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Challenges in the assignment of relative and absolute configurations of complex molecules: computation can resolve conflicts between theory and experiment



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Jie Ren^a, Guo-You Li^b, Lan Shen^a, Guo-Lin Zhang^{b,*}, Laurance A. Nafie^c, Hua-Jie Zhu^{a,*}

^a Chinese Center for Chirality, Key Laboratory of Medicinal Chemistry and Molecular Diagnostics Education Committee of China, Hebei University, Baoding, 071002 Hebei Province, China

^b Chengdu Institute of Biology, Chengdu, Sichuan, China

^c Department of Chemistry, Syracuse University, Syracuse, NY 13244, USA

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1. Introduction

Absolute configuration (AC) determination for complex chiral compounds has challenged chemists for a long time. With the development of super-computer technology, to use theoretical methods to assign AC becomes more and more popular in the world. Especially, by means of modern quantum theory, researchers can now identify many complex chiral compounds' AC. This greatly accelerates the progress of different theoretical methods used in AC assignment in stereochemistry.

Recently, a novel bioactive alkaloid, brevianamide M (1), and its oxidation product **2** have been reported (Fig. 1).¹ The relative configuration of **1** was established as (2R,13R) or (2S,13S) by X-ray crystallography using Mo radiation. This compound can be hydrolyzed in acidic aqueous solution at 100 °C to afford L-phenylalanine, which strongly implied that C-13 should have an S-configuration. Therefore, the AC of **1** was assigned as (2S,13S).¹ This procedure for AC assignment is normally definitive and cogent. In our recent studies of structural properties of chiral molecules, we use density functional theory (DFT) with different basis sets to examine the relationship between optical rotation values of the target chiral

ABSTRACT

The configuration of (-)-brevianamides was assigned as (2S,13S) based on X-ray structure analysis and hydrolysis experiments. However, our theoretical investigation of its chiroptical properties strongly implied that the correct configuration should be (2R,13R). The reasons for the incorrect earlier assignment are analyzed by calculations of conversion energy barriers among different intermediates, starting materials and final products. This study demonstrates that conflicting theoretical and, experimental results suggest that it is premature to assign the configuration of a natural product.

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molecules and their structures.² The AC of **1** was selected as one of the examples in this study. After comparing measured to calculated chiroptical properties of **1**, we concluded that the reported AC was incorrect and should be re-assigned as (2*R*,13*R*)-**1**. This example of mis-assignment of AC is the most extreme case uncovered to date in our theoretical studies. It demonstrates that, given the power of current computational chemistry using DFT, chemists should now



Fig. 1. The structures of 1 and 2.



^{*} Corresponding authors. E-mail address: hjzhu@mail.kib.ac.cn (H.-J. Zhu).

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reexamine AC assignments based in part on indirect chemical evidence, such as the acid hydrolysis mentioned above. The details of how the new assignment of AC for **1** was systematically reached are explained below, including how the acid hydrolysis provided misleading evidence.

The experimental optical rotation (OR) of **1** is -147.7° in acetone.¹ However, it was found that (2*S*,13*S*)-**1** had positive OR values (Table 1) both in the gas phase and in chloroform using widely used DFT methods.³ Four DFT quantum chemistry models were used in the OR computations. Optimization of different conformations was

Table 1

OR values for (2	S)- 1 from	methods	1 - 4
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	Method 1 ^a	Method 2 ^b	Method 3 ^c	Method 4 ^d
[α] _D	+510.5	+532.9	+519.5	+600.7
[a] _{Den} e	+209.8	+222.4	+217.0	+354.0

^a B3LYP/6-311++G(2d,p)//B3LYP/6-31G(d).

^b B3LYP/6-311++G(2d,p)//B3LYP/6-31+G(d,p).

^c B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p).

^d B3LYP/6-311++G(2d,p)//PCM/B3LYP/6-311++G(2d,p).

