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Conformational Sensitivity of Chiroptical Spectroscopic Methods: 6,6′-Dibromo-1,1′-bi-2-naphthol

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The experimental vibrational circular dichroism (VCD), electronic circular dichroism (ECD), and optical rotatory dispersion (ORD) spectra for both enantiomers of 6,6′-dibromo-1,1′-bi-2-naphthol have been measured. The corresponding quantum chemical predictions for three different orientations of hydroxyl groups in this molecule were obtained using 6-31G*, 6-311G(2d,2p) and 6-311++G(2d,2p) basis sets and the B3LYP density functional. The absolute configuration inferred by comparing the predicted spectra with experimental data is the same in VCD, ECD, and ORD methods, but spectral sensitivity to conformation varies among these methods. It is found that predicted ECD in the 200−350 nm region does not change significantly for the three conformers. As a result, the sensitivity of ECD to the conformation of hydroxyl groups in 6,6′-dibromo-1,1′-bi-2-naphthol is rather limited. Similarly, a comparison between experimental and predicted ORD spectra indicated that ORD spectral prediction is not the best method of choice for discrimination among different conformations of O−H groups. On the other hand, the predicted VCD, and associated absorption, spectral patterns in the 1600−900 cm^{-1} region are found to change significantly for the three conformations, and the experimental spectra correlate well with those predicted for only one conformation. These observations suggest that, among the three chiroptical spectroscopic methods investigated, VCD provides better sensitivity to the conformation of hydroxyl groups. The use of PCM model for exploring the influence of CH_2Cl_2 solvent on vibrational spectra indicated that this model is not appropriate for modeling the CH_2Cl_2 solvent influence on the vibrational absorption and VCD spectra of 6,6′-dibromo-1,1′-bi-2-naphthol.

Introduction

Substituted enantiomeric 1,1′-bi-2-naphthol compounds have been usefully employed as chiral auxiliaries and as chiral catalysts in many asymmetric syntheses.[1] Poly(1,1′-bi-2-naphthol) has been used[2] to prepare novel polymeric Lewis acid complexes with greatly enhanced catalytic activity. The determination of the absolute configuration of compounds containing binaphthol groups has attracted considerable attention in the literature. The X-ray diffraction method has been the preferred approach, if the compound of interest could be crystallized. Alternately, different solution phase methods, including resolution,[3] electronic circular dichroism (ECD)[4] spectroscopy, and nuclear magnetic resonance (NMR),[5] have also been employed for this purpose.

One important question for these binaphthol compounds is the magnitude of dihedral angle around the C−C bond connecting the two naphthol groups. This information has been inferred[6] from ECD spectroscopy by noting that the exciton couplet originating from the ^1B electronic transition of the naphthalene chromophore gives rise to bisignate ECD signals at about 230 nm. For the (a*S*)-configuration with this dihedral angle between $>0°$ and $<110°$, the positive portion of this ECD couplet appears at lower energy and the negative portion at higher energy. For the same configuration with this dihedral angle between $>110°$ and $<180°$, the opposite pattern is expected.[6,7] Therefore if the absolute configuration is known, then the range for the magnitude of this dihedral angle could be inferred from ECD spectral appearance. A second approach is based on the induction of helical twist, by the compound of interest, in nematic liquid crystals.[7] A third approach, based on the approximate semiclassical models of ECD, uses the wavelength separation[8] of positive and negative portions of the ECD couplet to suggest the magnitude of dihedral angle. These approaches[6−8] depend on the assumption that ^1B transitions of the naphthalene chromophore can be identified in the experimental spectrum and that approximate semiclassical models of ECD are applicable.

The conformational mobility of the hydroxyl groups in isolated 1,1′-bi-2-naphthol has been addressed before,[9] and it was found that one orientation of hydroxyl groups has significantly lower energy than other orientations. However, when compounds containing binaphthol groups are dissolved in solvents that participate in hydrogen bonding (such as alcohols, dimethyl sufoxide, etc.), the conformational preference can alter from that in an isolated molecule. This situation is less clear when solvents (such as CH_2Cl_2, CCl_4, etc.) that do not participate in hydrogen bonding are used. As a result, the conformation preferred for an isolated molecule may or may not remain as the lowest energy conformer in solution. For this reason, when experimental data are compared to those predicted for an isolated molecule, it is necessary to investigate the conformational dependence of predicted properties. In this manuscript we address the sensitivity of chiroptical spectroscopic methods to the hydroxyl group orientations using 6,6′-dibromo-1,1′-bi-2-naphthol as a test case.

The absolute configuration of 6,6′-dibromo-1,1′-bi-2-naphthol has been determined,[10] from the synthetic scheme used to prepare this compound from 1,1′-bi-2-naphthol, as (−)-(a*R*). The magnitude of the dihedral angle between the planes of two naphthyl groups and the orientation of hydroxyl hydrogen atoms

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in 6,6′-dibromo-1,1′-bi-2-naphthol are of interest not only from structural point of view but also for applications in asymmetric syntheses, liquid crystal properties, and chiral separations.[11−13]

In recent years, chiroptical spectroscopic methods have emerged[14] as powerful tools to determine the absolute configuration and predominant conformations of chiral molecules in the solution phase. The successful use of chiroptical spectroscopic methods depends on a reliable theoretical prediction of corresponding properties, and therefore quantum chemical predictions of chiroptical properties are needed along with experimental measurements. These chiroptical spectroscopic methods include vibrational circular dichroism (VCD), vibrational Raman optical activity (VROA), electronic circular dichroism (ECD), and optical rotatory dispersion (ORD). Although all four methods need not be used simultaneously, the use of more than one method certainly helps[15] remove any uncertainty in the conclusions emerging from individual methods. Furthermore, as the sensitivity to conformational details varies among these methods, sometimes a clear insight can only be obtained using multiple methods.

