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Configurational assignment of sugar *erythro*-1,2-diols from their electronic circular dichroism spectra with dimolybdenum tetraacetate

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ABSTRACT

An extension of the dimolybdenum circular dichroism methodology for the determination of absolute configuration of *erythro*-*vic*-diols is presented. This straightforward, simple, and reliable approach consists of mixing a non-racemic transparent *vic*-diol with dimolybdenum tetraacetate acting as an auxiliary chromophore. Generally, the application of the helicity rule relating the sign of the O–C–C–O torsional angle with the sign of the Cotton effects arising in the 300–400 nm spectral range allows an unequivocal assignment of the stereostructure of the investigated diols. For *erythro vic*-diols, however, an additional assumption regarding the preferred conformation of the diol unit in its complexed form had to be made. The molecular modeling calculations provide adequate support to resolve this issue.

1. Introduction

During our study on the application of dimolybdenum tetraacetate as an auxiliary chromophore in chiroptical studies of *vic*-diols, we have demonstrated that this in situ methodology can be successfully applied in determining the absolute configuration of several types of *vic*-diols.[1–4] In this approach, prior to measuring the circular dichroism (CD) spectra, a transparent chiral diol has to be transformed into a chromophoric derivative by mixing with dimolybdenum tetraacetate, which acts as an chromophore auxiliary. Subsequently, it is possible to record the CD spectra of components dissolved in DMSO in the 250–650 nm spectral range. The resulting CD spectra are suitable for the assignment of the absolute configuration, since the determining factor of the signs of Cotton effects (CEs) arising within the d–d absorption bands of the metal cluster is the sense of twist within the diol moiety. Based on such CD results, the molecular stereostructure of *vic*-diols can be determined with confidence through the helicity rule. The rule, formulated on the basis of empirical results procured for a large variety of *vic*-diols, correlates the sign of the O–C–C–O torsional angle with the sign of CEs occurring in the 300–400 nm spectral range. According to the rule, a positive (negative) sign of the CEs arising at around 310 and 400 nm is related to a positive (negative) sign of O–C–C–O torsional angle of the diol subunit. The rule finds application for both rigid as well as conformationally flexible diols. In the latter case however, the determination of the absolute configuration requires us to know of the diol conformation in its complexed form. It is commonly known that any chiroptical method typically yields either the absolute configuration or the conformation.[5] Establishing a correlation between both properties (absolute configuration and the conformation) calls for an access to additional information, which can be deduced only in very rare cases from the CD-measurements alone. After ligation to the Mo_2-core, however, an internal conformational mobility of the flexible diol molecule becomes substantially reduced owing to the steric requirements of the stock complex.[1,6] Therefore, the molecule appears to exist only as a single conformer, in most cases. The preferred conformation of a *vic*-diol molecule in the chiral Mo_2-complex is the one with an antiperiplanar orientation of both O–C–C–R units. This is very reasonable, because only in such a conformation do the bulky R-groups point away from the rest of the complex and tend to avoid the steric interaction with the remaining acetate ligands in the stock complex. Additional evidence in support of such a preferred conformation is given by the quantum-mechanical calculations.[7] These calculations, made for the model systems of *vic*-diols, indicate that the lowest energy *gauche* conformer (O–C–C–O $\approx 60°$) is ca. 8 kJ mol^{-1} (1.92 kcal mol^{-1}) lower in energy than the lowest energy *trans*-conformer (O–C–C–O $\approx 180°$). Thus, the relative configuration of *vic*-diol after ligation to the Mo_2-core is established to be *gauche* with an antiperiplanar orientation of each O–C–C–R group, as presented in Figure 1. Consequently, the sign of the particular CEs obtained from the CD spectrum allows us to unequivocally assign the absolute configuration. In this manner, the determination of the absolute configuration becomes possible on the basis of the chiroptical data alone. In

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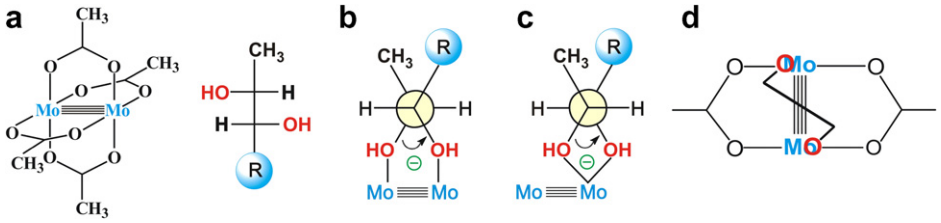