^e Single point energy at the B3LYP/aug-cc-pVDZ level in the chloroform using PCM model was used in OR computations.

performed at the B3LYP/6-31G(d) level in the gas phase; the OR computations were then performed at the B3LYP/6-311++G(2d,p) level in the gas phase (methods 1, B3LYP/6-311++G(2d,p)//B3LYP/6-31G(d)). Three additional models were used for OR calculations as indicated in Table 1. They were B3LYP/6-311++G(2d,p)//B3LYP/6-31++G(2d,p), method 2, B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p), method 3, and B3LYP/6-311++G(2d,p)//PCM/B3LYP/6-311++G(2d,p), method 4. The total electronic energy (TEE) was used in OR computations using Boltzmann statistics. All conformations were used in a single point energy (SPE) calculation at the B3LYP/aug-cc-pVDZ level in chloroform using the PCM model. The SPE were then used in OR computations again to afford [α]_{Dspe} shown in Table 1. The methods used were validated in our recent study.⁴ All OR values are summarized in Table 1.

All OR predictions for (25,13S)-1 are positive ranging from about +210 to +600. The absolute values of OR are much bigger than the experimental OR (-147.7 in acetone), which is typical for DFT-level calculations. Since the relative configuration was well established using X-ray, the positive OR values of from +210 to +600 suggest that 1 should have the absolute configuration of (2R,13R). However, there would be concern that the computation of OR values is based on the determination of electronic transitions in the inaccessible far-UV region, which is not easy to calculate with reliability. By contrast, the relative configuration of the structure of (2R,13R) or (2S,13S)-1 was well established by X-ray and its absolute configuration was confirmed by hydrolysis of 1 to afford the L-amino acid. Thus, we questioned whether the DFT methods may have given a wrong prediction in this example.

However, after we carefully examined the structure **1**, we found that the previously assigned absolute configuration was indeed incorrect. A possible reason for this discrepancy is that the H on C-13 could be enolized under strong acid conditions (6 N HCl aqueous solution, 100 °C for 12 h), and thus epimerized (Scheme 1). Theoretically, if the diastereomer (2R,13S)-**1** had lower energy than (2R,13R)-**1**, this isomerization conversion could explain the hydrolysis result. Thus, relative energetics of (2R,13S)-**1** and (2R,13R)-**1** were examined. After conformational searches using the MMFF54S force field, all accessible conformations were used in optimizations at the B3LYP/6-31G(d) level in the gas phase. The low energy conformations from 0 to 2.5 kcal/mol were then used for further optimizations at the B3LYP/6-311++G(2d,p) level in the gas phase. It was found that the energy of (2R,13S)-**1** is really lower than that

of (2R,13R)-1 by 1.66 kcal/mol at the B3LYP/6-311++G(2d,p) level in TEE. This energy decreased to 0.80 kcal/mol in Gibbs free energy (GFE), or 1.46 kcal/mol with zero-point energy (ZPE) correction at the B3LYP/6-311++G(2d,p) level in the gas phase. Thus, if the transition state barriers are not high enough to maintain the configuration at C-13, (2R,13R)-1 can convert into the more stable epimer (2R,13S)-1 with almost 92% conversion yield from (2R,13R)-1 to (2R,13S)-1 using ZPE energy, or 80% conversion using GFE. Finally, (2R,13S)-1 could hydrolyze to afford 80–92% of L-phenylalanine under strong HCl conditions at 100 °C.



Scheme 1. The plausible isomerization from (2R,13R)-1 to (2R,13S)-1.

We determined experimentally that L-phenylalanine cannot be converted into D-phenylalanine in 6 N HCl at 100 °C over 12 h since all recovered product showed no loss of OR. Therefore, this excluded both the possibility of conversion of D-phenylalanine to Lphenylalanine or vice versa. Accordingly, the obtained L-phenylalanine must originate from the hydrolysis procedure instead of an inter-conversion under HCl catalysis.