Optical rotation at 589 nm is routinely reported by synthetic chemists whenever a compound is synthesized. However, ORD data are not routinely reported. There are no prior combined studies on the experimental and quantum theoretical ORD spectra of any of the binaphthol compounds. Although several papers in the literature dealt with interpreting the ECD spectra of binaphthol compounds using semiempirical methods,[4,6−8] there appears to be no quantum chemical predictions of ECD for binaphthol compounds. Also, there are only a limited number of VCD studies on binaphthol and related compounds.[16−20] Sugeta and co-workers[16] have measured the VCD in the O−H stretching region of 1,1′-bi-2-naphthol in different solvents and interpreted the observed spectra using a coupled oscillator model. Urbanova and co-workers[17] measured the VCD in the mid-infrared region for 1,1′-bi-2-naphthol, 1,1′-bi-2-naphthol-3-carboxylic acid, and 1,1′-bi-2-naphthol-3-carboxylate and interpreted the observed spectra using quantum chemical predictions with BPW91 functional and 6-31G* basis set. Starting from 1,1′-bi-2-naphthol, a bis(ether ketone) macrocyle[18] was prepared by Cao et al. and its absolute configuration was determined using VCD spectroscopy. A related molecule, 1,1′-binaphthyl dimer,[19] was also subjected to VCD investigations. Although not directly related to binaphthol series of molecules, the absolute configuration and predominant conformation of a related axially chiral molecule, 2,2′-diphenyl-[3,3′-biphenanthrene]-4,4′-diol,[20] has been investigated in this laboratory using VCD, ECD and ORD methods.

From the literature survey provided in the previous paragraphs, it is clear that the spectroscopic and structural information on chiral molecules containing 1,1′-bi-2-naphthol groups is quite limited. The latest developments in chiroptical spectroscopic methods[14] can be used to fill some of these gaps. These developments include theoretical formalism[21] and its subsequent implementation in the quantum chemical programs[22] within the density functional framework for VCD. Additionally, following the first quantum chemical prediction of optical rotation,[23] remarkable advances have taken place in the prediction of ORD using density functional and coupled cluster theories.[24] The experimental measurement of gas phase optical rotations[25] is another significant development in this period. Around the same time, density functional and coupled cluster theoretical methods for ECD predictions[24a,26] have also been developed.

In this manuscript we report structural investigations on one of the chiral 1,1′-bi-2-naphthol compounds, namely, 6,6′-dibromo-1,1′-bi-2-naphthol, using VCD, ECD and ORD spectroscopies. The absolute configuration of this compound was previously determined[10] as (−)-(a*R*). Although this conclusion is clearly supported by the present investigation, the emphasis in this article is placed on conformational sensitivity of chiroptical spectroscopic methods and identification of predominant conformation of 6,6′-dibromo-1,1′-bi-2-naphthol.

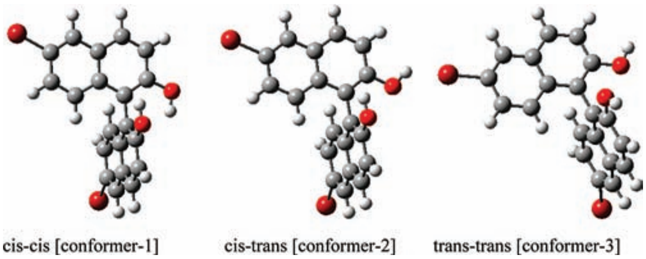

Figure 1. Three conformers of (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol: (a) cis−cis (conformer 1); (b) cis−trans (conformer 2) and trans−trans (conformer 3).

Calculations

All calculations were undertaken with a Gaussian program[22a] using the B3LYP functional and 6-31G*, 6-311G(2d,2p) and 6-311++G(2d,2p) basis sets. The influence of CH_2Cl_2 solvent on predicted vibrational spectra was investigated using the PCM model implemented in the Gaussian program. For 1,1′-bi-2-naphthol molecules with axial chirality, the absolute configuration is assigned[27] on the basis of the priorities for two pairs of ortho carbons using Cahn and Ingold rules. Starting from the structure with (a*S*)-configuration, three different conformations of hydroxyl groups (Figure 1) were used for geometry optimization. These conformers are labeled as cis−cis (conformer 1), cis−trans (conformer 2), and trans−trans (conformer 3), where cis refers to the H−O bond in cis orientation to the C_2-C_1 bond and trans refers to the H−O bond in trans orientation to the C_2-C_1 bond (C_1-C_1' is the C−C bond connecting the two naphthyl groups; C_2 and C_2' are two ortho carbon atoms to which the two OH groups are attached). The optimized geometries of three conformers, obtained with each of the three basis sets, are used for predicting VCD, ECD, and ORD spectra using the same basis set that was used for geometry optimization. From the calculated vibrational frequencies, all three conformations considered were found to represent the minima on the potential energy surface, as there are no imaginary frequencies. The calculated dipole moments of these conformers vary from 1.4 D (cis−cis conformer) to 3.9 D (cis−trans conformer) to 4.0 D (trans−trans conformer).

Selected structural parameters obtained from the B3LYP/6-311++G(2d,2p) optimized structures are summarized in Table 1. The energies of three conformers at all levels of calculations are summarized in Table 2. The theoretical absorption and VCD spectra were simulated, using predicted frequencies as such without any scaling, with Lorentzian band shapes and 5 cm^{-1} half-width at half-peak height. The theoretical ECD spectra were simulated from the first 30 singlet → singlet electronic transitions using Lorentzian band shapes and 20 nm half-width at half-peak height. The use of 40 electronic transitions did not introduce any significant changes in the simulated EA and ECD spectra at the B3LYP/6-31G* level. The predicted electronic transition wavelengths are used as such without any scaling. The electronic absorption spectra are presented as molar extinction coefficient (in L mol^{-1} cm^{-1}), derived from dimensionless oscillator strength. The peak extinction coefficient of

TABLE 1: Selected Structural Parameters for Three Conformers of 6,6′-Dibromo-1,1′-bi-2-naphthol at the B3LYP/6-311++G(2d,2p) Level

	conformers					
	cis−cis		cis−trans		trans−trans	
parameter	isolated	PCM	isolated	PCM	isolated	PCM
$H-O-C_2-C_1$[a]	0.86	0.84	180	180	180	180
$H-O-C_2'-C_1'$[a]	0.86	0.84	−0.95	−0.93	180	180
$C_2-C_1-C_1'-C_2'$[a]	90	91	88	88	88	89
C_1-C_2[b]	1.49	1.49	1.49	1.49	1.49	1.49
$C-Br$[b]	1.92	1.92	1.92	1.92	1.92	1.92

[a] Dihedral angle (in deg). [b] Bond length (in Å).

