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Theoretical Study of the Circular Dichroism of (+)-(*S*)-2-Butanol in the Vacuum Ultraviolet

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Abstract: Ab initio configuration interaction calculations on the electronic states of (+)-(*S*)-2-butanol have been carried out with the aim of studying the circular dichroism spectrum of the hydroxyl chromophoric group in the vacuum ultraviolet. The calculations involving more than a million distinct spatial configurations were carried out at a number of molecular geometries and with two basis sets. Good agreement is found with the optical absorption spectrum to 70 000 cm^{-1} and with the circular dichroism spectra of the first two absorption bands. The large negative rotation observed for the third absorption band of (+)-(*S*)-2-butanol is not reproduced, but good agreement is found with the observed spectrum of all bands of a related compound, 1-borneol, leading to the suspicion that the missing feature is due to something other than gas-phase (+)-(*S*)-2-butanol.

I. Introduction

In the early 1970's, advances in experimental techniques extended vapor-phase measurements of circular dichroism (CD) to 1350 Å in the vacuum UV.[1] Since then, CD has become an increasingly useful tool for the molecular structural analysis of optically active molecules. A chromophore transition will be optically active if it is inherently dissymmetric and the molecule as a whole has no plane or center of symmetry. For a molecule of known conformation, the CD spectrum provides information on its electronic properties. Alternatively, a good knowledge of the excited state electronic structure of a chromophore and the way its circular dichroism depends upon geometry can, at least in principle, aid in the determination of the conformation of a complex molecule.

The CD spectra of many molecules containing commonly occurring chromophores have been measured in the vacuum UV in the last decade. Because molecules exhibiting circular dichroism are inherently large, ab initio theoretical methods for examining their excited states were prohibitively expensive or impossible. Recently, however, advances in theoretical techniques have rendered reliable configuration interaction calculations possible for molecules of some size.

Among the compounds widely studied experimentally with CD are alcohols; the lowest energy singlet–singlet transition of the hydroxyl chromophore occurs in the now accessible near UV. Here, we present the results of configuration interaction calculations on the electronic states of (+)-(*S*)-2-butanol, an especially simple asymmetric molecule. The basic assumption of the use of chromophoric CD for the determination of molecular conformation is the transferability of chromophoric behavior from molecule to molecule. If this assumption is justified, our results for (+)-(*S*)-2-butanol, taken as a function of conformation, should be transferable to other alcohols. We show that this is so for 1-borneol.

In the next section, we discuss experimental CD studies of (+)-(*S*)-2-butanol and other alcohols, the available UV spectra of simple alcohols, and relevant theoretical studies. In section III, we present the details and results of our calculational method. In section IV, we compare our results with the available experimental and theoretical data. In section V, we briefly summarize our findings.

II. Previous Experimental and Theoretical Studies

For convenience, we divide this discussion into three sections: first, we review the relevant CD experiments; second, we discuss the experimental UV spectra for simple alcohols; third, we present the results of pertinent theoretical investigations.

CD Experiments. There have been a number of vacuum UV CD studies of molecules containing hydroxyl groups in recent years in both the aqueous[2-4] and vapor phases.[4,5] The CD spectrum of (+)-(*S*)-2-butanol, as presented in ref 5, is shown in Figure 1. It contains three main features between 50 000 and 70 000 cm^{-1}. The first is a very small broad, positive CD band extending from about 50 000 to 59 000 cm^{-1}, and centered at approximately 55 000 cm^{-1}. Its rotational strength is reported to be 1.7×10^{-6} e^2 Å^2.[5] The second band is also positive, but larger; its range is from about 59 000 to 64 000 cm^{-1}, and its maximum occurs at approximately 62 000 cm^{-1}. The reported rotational strength for this band is 5.2×10^{-6} e^2 Å^2.[5] The third CD band is larger yet, negative, and centered around 67 000 cm^{-1}. It extends from about 64 000 to 69 000 cm^{-1}. Its rotational strength is not reported. At higher energy (>69 000 cm^{-1}), there is increasingly positive CD absorption.

Reference 4 presents a spectrum of the first CD band of 2-butanol in both water and 1,1,1,3,3,3-hexafluoro-2-propanol. The vapor phase and solution phase (in 1,1,1,3,3,3-hexafluoro-2-propanol) of several CD bands of 1-borneol are presented as well. The low-energy band for 2-butanol is negative in solution,[4] but positive in the vapor phase (see Figure 1).[5] For 1-borneol, in contrast, the low-energy band is negative in the vapor phase and positive in the liquid phase. The second and third CD bands of 1-borneol appear to be negative in both the vapor phase and solution CD spectra.