The electronic circular dichroism (ECD) of (2R,13R)-1 was computed at the B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p) level to further explore the AC of 1.⁵ All conformations were used for frequency computations to obtain GFE data. Then, GFE magnitudes were used in the Boltzmann statistics in ECD simulations. As expected, the computed ECD for (2R,13R)-1 was in good agreement with the experimental ECD (Fig. 2). The theoretical prediction of



Fig. 2. Comparison of the computed ECD with the experimental CD.

positive and negative Cotton effect matched very well with those in the experimental ECD. Therefore, both of OR and ECD provide evidence that the previously assigned AC (-)-(2S,13S)-1 is not correct. The actual absolute configuration of (-)-1 must be (2R,13R).

Why did the early experiments provide the wrong predictions? The major reason must be low barriers of the isomerization from (2R,13R)-1 to (2R,13S)-1. Therefore, conversion barriers were investigated. All possible transition state (TS) structures were analyzed using DFT methods similar to those recently used (Fig. 3).⁶ Theoretically, four TS structures were plausible for the formation of (2R,13S)-1. However, only **TS-1**, **TS-2**, and **TS-4** were found in the calculations, **TS-3** does not exist in the computations.



Fig. 3. The four TS structures used in TS computations.

In the absence of H⁺ catalysis (**TS-1**), a 33.4 kcal/mol barrier was found at the B3LYP/6-311++G(2d,p) level in the gas phase using TEE. The barrier is 32.9 kcal/mol using GFE, or 31.5 kcal/mol using zero-point energy corrections in the gas phase. Here, all the barriers are quite high, and it is difficult to get conversion via **TS-1**. The energy barrier decreased to 25.1 kcal/mol at the B3LYP/6-311++G(2d,p) level in water with the PCM model using SPE data. However, in the presence of another H⁺, e.g., **TS-2** and **TS-4**, the conversion benefits from a lower TS barrier of 23.1 kcal/mol (**TS-4**) in the gas phase in TEE, or 17.9 kcal/mol in SPE in water (Table 2). If

Table 2

The TS activation energy magnitudes for the four different procedures computed at the B3LYP/6-311++G(2d,p) level in the gas phase or in water

	ΔE_0^a	$\Delta G^{\mathbf{b}}$	ΔE^{c}	ΔE_l^d
TS-1	31.5	32.9	33.4	25.1
TS-2	26.8	28.6	28.2	16.5
TS-4	21.5	23.3	23.1	17.9
TS-5	25.4	26.7	27.7	21.3

^a Using zero-point energy correction.

^b Using Gibbs free energy.

^c Using total electronic energy.

^d Using single point energy obtained in water via PCM model.

the reaction involves**TS-2**, the barriers in the gas phase are higher by about 5.1–5.3 kcal/mol than those in **TS-4**. However, **TS-2** decreased to 16.5 kcal/mol in water and is about 1.4 kcal/mol lower than **TS-4**. Both barriers are low enough for the isomerization. The 3D TS structure (**TS-4**) is illustrated in Fig. 4a. Once the isomerization completed, the intermediate could convert into (2*R*,13*S*)-**1** via **TS-5** as illustrated in Fig. 4b and c. The procedure involved HCI again. This energy barrier is only 25.4 kcal/mol in ZPE, 26.7 kcal/mol in GFE, or 27.7 kcal/mol in TEE. The barrier decreased to 21.3 kcal/ mol in water using the PCM model. The reaction coordinate for the



Fig. 4. The 3D structures of TS-4, TS-5, and the coordinates for the conversion from (2R,13R)-1 to (2R,13S)-1.

whole procedure is illustrated in Fig. 4c. (2*R*,13*S*)-1 finally decomposed into L-phenylalanine as reported previously.