TABLE 2: Energies of Three Optimized Conformers of 6,6′-Dibromo-1,1′-bi-2-naphthol Obtained with the B3LYP Functional

		Electronic Energy (au)		Gibbs Energy (au)		Relative Gibbs Energy (kcal/mol)	
basis set	conformer	isolated molecule	PCM model	isolated molecule	PCM model	isolated molecule	PCM model
6-31G*	cis−cis	−6063.23709	−6063.25249	−6063.02369	−6063.41634	0	0
	cis−trans	−6063.23117	did not converge	−6063.01884	did not converge	3.0	
	trans−trans	−6063.22628	−6063.252393	−6063.01537	−6063.04044	5.2	0.8
6-311G(2d,2p)	cis−cis	−6068.37127	−6068.386781	−6068.15905	−6068.17755	0	0
	cis−trans	−6068.36576	−6068.387586	−6068.1547	−6068.17584	2.7	1.1
	trans−trans	−6068.36127	−6068.38705	−6068.15010	−6068.17564	5.6	1.2
6-311++G(2d,2p)	cis−cis	−6068.38455	−6068.40079	−6068.17181	−6068.19068	0	0
	cis−trans	−6068.37957	−6068.401503	−6068.1682	−6068.18986	2.3	0.5
	trans−trans	−6068.37557	−6068.40216	−6068.16408	−6068.19052	4.8	0.1

ith band, ε_i^0, is related to oscillator strength, f_i, as $\varepsilon_i^0 = 7.369 f_i(\lambda_i^2)/(\Delta_i)$ where Δ_i is the half-width at half-height of Lorentzian band. The ORD spectra are obtained by predicting specific rotations at six discrete wavelengths. The VCD and ECD spectra obtained at the B3LYP/6-311++G(2d,2p) level are shown in Figures 2−7, whereas these spectra obtained at B3LYP/6-31G* and B3LYP/6-311G(2d,2p) level are provided as Supporting Information. The ORD spectra predicted with B3LYP functional and all three basis sets are shown in Figure 8.

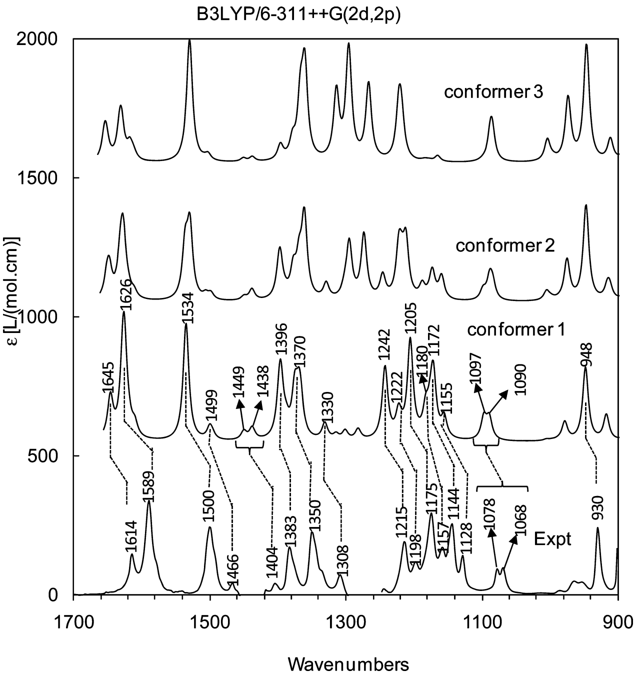

Figure 2. Comparison of the experimental vibrational absorption spectrum in CH_2Cl_2 solvent with B3LYP/6-311++G(2d,2p) predicted vibrational absorption spectra for three conformations of 6,6′-dibromo-1,1′-bi-2-naphthol.

Experimental Measurements

Both enantiomers and racemic mixture of 6,6′-dibromo-1,1′-bi-2-naphthol have been purchased from Aldrich Chemicals and used as received. The enantiomers used for experimental measurements are labeled as $(+)_{589}$- and $(-)_{589}$-enantiomers, where $(+)_{589}$ and $(-)_{589}$ refer respectively to the positive and negative optical rotations at 589 nm in CH_2Cl_2 solvent. The absorption and VCD spectra were recorded on a commercial Fourier transform VCD spectrometer, Chiralir, in the 2000−900 cm^{-1} region. The VCD spectra were recorded with 1 h data collection time at 4 cm^{-1} resolution. Spectra were measured in CH_2Cl_2 solvent at 16 mg/mL (3.6×10^{-2} M) concentration.

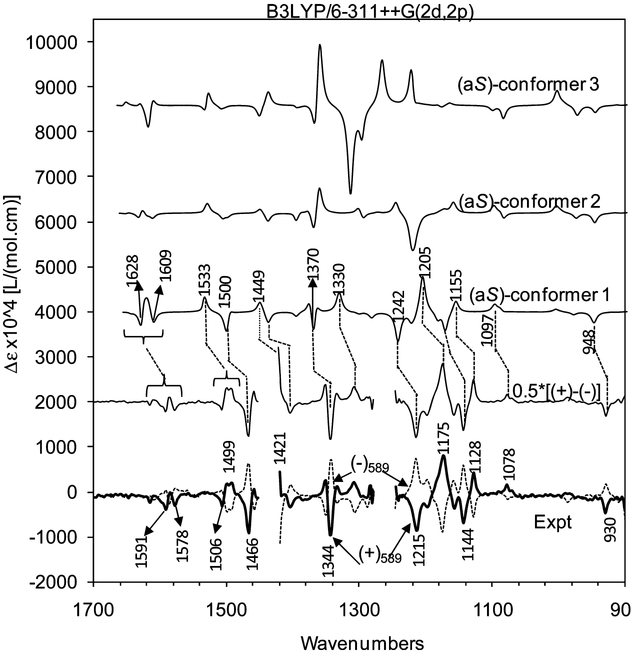

Figure 3. Comparison of the experimental VCD spectrum in CH_2Cl_2 with B3LYP/6-311++G(2d,2p) predicted VCD spectra for three conformations of (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol.