Figure 1. Dimolybdenum tetraacetate (a) and preferred antiperiplanar conformation of an aliphatic *threo*-1,2-diol with a negative torsional angle when complexed to the Mo_2-dimer: (b) a bridging mode of ligation; (c) a chelating mode of ligation; (d) a view from the top on the bridging chiral complex.

addition, the conformational preferences of the resulting Mo_2-containing rings impose a twist about the Mo–Mo bond so that the core is no longer in an eclipsed form. Thus, the achiral chromophore is incorporated into a chiral ring ('chiral second sphere' according to Snatzke[8]) which implies that the CD is mainly governed by a 'helicity rule', which means that the sign of the torsional angle determines the signs of particular CEs, and also, to a great extent, their observed magnitudes.

We have demonstrated recently that this in situ methodology can be extended successfully to sterically demanding *sec*/*tert* and *tert*/*tert* *vic*-diols.[9,10] Thus, it can be concluded that the dimolybdenum methodology is a straightforward, reliable, convenient, and very easy to apply technique in the determination of the absolute configuration of a variety of *vic*-diol classes.

Among glycols, recently researched by us, are the *erythro vic*-diols.[9,10] However, all of them were conformationally rigid as they belonged to the steroidal or cyclic terpenoid diols. Thus, the molecular conformation was clearly defined while the application of the helicity rule to assign the configuration of the diol unit was straightforward. To the best of our knowledge, there is only one additional example of a rigid *erythro*-1,2-diol investigated by the in situ dimolybdenum method.[11] Thus, the question arises as to whether the same regularity is applicable to the conformationally flexible *erythro*-*vic*-diols? To answer this question one must bear in mind that in *erythro*-1,2-diols the two O–C–C–R groups cannot adopt an antiperiplanar conformation simultaneously. Two possible arrangements of the diol unit leading to opposite signs of the decisive CD bands for the same absolute configuration are shown in Figure 2. It is very likely that in *erythro*-1,2-diols, for steric reasons, the relative dimensions of substituents play a primary role. Frequently, however, the determination which substituent dominates it is not an easy task.

Figure 2. Two possible arrangements of the *erythro*-1,2-diol unit in the chiral complex formed after complexation with the Mo_2-dimer.

There are several reported possible strategies for assigning the stereochemistry of *threo*-*vic*-diols. Among them the exciton-coupled circular dichroism (ECCD), introduced by Harada and Nakanishi, should be mentioned.[12,13] A few suitable red-shifted chromophores have been proposed to convert the hydroxyl groups of diols into derivatives that absorb light in the visible spectral region.[14,15] For the transformation of acyclic *vic*-diols into conformationally defined derivatives, their conversion into dioxolanes[16,17] or 4-biphenylborates[18,19] was also proposed. The ECCD method has also been applied successfully to the absolute stereochemical assignment of *vic*-diols in the form of their macrocyclic host–guest complexes with a host porphyrin tweezer.[20,21] However, a method for the reliable and unambiguous determination of the absolute configuration of flexible *erythro*-1,2-diols based on CD spectroscopy was, in general, lacking. Very recently, Borhan et al. proposed a protocol to determine, among others, the absolute configuration of both *threo*- and *erythro*-*vic*-diols.[22] This newly proposed protocol is based on the ECCD spectroscopy and employs a fluorinated porphyrin tweezer to form supramolecular complexes with chiral diols. The conformation adopted by a ligand after binding to the fluorinated tweezer is the determining factor of the stereochemical outcome of the host–guest complex. The proposed conformational model is one of several possible modes of binding. Nonetheless, for

