9, 28.9, 30.1, 44.1, 53.8, 55.1, 92.3, 122.5, 123.0, 125.2, 125.8, 126.5, 128.5, 128.9, 130.9, 133.9, 137.5, 165.9, 178.3. Anal. for $C_{22}H_{25}NO_3$ (351.446), calcd: C 75.19, H 7.17, N 3.98; found: C 75.06, H 7.19, N 4.20.

Data for compound **5B**: mp 64.3–66.0°C (dec.); $[\alpha]_D$=−39.8 (c 2.0, CH_2Cl_2); IR: 3380, 2980, 1790, 1665, 1535, 1450, 1190, 1060, 920, 770 cm^{-1}; ^1H NMR: 0.72 (s, 3H), 1.06 (s, 3H), 1.10 (s, 3H), 1.69 (d, 3H), 1.90–1.98 (m, 3H), 2.53–2.59 (m, 1H), 5.93–6.03 (m, 1H), 6.73 (d, NH), 7.43–8.14 (m, 7H); ^{13}C NMR: 9.4, 16.3, 16.5, 20.6, 28.9, 30.2, 44.2, 53.9, 55.1, 92.4, 122.5, 123.2, 125.2, 125.8, 126.3, 128.5, 128.9, 130.8, 133.9, 137.8, 165.9, 178.3. Anal. for $C_{22}H_{25}NO_3$ (351.446), calcd: C 75.19, H 7.17, N 3.98; found: C 75.11, H 7.09, N 4.09.

3.4. (1S,3R)-N-[(1′S)- and -(1′R)-Anthran-9′-yl-ethyl-1-carboxamido-1-hydroxy-2,2,3-trimethylcarboxylic acid lactone (6A and 6B)

Starting from 1.20 g (6.0 mmol) of camphanic acid and 2.40 g (10.8 mmol) of (±)-1-anthracenylethylamine was obtained 2.40 g (99%) of **6A,B**, HPLC asssay 89%. Separation was performed on a silica gel column (140 g) using cyclohexane:diisopropylether (1:1) as eluent. Obtained were 1.10 g of **6A** and 1.00 g of **6B**, both with ≥99% HPLC purity.

Data for compound **6A**: mp 137.5–140.0°C; $[\alpha]_D$=−95.2 (c 1.4, CH_2Cl_2); IR: 3440, 2960, 1795, 1680, 1515, 1445, 1170, 1015, 920, 730 cm^{-1}; ^1H NMR: 1.12 (s, 3H), 1.14 (s, 3H), 1.17 (s, 3H), 1.56–1.92 (m, 2H), 1.98 (d, 3H), 2.34–2.43 (m, 1H), 6.62–6.71 (m, 1H), 7.44–8.46 (m, 9H); ^{13}C NMR: 9.4, 16.4, 16.6, 21.5, 28.8, 29.9, 44.6, 53.8, 55.1, 92.4, 123.6, 124.8, 126.3, 128.3, 128.8, 129.8, 131.7, 132.9, 166.5, 178.3. Anal. for $C_{26}H_{27}NO_3$ (401.506), calcd: C 77.78, H 6.78, N 3.49; found: C 77.61, H 6.57, N 3.41.

Data for compound **6B**: mp 129.5–133.5°C; $[\alpha]_D$=+32.2 (c 1.5, CH_2Cl_2); IR: 3440, 2970, 1790, 1675, 1520, 1450, 1165, 1015, 920, 730 cm^{-1}; ^1H NMR: 0.47 (s, 3H), 0.91 (s, 3H), 1.03 (s, 3H), 1.66–2.05 (m, 3H), 1.96 (d, 3H), 2.52–2.59 (m, 1H), 6.57–6.66 (m, 1H), 7.39–8.45 (m, 9H); ^{13}C NMR: 9.4, 16.1, 16.3, 21.2, 28.9, 30.1, 44.9, 53.7, 55.1, 92.5, 123.7, 124.8, 126.2, 128.2, 128.8, 129.7, 131.7, 133.4, 166.6, 178.4. Anal. for $C_{26}H_{27}NO_3$ (401.506), calcd: C 77.78, H 6.78, N 3.49; found: C 77.53, H 6.76, N 3.57.

3.5. (1S,3R)-N-Phenylmethyl-1-carboxamido-1-hydroxy-2,2,3-trimethylcarboxylic acid lactone (7)

Compound **7** was prepared as described above for diastereomeric mixtures. Obtained were 594 mg (96%) of crude **7**, dense oil that slowly crystallized: mp 110.6–112.2°C; $[\alpha]_D=-6.3$ (c 1.9, CH_2Cl_2); IR 3360, 2960, 1770, 1670, 1540, 1450, 1260, 1065, 920, 725 cm^{-1}; ^1H NMR: 0.91 (s, 3H), 1.10 (s, 3H), 1.13 (s, 3H), 1.63–1.72 (m, 1H), 1.88–2.00 (m, 2H), 2.51–2.61 (m, 1H), 4.43 (dd, 1H, J=14.4, 5.7 Hz), 4.53 (dd, 1H, J=14.4, 5.7 Hz), 6.79 (s, 1H), 7.27–7.36 (m, 5H); ^{13}C NMR: 9.4, 16.3, 16.5, 28.8, 30.1, 42.9, 53.8, 55.1, 92.4, 127.6, 127.7, 128.7, 137.5, 166.9, 178.2. Anal. for $C_{17}H_{21}NO_3$ (287.359), calcd: C 71.06, H 7.37, N 4.87; found: C 71.16, H 7.20, N 5.03.

3.6. Calculations

The force field calculations were performed using a standard procedure by the SYBIL software package of TRYPOS Assoc. (Munchen, Germany).

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