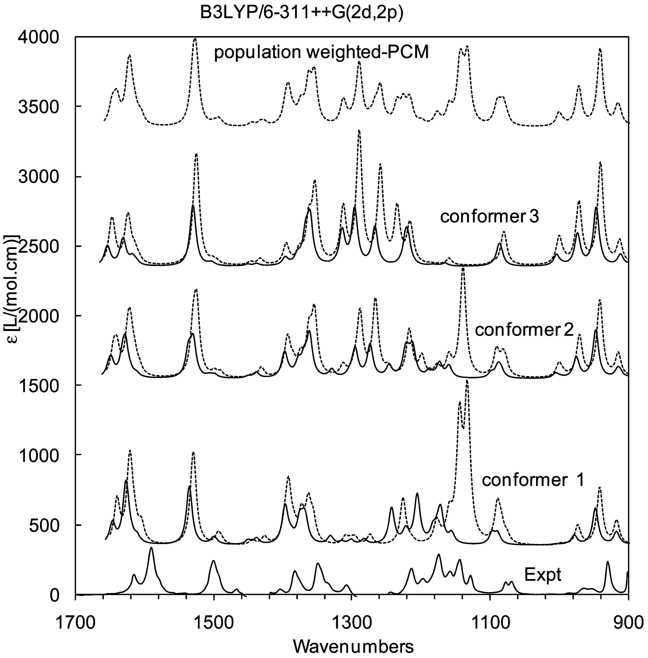

Figure 4. Comparison of the experimental vibrational absorption spectrum (bottom) in CH_2Cl_2 solvent with the absorption spectra obtained using the PCM model (dotted traces) at the B3LYP/6-311++G(2d,2p) level for 6,6′-dibromo-1,1′-bi-2-naphthol. The predicted spectra for isolated conformers (solid traces) at the B3LYP/6-311++G(2d,2p) level are also shown for comparison.

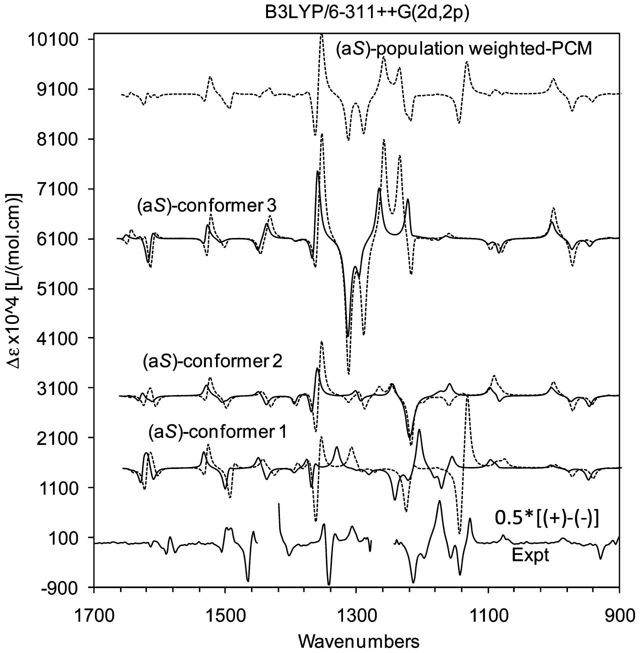

Figure 5. Comparison of the experimental VCD spectrum (bottom) in CH_2Cl_2 solvent with VCD spectra obtained using the PCM model (dotted traces) at the B3LYP/6-311++G(2d,2p) level for (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol. The predicted spectra for isolated cis−cis conformers (solid traces) at B3LYP/6-311++G(2d,2p) level are also shown for comparison.

The sample was held in a variable path length cell with BaF_2 windows. In the absorption spectra presented (Figures 2 and 4), the solvent absorption was subtracted. In presenting the VCD spectra of individual enantiomers (Figure 3), the VCD spectrum of racemic mixture was subtracted. The ~1450−1421 and ~1294−1248 cm^{-1} regions have been removed from the experimental traces due to interference from strong solvent absorption. Because the region blocked from solvent absorption is very small, no attempts were made to measure the spectra in CD_2Cl_2 solvent.

The vibrational absorption spectra were also measured as a function of concentration in CH_2Cl_2 solvent in the concentration range 3.7−16 mg/mL (the use of higher concentrations was not possible due to limited solubility in CH_2Cl_2) to investigate the possible concentration dependence. Neither conformational changes nor aggregation are apparent in these concentration dependent absorption spectra. Due to the presence of intermolecular hydrogen bonding in dimethyl sulfoxide (DMSO) solvent, the VCD spectra obtained in DMSO solution are found to be significantly different from those in CH_2Cl_2 and the analysis of the spectra in DMSO solution is deferred to a future report.

The electronic absorption (EA) and ECD spectra (Figures 6 and 7) were recorded on a JASCO J720 spectrometer, using 0.01 cm path length quartz cell, in both dichloromethane and acetonitrile solvents. However, the absorption of dichloromethane prevented the measurements at wavelengths shorter than 230 nm. EA and ECD spectral profiles in the 350−230 nm region (that is accessible in both solvents) appeared similar in both solvents. Therefore only the spectra measured in acetonitrile solvent, at a concentration of 0.4 mg/mL (~9.3 × 10^{-4} M), are presented here. The optical rotations at six discrete wavelengths (633, 589, 546, 436, 405, and 365 nm) have been measured with a 0.5 dm cell using an Autopol IV polarimeter and displayed (Figure 8) as specific rotation (in deg cm^3 g^{-1} dm^{-1} units). ORD measurements were obtained at a concentration of 1.5 mg/mL (3.38 × 10^{-3} M) in CH_2Cl_2 solvent. Due to the presence of intermolecular hydrogen bonding in DMSO solvent, the signs of experimental optical rotation in DMSO solution are found to be opposite to those in CH_2Cl_2 solution, which will be analyzed in a future report.