The first negative band in the vapor-phase spectrum of 1-borneol extends from about 50 000 to 55 000 cm^{-1} and is centered around 52 000 cm^{-1}.[4] Its rotational strength is reported to be -8.6×10^{-6} e^2 Å^2. The second negative band falls between 55 000 and 62 000 cm^{-1} and its maximum lies at about 59 000 cm^{-1}. The experimental rotational strength is -2.7×10^{-6} e^2 Å^2. The third band, also rotationally negative, falls between 62 000 and 67 000 cm^{-1} and is centered around 63 000 cm^{-1}.

UV Spectra. The electronic spectra of various simple alcohols have been experimentally determined in a number of laboratories. In 1971, Salahub and Sandorfy reported the vacuum UV spectra of methanol, ethanol, *n*-propanol, and 2-propanol.[6] In a later work, Robin and Kuebler reported vacuum UV results for methanol.[7] The UV spectrum of (+)-(*S*)-2-butanol was presented by Snyder and Johnson in 1973.[5]

The latter spectrum, that of (+)-(*S*)-2-butanol, is also shown in Figure 1.[5] It exhibits three dominant features. The first is a broad, diffuse transition in the 50 000–59 000-cm^{-1} region, with a maximum at about 56 000 cm^{-1}. The second is a stronger, sharp band centered at approximately 64 000 cm^{-1}, extending over the 59 000–67μtc000-cm^{-1} frequency range. The third feature is an extremely strong, sharp band indicating increasingly significant absorption above 67 000 cm^{-1}.

The spectra of methanol,[6,7] ethanol,[6] n-propanol,[6] and 2-propanol[6] all contain similar features. The weak, broad transition centered at about 55 000 cm^{-1} is followed by a stronger band between 60 000 and 70 000 cm^{-1}. Above 70 000 cm^{-1}, increasing absorption is observed.

In analogy to the band assignments in methanol, Snyder and Johnson[5] attribute the first transition at 55 000 cm^{-1} in 2-butanol to the $n \rightarrow \sigma_{OH}$ transition. The low-energy part of the second UV band at about 64 000 cm^{-1} is assigned to the $n \rightarrow \sigma_{CO}$ transition; the high-energy portion of the

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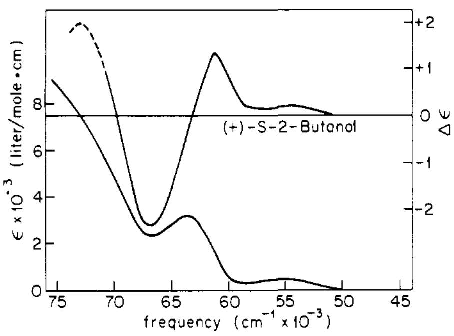

Figure 1. The absorption and circular dichroism spectra of (+)-(S)-2-butanol in the vapor phase (after ref 5).

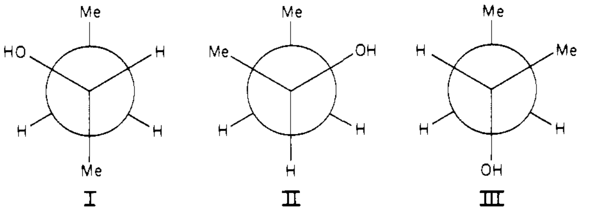

Figure 2. Conformation of the carbon backbone of 2-butanol.

band is attributed to the n → $3s_0$ transition.

Theoretical Calculations. Salahub and Sandorfy performed INDO calculations on methanol, ethanol, n-propanol, and 2-propanol and a RCNDO calculation, including Rydberg orbitals, on methanol.[6] For each molecule, the lowest transition fell in the 53 500–55 100-cm^{-1} range. This band was assigned as an n → σ* transition. The lone-pair MO was judged delocalized to a considerable extent, whereas the σ* MO was identified primarily as a C–H antibonding orbital. Two higher energy transitions at 62 267 and 67 114 cm^{-1} were calculated in methanol and assigned as n → 3s and n → 3p transitions, respectively.

Wadt and Goddard present the results of a Hartree–Fock improved virtual orbital calculation on methanol.[8] The lowest energy singlet transition, a 2a″ → 3sa′, occurs at 6.72 eV; this compares very favorably with the experimental value of 6.7 eV. The calculated oscillator strength of 0.002 also agrees fairly well with the experimental value of 0.005. Three additional transitions, all 2a″ → 3pa′, were calculated at 8.2, 8.6, and 8.63 eV. Two of these, at 8.2 and 8.63 eV, are assigned to the experimental bands at 7.8 and 8.41 eV. The lowest transition is oriented along the OH bond, whereas the second transition is oriented along the CO axis and is antibonding along the CO bond. These descriptions agree with the transition assignments of ref 5 for 2-butanol. The third calculated transition in methanol[8] is not, however, the n → $3s_0$ transition attributed to the third CD band of 2-butanol in ref 5.