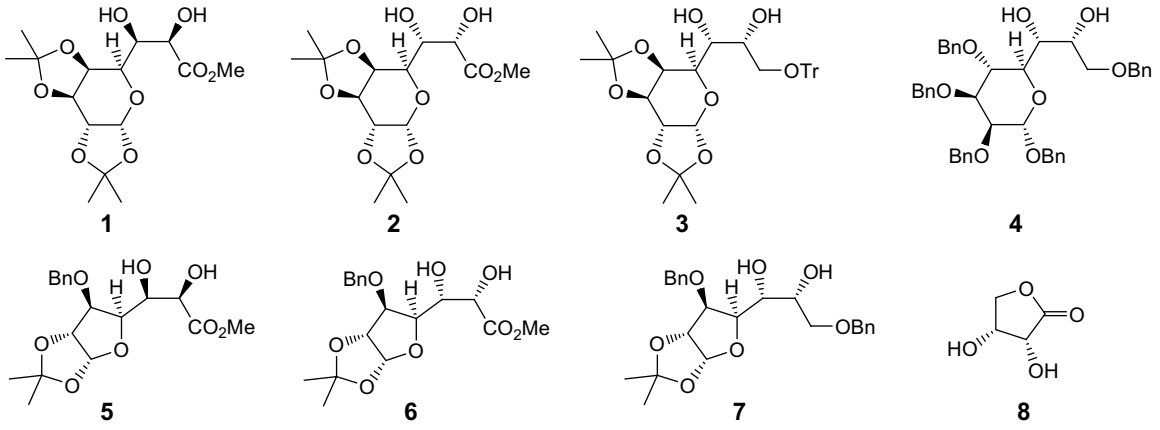

Chart 1.

the diols investigated this model correlates successfully the experimental chiroptical data with the stereochemistry of the complex.

Herein, we report an application of the in situ dimolybdenum methodology to the assignment of the absolute configuration of flexible *erythro*-1,2-diols. This study is undertaken for two main reasons. Firstly, to verify that the dimolybdenum methodology has a more general applicability and can be successfully applied to this type of diols as a reliable, versatile, and simple procedure. Secondly, to find an alternative protocol to the work of Borhan[22] in order to enhance the potential and reliability of the assignment. As model compounds for our systematical study, we used a series of acyclic *erythro-vic*-diols synthesized by us [except commercially available D-erythronic acid γ-lactone **8**] and presented in Chart 1.

2. Results and discussion

Analogously to the *threo*-1,2-diols, up to five CEs (I – V), arising in the 550–250 nm range were observed for a chiral *erythro-vic*-diol (Table 1) in the presence of dimolybdenum tetraacetate. The CD spectrum of Mo_2-complex of each compound has three prominent bands, as can be seen in Figure 3. For comparison, the CD spectrum of the Mo_2-complex of (2*R*,3*R*)-butane-2,3-diol, a representative of *threo vic*-diols, is presented additionally. Two bands with the same sign appear near 300 nm (band IV) and 400 nm (band II) and a third one, of opposite sign to the first two, occurs at ca. 350 nm (band III). Band III, however, is detectable as a distinct minimum or maximum only for diols **2**, **3**, **6**, and **8**. Most probably, this CE is too small to overcome the contributions of the relatively strong neighboring bands II and IV and therefore, in the case of remaining compounds, it can be observed only as an inflexion point (Table 1, Fig. 3). Nevertheless, the tendency to form a minimum or a maximum by these bands is clearly visible.

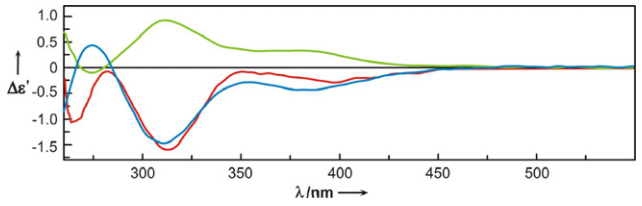

Figure 3. CD spectra of in situ formed Mo_2-complexes of *erythro*-diols **1** (——) and **7** (——) as well as *threo*-(2*R*,3*R*)-butane-2,3-diol (——).

CD bands II–IV, as was the case for *threo-vic*-diols, appear to be the most useful for correlation between the stereostructure of the diol and its CD. These bands are relatively strong in comparison with the other bands and appear in the spectra of all compounds studied.

On the basis of the data presented in the Table 1, investigated compounds **1-8** may be divided into two groups differing in sign of the diagnostic bands. In the first group, which contains diols **1**, **5**, and **8**, the CEs at around 300 and 400 nm are negative with a positive one, or occurring as a negative minimum, at ca. 350 nm. In the second group, represented by diols **2**–**4**, and **6** and **7**, the opposite relationship of sign pattern is observed, for example, both CD bands at ca. 300 and 400 nm are positive and the one near 350 nm is negative.