Results and Discussion

Structures. The optimized structures of three conformers are shown in Figure 1. Referring to the structural parameters in Table 1, it can be noted that the C_1−C_2 and C−Br bond lengths are essentially the same among different conformers and that they are not influenced by the inclusion of solvent in the calculations with the PCM model. The orientation of OH groups influences the relative orientation of the naphthyl groups only slightly. For an isolated molecule, the two naphthyl groups are at 90° to each other in the cis−cis conformer, but this angle decreases by ~2° for cis−trans and trans−trans conformers. With the inclusion of solvent, using the PCM model, the angle between two naphthyl groups in the cis−cis conformer is 91°, and this angle decreases by ~2−3° for cis−trans and trans−trans conformers. A reviewer suggested the possibility of energy minima for the dihedral angles of 69° and 103° between two naphthyl groups. However, single point energy calculations at the B3LYP/6-311++G(2d,2p) level, as a function of the dihedral angle between naphthyl groups indicated significant energy increase on either side of the energy minimum at an ~90° dihedral angle.

Energies of Conformers. Referring to the energies in Table 2, the cis−cis conformer (where H−O groups connected to C_2 and C_2' carbons are respectively in cis orientation to C_2−C_1 and C_2'-C_1' bonds; C_1−C_1' is the bond connecting the two naphthyl groups) is seen to be the most energetically favored conformation for an isolated molecule. The cis−trans conformer is higher in energy by about 2−3 kcal/mol, and the trans−trans

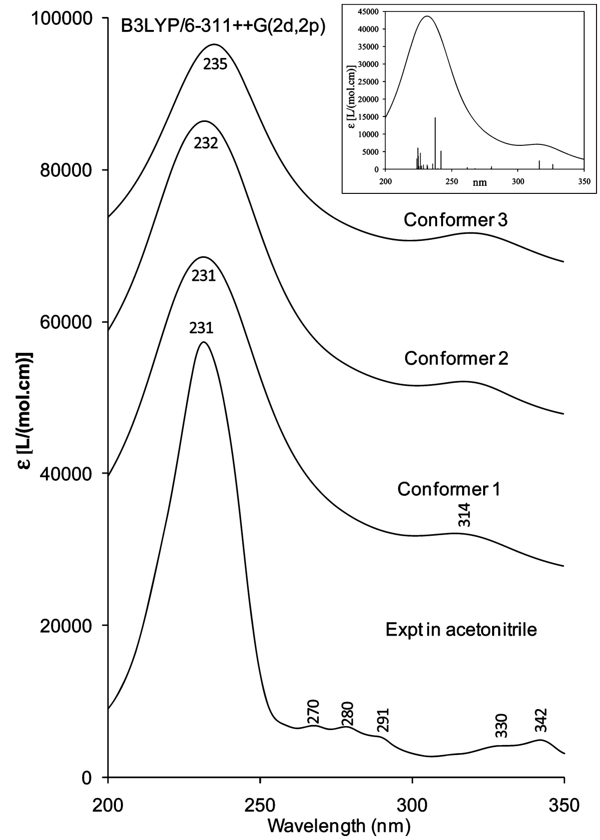

Figure 6. Comparison of the experimental electronic absorption spectrum in acetonitrile solvent with B3LYP/6-311++G(2d,2p) predicted electronic absorption spectra for three conformations of 6,6′-dibromo-1,1′-bi-2-naphthol. The inset depicts stick-line traces for individual transition intensities in the predicted spectrum for conformer 1.

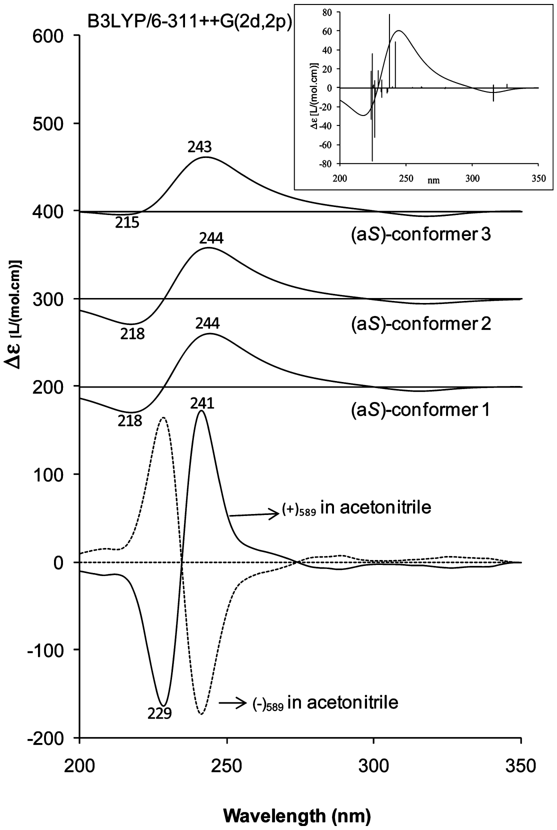

Figure 7. Comparison of experimental ECD spectra in acetonitrile solvent with B3LYP/6-311++G(2d,2p) predicted ECD spectra for three conformations of (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol. The inset depicts stick-line traces for individual transition intensities in the predicted spectrum for conformer 1.

conformer is higher in energy by about 5 kcal/mol. The energy difference between these conformers is greater than the thermal energy at room temperature, so it would appear that only the cis−cis conformer is dominant for an isolated molecule at room temperature. However, for experimental measurements in solution, the solute−solvent interactions can influence the relative populations of conformers. To assess the solvent influence, the PCM model implemented in the Gaussian program has been used and the Gibbs energies of optimized conformers obtained with this model are also included in Table 1. Although the cis−cis conformer still has the lowest Gibbs energy, the energy difference between three conformers has been lowered significantly and these energy differences change with the basis set. At the highest B3LYP/6-311++G(2d,2p) level used in the present calculations, the Gibbs energy difference for the conformers in CH_2Cl_2 solvent, obtained with the PCM model, is comparable to or lower than the thermal energy at room temperature; as a result, the B3LYP/6-311++G(2d,2p) predicted populations of conformers 1−3, in CH_2Cl_2 solvent, are 44%, 19%, and 37%, respectively. Then it would appear that all three conformations would be favored in CH_2Cl_2 solution with significant populations—a conclusion that is quite different from that for isolated molecule.