Another feasible route for the AC conversion involves an S_N2 procedure (Scheme 2). At the first step, H⁺ catalysis leads the loss of a water molecule to form an imine (**3**), the imine then hydrolyzed into an amide (**4**) after cleavage of the C2–N. Under HCl catalysis, **4**

Indeed, the possibility for **1** to lose a molecule of water to **3** existed. The size of the barrier for dehydration to form **3** via **TS-7** is therefore of immediate interest. If the barrier is lower than that leading through **TS-4**, the loss of a water, while reversible, could determine the reaction pathway. However, if the barrier via **TS-7** is higher than that via **TS-4**, the loss of a molecule of water to **3**would



Scheme 2. The possible conversion from 1 to L-phenylalanine 7.

can go through **TS-6** to give intermediate **6**. In this procedure, the AC of C-13 may change from *R* to *S*. After reaction with a molecule of water, phenylalanine **7** formed. Therefore, to obtain L-phenylalanine, the **TS-6** conversion must change the AC of C-13.

The barriers via **TS-6** were investigated at the B3LYP/6-31G(d) level in the gas phase; the effect of the phenyl ring on the barriers were also carefully considered. Finally, the lowest barrier TS structures were further computed at the B3LYP/6-311++G(2d,p) level. However, it was found that the energy barrier via **TS-6** is 64.9 kcal/mol in free energy when the energy of a complex of HCl and **4** was used as the relative zero-point reference. On the other hand, the relative energy of the complex of HCl and **4** is higher by 8.0 kcal/mol in GFE than that of the complex of HCl and **1**. Thus, the TS barrier was about 72.8 kcal/mol when the energy of the complex of HCl and **1** was used as the relative zero-point reference. This may be due to the ring strain in the aziridinium TS structure. This conversion is therefore quite difficult. The 3D TS structure of **TS-6** is illustrated below (Fig. 5).



Fig. 5. The plausible transition state for TS-6.

be inconsequential. The process should go through **TS-4** and **TS-5**. Therefore, the pathway via **TS-7** was investigated at the B3LYP/6-311++G(2d,p) level (Fig. 6). The position of a phenyl ring in TSs was investigated to study the effect of phenyl ring on the barriers.



Fig. 6. The plausible transition state for TS-7.

The predicted barrier (33.78 kcal/mol) via **TS-7** was higher than that (23.28 kcal/mol) via **TS-4** by a value of 10.5 kcal/mol at the B3LYP/6-311++G(2d,p) level in the gas phase. This barrier is also higher by 7.0 kcal/mol than that via **TS-5**. Since the barriers in **TS-7** were bigger than those via **TS-4** and **TS-5**, respectively, this suggests the favorable route to the final products should proceed via **TS-4** and **TS-5**. The specific TS barriers involved in **TS-6** and **TS-7** are summarized in Table 3.

After careful examination of the possible procedures, the whole sequence from **1** to **7** is illustrated below (Scheme 3).

In route A, after (2*R*,13*S*)-**1** formed, it could be hydrolyzed into **8a** or **8b**. Under the H_3O^+ - CI^- system, either **8a** or **8b** should be further hydrolyzed into **9** and **10**. Compound **9** would not change anymore. However, intermediate **10**, which is stable due to the transorientation, should be hydrolyzed into **7** and **11** including a molecule of NH₄Cl. Another possible way is route B, after (2*R*,13*S*)-**1** formed, it could be hydrolyzed into **4**. In the H_3O^+ - CI^- system, intermediate **12** formed and it should be further hydrolyzed into **9** and **7**.

Table 3

The corresponding barriers involved in **TS-6** and **TS-7** at the B3LYP/6-311++G(2d,p) level in the gas phase and in water using PCM model

	ΔE_0^a	ΔG^{b}	ΔE^{c}	ΔE_l^d
TS-6	65.1	64.9	67.1	51.7
TS-7	32.0	33.8	32.9	29.1
$\Delta(\Delta E)^{e}$	10.6	10.5	9.9	11.2
$\Delta(\Delta E)^{f}$	6.6	7.1	5.3	7.8

^a Using zero-point energy correction.

^b Using Gibbs free energy.

^c Using total electronic energy.

^d Using single point energy obtained in water via PCM model.

^e The barrier energy via **TS-7** was subtracted from that via **TS-4**. The positive values exhibit that the barrier via **TS-7** is higher than that via **TS-4**.