The shapes of CD spectra of *threo*- and *erythro*-diols are similar (Fig. 3), indicating that the complexation mode for the both groups is similar. Thus, the correlation between the stereostructure and the CD data could be made applying the helicity rule also for *erythro*-diols. An important point is, however, to find which conformation (of the two presented in Figure 2) is the preferred one. In other words, it is imperative to ascertain if the favored conformation in the chiral Mo_2-complex formed in situ is the one with the sugar unit or the ester/ether group in an antiperiplanar arrangement in respect to one of hydroxyl group.

Building on the assumption that the helicity rule is valid also for *erythro*-diols, compounds from the first group, that is, diols **1**, **5**, and **8** with a negative CE at around 300 and 400 nm, should have the negative sign of the O–C–C–O unit. Consequently, the positive sign of these decisive CEs for the second group, that is, diols **2**–**4**, **6** and **7**, would indicate the positive sign of the same unit. Therefore, diols from the first group in their complexed form may adopt conformation I or IV (Fig. 4) while the diols from the second group may adopt conformations II or III (Fig. 4). If the relative dimension of the substituents is crucial in the case of diols studied, it can be concluded that the sugar part of the molecule does play the decisive role in adopting a preferred conformation in the chiral Mo_2-complex. Thus, for both the first and the second groups of diols the conformation I and III as depicted in Figure 4 should be the favorable ones, respectively.

Table 1
CD data of in situ formed Mo-complexes of *vic*-diols **1**–**8**

Compound	A	B	CD band V	CD band IV	CD band III	CD band II	CD band I
1	–	–	+0.43 (275.0)	−1.47 (310.5)	a (355.5)	−0.44 (387.5)	+0.03 (499.0)
2		+		+0.78 (290.5)	−0.53 (344.0)	+0.07 (410.0)	−0.07 (476.0)
3	+[$]	+	−0.10 (270.5)	+0.26 (285.0)	−0.15 (352.0)	+0.17 (410.5)	
4		+	−0.08 (273.5)	+0.23 (311.0)	b (351.5)	+0.05 (385.5)	
5	–	–	+0.15 (273.5)	−0.57 (310.5)	a (357.0)	−0.13 (385.0)	
6		+		+0.27 (285.0)	−0.18 (348.0)	+0.05 (420.0)	−0.03 (489.0)
7		+	−0.02 (272.5)	+0.25 (308.5)	a (356.0)	+0.11 (389.0)	+0.05 (468.0)
8	–	–	a (275.5)	−0.70 (302.5)	+0.58 (346.5)	−0.03 (418.5)	−0.05 (481.0)

Values are given as $\Delta\varepsilon'$(nm)[*]. A—predicted sign of the O–C–C–O torsion angle; B—sign of the O–C–C–O torsion angle from CD; [$]—X-ray data; a—negative minimum; b—positive minimum; *—since the real complex structure as well as the concentration of the chiral complex formed in solution is not known the CD data are presented as the artificial $\Delta\varepsilon'$ values which are calculated in the usual way as $\Delta\varepsilon' = \Delta A/c \times d$, where c is the molar concentration of the chiral ligand, assuming 100% complexation.

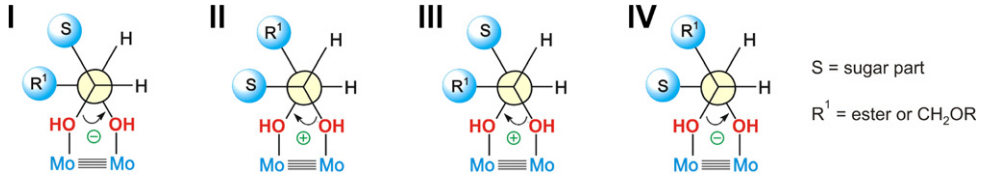

Figure 4. Four possible conformations adopted by *erythro-vic*-diols in their complexed form with Mo_2-dimer.

This is in line with an intuitive feeling that, for steric reasons, the sugar part is larger than the ester or ether group. Additional evidence in favor of the above empirical statement is given by the X-ray data for diol **3**.[23] The ORTEP diagram of compound **3**, shown in Figure 5, demonstrates that in the crystalline form the sugar part adopts an antiperiplanar arrangement versus one of the OH group, as evidenced by the O–C–C–C(sugar) torsional angle of 177.89°. The trityl ether group is in a *gauche* conformation relative to the second hydroxyl according to the O–C–C–C(ether) torsional angle amounting −59.20°.