Conformational Sensitivity of Vibrational Absorption and VCD Spectra. The experimental vibrational absorption spectrum in the 1700−900 cm^{-1} region is compared in Figure 2 to the corresponding predicted spectrum at the B3LYP/6-311++G(2d,2p) level. This mid-infrared region is dense with numerous vibrational bands, as would be expected for similar molecules. These absorption bands exhibit one-to-one visual correspondence (Figure 2) between experimental absorption spectrum and that predicted for the cis−cis conformer of 6,6′-dibromo-1,1′-bi-2-naphthol. Although there are differences in relative intensities among some of the experimental and predicted absorption bands, the overall correlation between experimental absorption spectral features and those predicted for isolated cis−cis conformer is remarkably good. On the other hand, the correlation between the experimental absorption spectrum and those predicted for the cis−trans or trans−trans conformers is not satisfactory. The qualitatively satisfactory agreement seen between the experimental vibrational absorption spectrum and that predicted for the cis−cis conformer, and lack of such agreement with predicted spectra for the other two conformers, can be used to suggest two points: (a) the vibrational absorption spectra are very sensitive to the conformation of O−H groups, and (b) the cis−cis conformation used for the calculations is probably close to that adopted by 6,6′-dibromo-1,1′-bi-2-naphthol in CH_2Cl_2 solvent. The same conclusion can be reached from the vibrational spectra predicted at B3LYP/6-311G(2d,2p) and B3LY/6-31G* levels of theory (see Supporting Information).

The assignment of absolute configuration depends on the satisfactory comparison between experimental and calculated VCD band signs and relative intensities. The predicted VCD spectra for three conformers of isolated (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol are compared to the experimental VCD spectrum of both enantiomers of 6,6′-dibromo-1,1′-bi-2-naphthol in Figure 3. Note that the calculated spectra for the conformers of (a*R*)-6,6′-dibromo-1,1′-bi-2-naphthol would be mirror images of those

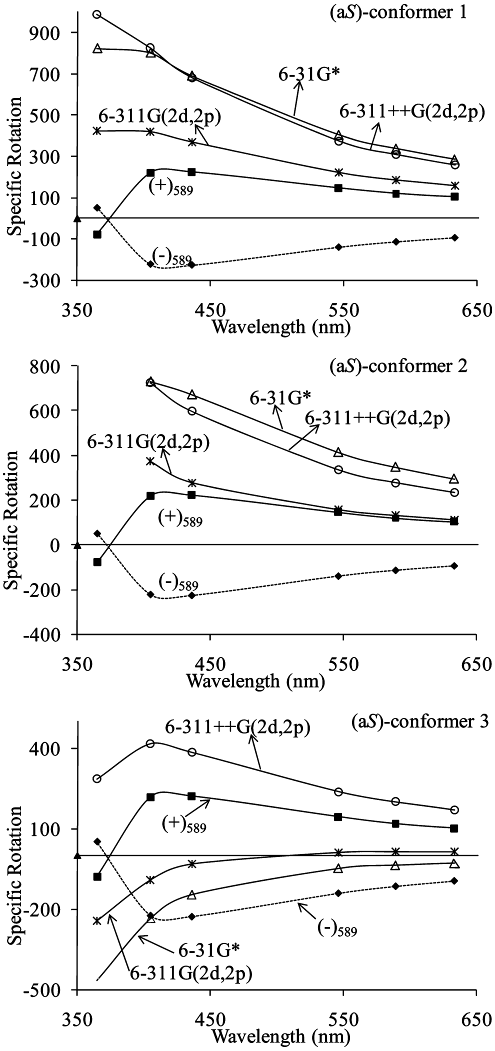

Figure 8. Comparison of experimental ORD spectra in CH_2Cl_2 solvent with predicted ORD spectra for three conformations of (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol. For conformer 2, the predicted specific rotations at 365 nm are not displayed as they are too large (−1375, +4512, and +2564 with 6-31G*, 6-311G(2d,2p), and 6-311++G(2d,2p) basis sets, respectively) and are off-scale. These large magnitudes could have resulted from the wavelength being too close to a transition at ~331 nm.

shown in Figure 3. Several VCD bands with one-to-one sign correspondence, and a good correlation of relative intensities, between the experimental VCD spectrum of $(+)_{589}$-6,6′-dibromo-1,1′-bi-2-naphthol and that predicted for cis−cis conformer of (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol can be seen in Figure 3. There is no such satisfactory correlation with the spectra predicted for the other two conformers. This observation leads to an unambiguous assignment that the (a*S*)-configuration corresponds to the $(+)_{589}$-enantiomer of 6,6′-dibromo-1,1′-bi-2-naphthol and that the conformation adopted by 6,6′-dibromo-1,1′-bi-2-naphthol in CH_2Cl_2 solvent is probably close to that of the cis−cis conformer. The satisfactory agreement seen between the experimental VCD spectrum of the $(+)_{589}$-enantiomer and that predicted for the cis−cis conformer with the (a*S*)-configuration, and lack of such agreement with the predicted spectra for other two conformers, can be used to suggest that: (a) VCD spectra are also very sensitive to the conformation of O−H groups (in addition to the absolute configuration), and (b) the cis−cis conformation, whose predicted VCD spectrum matched the experimental VCD spectrum, is probably close to that adopted by 6,6′-dibromo-1,1′-bi-2-naphthol in CH_2Cl_2 solvent. The same conclusion can be reached from the VCD spectra predicted at B3LYP/6-311G(2d,2p) and B3LY/6-31G* levels of theory (see Supporting Information). This conclusion is consistent with chemical intuition that the cis−cis conformer with intramolecular hydrogen bonding is likely to be favored in non-hydrogen bonding solvents.