A third theoretical calculation, an independent systems theory treatment[9,10] of CD in (+)-(S)-2-butanol, was performed by Snyder and Johnson.[5] This group attains good agreement with the experimental CD spectrum for the lowest two bands, assuming contributions from various conformations of the carbon backbone and hydrogen rotation angle. The calculation, however, does not explain the third experimental feature, the strong negative CD band at about 67 000 cm^{-1}. Indeed, the authors allow that the theoretical calculation explains the observed experimental results only if the third negative CD band is terminated at 66 000 cm^{-1} while it is apparent from Figure 1 that this band, in fact, extends as far as about 70 000 cm^{-1}.

The independent systems theory is a semiempirical method which requires that one assume which excited states are involved in the CD spectrum. Snyder and Johnson limited their consideration to the excited states of the chromophore group OH and concluded that the remainder of this band is due to unknown σ → σ* transitions of the hydrocarbon backbone. Such transitions are, of course, automatically included in a large-scale CI calculation (see below).

Snyder and Johnson also applied the independent system theory approach to the calculation of the rotational strength of the transitions in 1-borneol.[4] They concluded that if the lowest two CD transitions are to be negative as observed experimentally, the hydroxyl rotation angle must be either between 30° and 100° or at about 290°. On the basis of a space-filling model, Snyder and Johnson conclude that the most favorable hydroxyl position is 60° in the vapor phase.

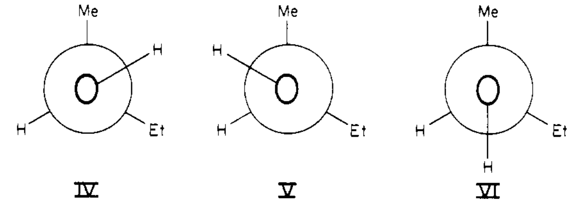

Figure 3. Staggered hydroxylic hydrogen conformations of 2-butanol.

Table I. SCF Characteristics

basis set A E_{SCF} = −231.5566 au		basis set B E_{SCF} = −231.5594 au	
MO no.	eigenvalue, au	MO no.	eigenvalue, au
14	−0.4523	14	−0.4544
15	−0.4221	15	−0.4243
16	−0.4039	16	−0.4058
17	0.0176	17	0.0104
18	0.0231	18	0.0219
19	0.0237	19	0.0231
20	0.0246	20	0.0239
21	0.0823	21	0.0450
22	0.1006	22	0.0545
23	0.1038	23	0.0554
24	0.1292	24	0.0559
25	0.2919	25	0.0565
		26	0.0598
		27	0.0858
		28	0.1024
		29	0.1124
		30	0.1528
		31	0.3113

III. Details and Results of the Calculations

Figure 2 illustrates the three possible conformations of the carbon backbone of 2-butanol. Conformation I was verified to be of lowest energy through Hartree–Fock STO-3G calculations using the GAUSSIAN 80 program. This conformation was used in all calculations subsequently described here.

The molecule was assumed to be of C_1 symmetry with R_{CC} = 1.54 Å, R_{CH} = 1.09 Å, R_{CO} = 1.43 Å, R_{OH} = 0.97 Å, ∠HCH = 109.5°, and ∠COH = 105.9°. Terminal methyl groups were staggered relative to the adjacent bonds, and three separate conformations of the hydroxyl hydrogen were considered; these are displayed in Figure 3. As we discuss in more detail later, of the three, conformation IV was determined through the CI calculations to be of lowest energy.

The atomic orbital basis set employed was Dunnings (9s 5p/3s 2p) contraction centered on three of the carbons and the oxygen and the (5s/1s) contraction centered on each hydrogen.[11,12] Since the molecule is large, we investigated the possibility of using an STO-3G basis for some of the backbone carbon atoms without serious degradation of the computed results. We concluded that the only carbon that could be described with the STO-3G was that farthest from the hydroxyl group, and the results reported use this contraction. In the first calculation, n = 3 and 4 (s and p) Cartesian Gaussians with $\delta_{3s,3p}$ = 0.02 and $\delta_{4s,4p}$ = 0.01 were added to the oxygen atom (basis set A). In the second calculation, an n = 3 d Cartesian Gaussian with δ_d = 0.015 was also added to the oxygen atom (basis set B).

For basis set A, there are 59 molecular orbitals generated; for basis set B, including the d atomic orbitals, there are 65. In both cases, the 1s carbon and oxygen molecular orbitals were frozen, leaving 54 and 60 molecular orbitals for transformation in basis sets A and B, respectively. Table I provides the SCF energy and lists a few relevant molecular orbitals together with their energies for the two basis sets.