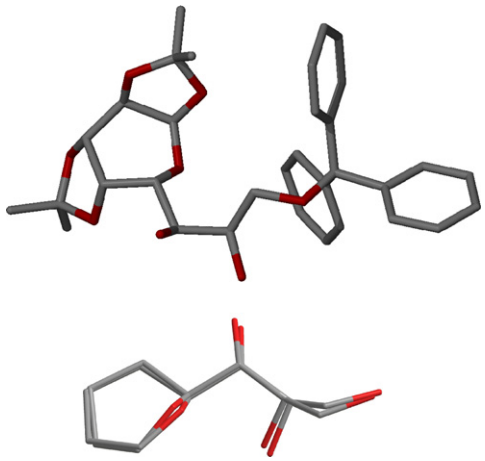

Figure 5. Top: ORTEP diagram of compound **3**. For clarity hydrogen atoms are omitted. Bottom: root mean square fit for the X-ray structure (top) and the calculated optimal conformation of compound **3** (bottom) and overlay. Hydrogen atoms and substituents (trityl and isopropylidenes) are omitted for clarity.

The results discussed above reflect perfectly the stereochemical situation of *erythro-vic*-diols **1**–**8** upon complexation with the Mo_2-core and the relationship with their CD spectra. As can be seen in Table 1, the sign of the O–C–C–C torsional angle for **1**–**8** predicted by the helicity rule is in excellent agreement with the sign of the decisive II and IV CEs in their CD spectra recorded in the presence of $Mo_2(OAc)_4$. This torsional angle was predicted under the assumption that the conformation adopted is dictated by the largest substituent, in this case the sugar substituent. Thus, it can be concluded that flexible *erythro-vic*-diols **1**–**8** also fall under our empirical helicity rule established before for other classes of glycols.

In an effort to corroborate the conclusions made on the basis of the relative dimensions of substituents, the conformational analysis using the molecular mechanics calculations was performed. A search of the conformational space was carried out using PC SPARTAN PRO.[24] For each of the structures **1**–**8** a corresponding model was built and its geometry optimized by applying the AM1 *semi*-empirical method. Next, a set of about 100 conformers was generated for each structure, using the MMFF94 method, except the compound **8** (a rigid structure), which gave only couple of conformers. This initial set of conformers was subjected to the geometry optimization (AM1 method), which reduced the aggregate number of conformers into a smaller set of optimized structures (approx. 10–20 per each structure). For each of the optimized sets of initially generated conformers for compounds **1**–**7** a second round of conformational space search has been conducted, also employing the MMFF94 method. This operation resulted in a generation of a large number of structures (each original, optimized conformer gave about 100 new structures), which were again subjected to geometry optimization (AM1 method). Finally, for each of the conformers related to structures **1**–**8**, values of *E* (kcal/mol) and the relevant dihedral angles (°) were tabulated. Invariably, conformers with a dihedral angle O–C–C–O close to ∼60° were amongst the most stable ones (within ∼0–2 kcal/mol range from the most stable structure). Generally, the number of distinct conformers for each compound is low (∼10–20), particularly if one disregards the variability arising from the existence of rotationally flexible benzyl groups in compounds **4**–**7** and the trityl group in compound **3**. Owing to the necessity of working with several large sets of structures it was not possible to model structures ligated to the Mo_2-core or to account for the solvent effects. However, the consistency of results obtained using the above methodology and similarity of calculated results for compound **3** with its respective X-ray data indicates adequacy of the presented results for the purpose in hand (Fig. 5).

The computed O–C–C–O torsion angle signs for compounds **1**–**8** and differences in energy between conformers are collected in Table 2. In general, the results presented in Table 2 are in line with the assumption that for *erythro-vic*-diols, the best conformations to coordinate to the Mo_2-core are conformations I and III (Fig. 4). In the case of diols **1** and **5** from the first group, the conformation I is found to be more than 1 kcal/mol lower in energy compared to the conformation II, thus providing good corroboration of our prediction. The same is true for diols **3** and **4** from the second group where predicted conformers III are lower in energy in comparison with conformers IV. Somewhat more varied are the results of conformational analysis for the second group of compounds, namely diols **2**, and **6** and **7**, as well diol **8**. In the cases of compounds **2** and **6**–**8** the calculated energies for the predicted conformer, that is, conformers III for diols **2**, **6**, **7** and conformer I for diol **8**, are higher in energy than for counterpart conformers. However, these differences in calculated energy equal 0.49, −1.28, 0.08, and −0.80 kcal/mol, respectively, are not significant for conformationally labile compounds. It should be noted that conformational analysis using molecular mechanics calculations was performed for the free diols and not for their complexes with the Mo_2-core.