However, this conclusion, that the cis−cis conformer of isolated 6,6′-dibromo-1,1′-bi-2-naphthol is close to that adopted by this molecule in CH_2Cl_2 solvent, is contradicted by the populations predicted with the PCM model, where all three conformations are predicted to have significant populations. To explore this further, the vibrational absorption and VCD spectra are also obtained with the PCM model and compared, along with the corresponding isolated molecule spectra, to the experimental spectra. The results obtained with all three basis sets are similar, so we will restrict the comments to those obtained with the PCM model at the B3LYP/6-311++G(2d,2p) level (Figures 4 and 5). (a). For the cis−cis conformer, some of the absorption bands in the 1150−1260 cm^{-1} range are shifted down in frequency and gained significant intensity. Accordingly, the PCM predicted VCD bands in this region have enhanced intensities. The absorption and VCD spectral predictions obtained with the PCM model, unlike those for an isolated molecule, do not match well with the experimental observations. In particular, two absorption bands with significant intensity at ~1140 cm^{-1} in the PCM model predicted spectra have no corresponding bands in the experimental spectrum; also, the positive VCD band predicted for the isolated molecule at 1205 cm^{-1}, which correlates well with the observed band at 1175 cm^{-1}, disappears in the spectrum predicted with the PCM model. (b) For the cis−trans conformer, one absorption band at ~1140 cm^{-1} has gained significant intensity in the PCM calculation. Overall intensities in the PCM predicted absorption spectra are higher than those predicted for the isolated molecule. In the 1100−1200 cm^{-1} region, the experimental absorption spectral patterns do not match either isolated or PCM model predictions for the cis−trans conformer. Neither the VCD spectrum predicted with the PCM model nor that predicted for the isolated cis−trans conformer matches the experimental VCD spectrum. (c) For the trans−trans conformer also, overall intensities in the PCM predicted absorption spectrum are higher than those in the spectrum predicted for the isolated molecule. The experimental absorption spectral patterns in the 1400−1100 cm^{-1} region do not match either isolated or PCM model predictions for the trans−trans conformer. As in the absorption spectrum, there is an overall VCD intensity enhancement in the VCD spectrum obtained with the PCM model. The experimental VCD bands seen in the 1100−1220 cm^{-1} region do not have correlating VCD bands for the trans−trans conformer in either the VCD spectrum predicted with the PCM model or that predicted for the isolated molecule.

In summary, a good correlation is seen between the experimental vibrational spectra and those predicted for the isolated cis−cis conformer, but this correlation is lost when the PCM model is used to predict the vibrational spectra. The correlation between the experimental vibrational spectra and those predicted for isolated cis−trans and trans−trans conformers is not satisfactory and this situation remains when the PCM model is used to predict the vibrational spectra.

Owing to the poor agreement between experimental and PCM predicted spectra for individual conformers, the population weighted spectra obtained with the PCM model are also compared to the experimental spectra in Figures 4 and 5. The overall correlation between the PCM predicted population weighted vibrational absorption (or VCD) spectrum and the experimental absorption (or VCD) spectrum is rather poor. The inability of the PCM model in correctly representing the influence of halogenated solvents has been noted before[28,29] in the context of specific rotations. However, we are not aware of prior studies reporting the inability of PCM model in correctly representing the influence of halogenated solvents on the vibrational spectra.

Because of the poor agreement between PCM predicted vibrational spectra and the corresponding experimental spectra, it is believed that the PCM model is not appropriate for modeling the CH_2Cl_2 solvent influence on the vibrational absorption and VCD spectra of 6,6′-dibromo-1,1′-bi-2-naphthol. Because the predicted vibrational spectra for the isolated cis−cis conformer resemble the experimental vibrational spectra quite well, it may be assumed that the chiroptical properties of binaphthol molecules in the presence of CH_2Cl_2 solvent are similar to those of isolated molecules (but PCM model fails to give this conclusion). Then one can calculate the chiroptical properties for individual conformers of isolated binaphthol molecule and compare them with corresponding experimental properties in CH_2Cl_2 solvent. The conformer which matches the experimental data most closely may be considered to be the dominant conformer in the presence of CH_2Cl_2 solvent as well.

Conformational Sensitivity of Electronic Absorption and ECD Spectra. The experimental electronic absorption spectrum (Figure 6) exhibits one set of two resolved components at ~342 and 330 nm of relatively weak intensity; another set of three resolved components at ~291, 280, and 270 nm; and strong absorption intensity at 231 nm. A weak band at 314 nm in the predicted spectra may correspond to the first set of resolved experimental bands at 342 and 330 nm. The predicted bands corresponding to the set of three resolved experimental bands at ~291, 280, and 270 nm are not resolved in the simulated spectra. The strong absorption band at 231 nm in the predicted spectra appears to correspond to the strong experimental absorption band at 231 nm. Nevertheless, an important point to note here is that the predicted electronic absorption spectra for all three conformers are identical to each other. Unlike in the predicted vibrational absorption spectra (Figure 3), no conformational discrimination is apparent in the predicted electronic absorption spectra. The same conclusion can be reached from the electronic absorption spectra predicted at B3LYP/6-311G(2d,2p) and B3LYP/6-31G* levels of theory (see Supporting Information).