^f The energy via **TS-7** was subtracted from that via **TS-5**. The positive values exhibits that the barrier via **TS-7** is higher than that via **TS-5**.

Route A:



As mentioned above, (2R,13R)-1 can be oxidized into (R)-2. Thus, conversion of (2R,13R)-1 was performed (Scheme 4), the obtained (R)-2 had OR values of -340. It had almost the same OR values as the one (-359) isolated from the broth. It exhibited the early ob-



Route B:



Scheme 3. Two plausible routes for the conversions of 1-7.

The experimental conversion of (2R,13R)-1 to (2R,13S)-1 was studied next. The starting material did not dissolve in water at room temperature. Once the temperature was raised to about 65 °C, it dissolved in water quickly and decomposed immediately, and L-phenylalanine formed with OR value of -32. This OR value is almost the same as that of pure natural L-phenylalanine. This exhibited that the conversion from (2R,13R)-1 to (2R,13S)-1 may be complete, or at least the conversion may be over 92% as predicted using ZPE energy.

Compound **2** was isolated from the same pathway as **1**. Logically, **2** is likely to have the same AC at C-13 as **1** based on a common precursor. For example, (2R,13R)-**1** can be oxidized into (R)-**2**. Thus, (R)-**2** was used in the OR computations. Theoretically, the computed OR for (R)-**2** was -619.2 at the B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p) level in the gas phase. The experimental OR was -359 for (R)-**2**. Thus, the early reported (-)-**2** should be (R) configuration (Scheme 4).

tained (-)-**2** has (*R*) configuration derived from (2*R*,13*R*)-**1** via oxidation. Furthermore, the (*R*)-(-)-**2** was used for ECD measurement. Three stable conformations were found and they were used in ECD computations at the B3LYP/6-311++G(2d,p)// B3LYP/6-311++G(2d,p) level in the gas phase using GFE after Boltzmann statistics. The recorded ECD agreed with the predicted ECD well (Fig. 7).

Furthermore, the three conformations of (*R*)-**2** were used in VCD computations at the B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p) in the gas phase in the gas phase based on methods described in a review of the application of VCD to the determination of AC in a wide variety natural product molecules,⁷ and a more recent review of the use of VCD and Raman optical activity (ROA) for the determination of AC in chiral molecules.⁸ Solvent-subtracted IR and VCD spectra were used. As shown in Fig. 8, the predicted IR and VCD spectra agree closely with the experimental IR and VCD spectra of (–)-**2**.



Fig. 7. The predicted ECD for (R)-**2** and experimental ECD for (-)-**2**.



Fig. 8. Predicted VCD and IR at the B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p) in the gas phase for (*R*)-**2**; comparison of experimental VCD for (-)-**2** and the calculated VCD for (*R*)-**2**. IR and VCD spectra of (-)-**2** in CDCl₃ (6 mg/0.3 mL); 100-µm path-length cell with BaF₂ windows; 19 h collection for sample and solvent; instrument optimized at 1400 cm⁻¹. Solvent-subtracted spectra are compared to the corresponding calculated spectra.

Efforts to prepare single crystals of **1** of sufficient quality for AC determination were successful, and X-ray diffraction data was obtained using a Cu-radiation source. The X-ray experiments confirmed that our theoretical predictions are correct (Fig. 9). The enantiomer (-)-**1** should be (2R,13R). Now, all evidences, both experimental and computational, agree well for the AC assignment of (-)-(2R, 13R)-**1**.

Experimental results are always the fundamental touchstone for different theories. However, if the interpretation of the experimental results is not correct, the conclusions reached will be affected, just as in our initial thinking in this study. With this idea in mind, the example analyzed in this paper, carries a high level of



Fig. 9. The X-ray structure for (-)-1.

significance for both experimental and theoretical chemists. All sources of evidence need to be considered carefully, and computational methods should be used, where possible, to confirm conclusions based only on chemical reasoning.

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