The computed O–C–C–O torsion angle signs for compounds **1**–**8** provide corroborating evidence for the validity of the helicity rule for *erythro-vic*-diols. The positive or negative sign of the decisive CD bands at around 300 and 400 nm can be predicted by both the helicity rule and the computational results. Thus, we can conclude that the applicability of the helicity rule can be extended for *erythro-vic*-diols.

Table 2
Selected torsional angles in deg (°) and energies (kcal/mol) for conformers I–IV calculated using the discussed method

Compound	Conformer I	Energy	Conformer II	Energy	Conformer III	Energy	Conformer IV	Energy	Δ*E*
1	−56.40/−179.19	107.56	+49.05/+177.16	110.01					2.45
2					+56.33/−178.80	109.26	−59.59/+174.20	108.75	0.49
3					+61.87/−173.81	−271.10	−44.86/−173.61	−268.66	2.44
4					+57.82/−178.53	165.84	−52.89/−177.85	171.27	4.33
5	−54.84/+179.37	−332.98	+52.08/+178.10	−331.71					1.27
6					+58.46/−177.25	120.80	−52.78/177.06	119.62	−1.28
7					+52.20/+174.65	−142.31	−51.88/−174.95	−142.23	0.08
8	−18.99/−140.74	−175.80	+5.50/+121.85	−176.50					−0.80

A = O–C–C–O; B = C–C–C–O; numbering of conformers according to Figure 4.

3. Conclusions

The present study demonstrates that (1) the scope of the dimolybdenum CD methodology can be extended to *erythro*-1,2-diols; (2) the absolute configuration can be determined unequivocally by means of the empirical helicity rule relating the sign of the CEs arising in the 300–400 nm spectral region with the helicity of the O–C–C–O subunit; (3) the method also allows us to establish the preferred conformation of *erythro vic*-diol after ligation to the Mo_2-core to be *gauche* with an antiperiplanar orientation of one of the O–C–C–R group, where R means the largest substituent; (4) no exception to the helicity rule has been found so far; (5) since the preferred conformation of the diol in the formed complex is determined by the largest substituent, we are able to establish the absolute configuration at the carbon atoms in the diol subunit, even in flexible *erythro*-*vic*-diols from the CD measurements only; (6) despite its empirical character this simple methodology allows for an easy, fast and effective determination of the absolute configuration of a variety of *vic*-diol classes, including the conformationally flexible *erythro*-diols. In other words, the empirical helicity rule finds application for the determination of the 3D molecular structure of this class of *vic*-diols as well. Nevertheless, a support of the experimental data obtained by molecular modeling calculations is recommended.

4. Experimental

The synthesis and spectral characterization of compounds **1**–**8** was published before.[23] The CD spectra were acquired at room temperature in DMSO (for UV-Spectroscopy, Fluka) on a Jasco J-715 spectropolarimeter and step scans were collected at 0.5 nm/step with an integration time of 1 or 2 s over the range 250–650 nm. For the CD standard measurements the chiral *vic*-diol (1–5 mg, ca. 0.002 M/L) was dissolved in a stock solution of the $[Mo_2(OAc)_4]$ (4–6 mg, ca. 0.002 M/L) in DMSO (10 mL) so that the molar ratio of the stock complex to ligand was about 1:1, in general. Since the real complex structure as well as the concentration of the chiral complex formed in solution was not known, the CD data are presented as the $\Delta\varepsilon'$ values. These $\Delta\varepsilon'$ values are calculated in the usual way as $\Delta\varepsilon' = \Delta A/c \times d$, where c is the molar concentration of the chiral ligand, assuming 100% complexation (A = absorption; d = path length of the cell). $\Delta\varepsilon'$ is expressed in $[M^{-1} \times cm^{-1}]$ units.

The molecular modeling was performed using 3 GHz Quad-core Xeon-based PC with 3.5 GB memory under a XP SP2 operating system. The PC SPARTAN PRO v.2.0 computational package distributed by Wavefunction, Inc. was used to obtain calculated data. The energy values (in kcal/mol) as well as appropriate dihedral angles (in degrees) for each conformer within each set of data related to each modelled structure were collected in a spreadsheet format and sorted by E value.

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