The predicted ECD spectra (Figure 7) at the B3LYP/6-311++G(2d,2p) level for all three conformers of (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol contain a positive couplet (positive CD at ~244 and negative ECD at ~218 nm), which matches the positive ECD couplet seen in the experimental spectrum (positive at 241 and negative at 229 nm). Thus, the B3LYP/6-311++G(2d,2p) predicted ECD spectra may be used to assign the absolute configuration of 6,6′-dibromo-1,1′-bi-2-naphthol as (a*S*)-$(+)_{589}$. The exciton chirality method[4−8] also predicts a positive ECD couplet for (a*S*)-configuration with dihedral angle less than 110°. However, these predicted ECD spectra are not useful for assigning the predominant conformation, because the ECD spectra predicted for all three conformers with (a*S*)-configuration are similar. One noticeable difference is present in the predicted ECD spectrum for conformer 3, where the negative portion of the positive couplet has diminished intensity. However, this difference is not present in the ECD spectra predicted at the B3LYP/6-311G(2d,2p) and B3LY/6-31G* levels of theory (see Supporting Information). Therefore it appears that predicted ECD spectra do not offer much discrimination for the conformations of O−H groups. This observation should not be surprising because ECD spectral signatures considered in 6,6′-dibromo-1,1′-bi-2-naphthol are attributable to the axial chirality between the naphthyl groups and originate from the electronic transitions of two naphthalene chromophores. The conformational freedom associated with secondary groups (hydroxyl in the present case) is not expected to offset these dominant contributions. We have not investigated the solvent influence on ECD predictions with the PCM model.

Conformational Sensitivity of ORD Spectra. The experimental ORD spectra for $(+)_{589}$- and $(-)_{589}$-6,6′-dibromo-1,1′-bi-2-naphthol have been compared in Figure 8 to the predicted ORD, at all three levels of theory, for three conformers of (a*S*)-6,6′-dibromo-1,1′-bi-2-naphthol. In principle, the wavelengths used for ORD predictions should be shifted[30] from those used for experimental ORD measurements because the predicted electronic transition wavelengths normally deviate[31] from those experimentally observed. However, no attempt has been made here to correct for the transition wavelength differences because the ORD spectra can be shifted along the wavelength scale as a whole relative to each other without influencing any conclusions derived here. The experimental ORD data of $(+)_{589}$-6,6′-dibromo-1,1′-bi-2-naphthol shows positive rotation values at 633, 589, 546, 436, and 405 nm (with magnitudes increasing with decreasing wavelength) and negative rotation at 365 nm. For the cis−cis conformer (conformer 1) with (a*S*)-configuration, the predicted specific rotations are positive at all wavelengths, at all three levels of theory, and increase with decreasing wavelength. Unlike in the experimental data, the predicted value at 365 nm for the cis−cis conformer does not become negative. The predicted specific rotations for the cis−trans conformer (conformer 2) with the (a*S*)-configuration are also positive and increase with decreasing wavelength until 405 nm. At 365 nm, a large negative value is predicted with the 6-31G* basis set and large positive values are predicted with the 6-311G(2d,2p) and 6-311++G(2d,2p) basis sets (see legend to Figure 8). The trend in predicted specific rotations for the trans−trans (conformer 3) with the (a*S*)-configuration varies with the basis set used. For the trans−trans conformer with the (a*S*)-configuration, negative specific rotations (increasing in magnitude with decreasing wavelength) are predicted with the 6-31G* basis set and bisignate specific rotations (small positive values at 633, 589, and 546 nm and negative values at the remaining three wavelengths) are predicted with the 6-311G(2d,2p) basis set. With the 6-311++G(2d,2p) basis set, however, all positive optical rotations (increasing in magnitude with decreasing wavelength until 405 nm and then decreased magnitude at 365 nm) are predicted.

With the exception of predicted specific rotation value at 365 nm, the predicted ORD spectra for both cis−cis and cis−trans conformers with the (a*S*)-configuration can be correlated with that observed for the $(+)_{589}$-enantiomer. The predicted ORD spectra for the trans−trans conformer with the (a*S*)-configuration are clearly wrong at B3LYP/6-31G* and B3LYP/6-311G(2d,2p) levels but can be reconciled at the B3LYP/6-311++G(2d,2p) level where the predicted ORD spectrum correlates with that observed for the $(+)_{589}$-enantiomer (except at 365 nm, where the magnitude decreases but does not become negative). The strong basis set dependence seen in the predictions of ORD for the trans−trans conformer raises the question if the predictions for this conformer are reliable even at the B3LYP/6-311++G(2d,2p) level. In any case, none of the predictions for any of the three conformers satisfactorily reproduces the observed rotation at 365 nm. It appears that the predictions of ORD, even at the B3LYP/6-311++G(2d,2p) level, may not be accurate enough to discern among different conformations of O−H groups in 6,6′-dibromo-1,1′-bi-2-naphthol. To predict ORD correctly, the theoretical predictions must account for the positions, and their spacing, of a large number of high energy electronic transitions correctly. Therefore ORD calculations with basis sets larger than those used here, and a different density functional, may shed additional light on the issues noted here. It appears that, when discrimination among different conformations of O−H groups is needed, ORD spectral prediction may not be the best method of choice.

Finally, the current conclusions should not be viewed as discouraging the use of certain method(s). Different methods have unique sensitivities to different structural issues. It will become possible to identify the merits or limitations of a given method only when multiple methods are applied simultaneously to interrogate a given structural problem. Thus the simultaneous use[15] of more than one chiroptical spectroscopic method for molecular structure determination should be strongly encouraged.

Conclusions

The comparisons of experimental VCD, ECD, and ORD spectra with those predicted for three different conformations of 6,6′-dibromo-1,1′-bi-2-naphthol suggested that its absolute configuration assignment is indeed $(+)_{589}$-(a*S*). The predicted vibrational absorption and VCD spectra revealed significant variations for different conformations of O−H groups in 6,6′-dibromo-1,1′-bi-2-naphthol. As a result, comparison of predicted vibrational absorption and VCD spectra of different conformations of O−H groups with experimental data provided a clear conformational discrimination. The use of PCM model for evaluating the CH_2Cl_2 solvent influence on vibrational properties of 6,6′-dibromo-1,1′-bi-2-naphthol indicated that this model is not appropriate for the stated purpose. The predicted electronic absorption and ECD spectra, do not show significant variations for different conformations of O−H groups in 6,6′-dibromo-1,1′-bi-2-naphthol, leading these methods to provide poor conformational discrimination. The comparison of predicted ORD spectra with experimental ORD spectra did not provide useful distinction among conformations of O−H groups.

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Supporting Information Available: VA, VCD, EA, and ECD spectra predicted at B3LY/6-31G* and B3LYP/6-311G(2d,2p) levels of theory. This information is available free of charge via the Internet at http://pubs.acs.org

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