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Table II. Basis Set A CI Results for Hydrogen Conformation IV

state	$E - E_{gs}$,[a] eV	oscillator strength	rotational strength, e^2 Å^2 × 10^6
16→17	7.10	0.005	1.3
16→18	7.68	0.005	6.9
16→19	7.85	0.021	−4.3
16→20	7.95	0.001	0.3
15→17	8.08	0.029	2.2
16→21	8.31	0.005	9.8
14→17	8.60	0.016	32.2
16→22	8.70	0.014	−2.1
15→18	8.75	0.017	−27.4
16→23	8.80	0.004	−12.8
15→19	8.91	0.004	4.6
16→24	8.98	0.002	4.1

[a] E_{gs} = −6312.80 eV.

Table III. Basis Set A CI Results for Hydrogen Conformation V

state	$E - E_{gs}$, eV	oscillator strength	rotational strength, e^2 Å^2 × 10^6
16→17	6.69	0.001	−3.4
16→18	7.45	0.029	−9.2
16→19	7.59	0.027	4.8
16→20	7.69	0.006	5.4
15→17	7.76	0.014	−1.0
16→21	8.09	0.002	−0.8
15→20	8.24	0.008	−5.5
14→17	8.39	0.007	8.4
15→18	8.47	0.011	1.4
15→19	8.62	0.004	−3.7
16→22	8.68	0.006	0.5
16→23	8.77	0.006	1.6

Table IV. Basis Set A CI Results for Hydrogen Conformation VI

state	$E - E_{gs}$, eV	oscillator strength	rotational strength, e^2 Å^2 × 10^6
16→17	6.65	0.009	11.8
16→18	7.19	0.016	2.4
16→19	7.30	0.017	−12.8
16→20	7.48	0.006	4.3
15→17	7.75	0.007	−0.5
16→21	8.00	0.010	15.9
15→18	8.28	0.025	−1.0
16→22	8.35	0.019	−23.8
16→23	~8.45[a]		
16→24	8.54	0.045	−0.7
15→19	8.59	0.007	0.9
15→20	8.74	0.002	0.2

[a] Estimated.

Table V. Basis Set B CI Results for Hydrogen Conformation IV

state	$E - E_{gs}$,[a] eV	oscillator strength	rotational strength, e^2 Å^2 × 10^6
16→17	7.24	0.004	3.0
16→18	7.72	0.008	5.3
16→19	7.91	0.024	−5.6
16→20	8.04	0.007	2.0
16→21	8.38	0.001	1.9
15→17	8.46	0.017	1.0
16→25	8.46	0.012	0.9
16→22	8.50	0.002	3.4
16→23	8.52	0.002	0.6
16→26	8.54	0.006	−7.0
16→24	8.69	0.001	−2.2
16→17	8.80	0.005	1.4
15→18	8.85	0.023	−15.8

[a] E_{gs} = −6312.89 eV.

The CI method, which is described in more detail elsewhere,[13] utilizes second-order Brillouin-Wigner perturbation theory within a large multireference configuration space, with a variational core space of 128 configurations. We estimate that numerical errors in the CI procedure for calculations of this size may amount to 1500 cm^{-1} in energy.

All CI calculations were performed in a similar manner. The results of initial CI calculations were used to identify significant contributors to each eigenvector. For basis set A, the 10 most important configurations formed the reference space; for basis set B, the number was 8. In all CI calculations, all single and double excitations from the reference configurations were generated. In general, additional contributing configurations were chosen to complete the interaction strip size of 46.[13] The full core size, in all cases, was 128 configurations.

For each root, the core vector comprised between 80 and 85% of the final vector. Because the calculations described here are huge (approximately 5 million matrix elements generated), the tail space is very large. The 15 to 20% of the vector contained within the tail appears large; it results, however, from the combined weight of many very small numbers so that one is well within the limits of perturbation theory. Indeed, no vectors important to the state of interest were missing from the core.

Table II–IV present the results of the CI calculations using basis set A, together with the oscillator strength and rotational strength of each transition. The values of Table II represent the lowest-energy hydrogen-rotation conformation (conformation IV in Figure 3). Tables III and IV give values for the other two higher-energy hydrogen-rotation conformations, V and VI in Figure 3. We include the results of the latter two conformations because of the possibility that they contribute to the CD spectrum. In Table V, we present the energy, oscillator strength, and rotational strength of the states generated in basis set B. We performed the CI calculations using basis set B for only the lowest conformation, IV in Figure 3.

It is to be emphasized that the conformation of the carbon backbone and, in particular, the terminal methyl groups is held frozen at the geometry favored for the most stable conformer, IV. This was done in order to limit our study to the effect on the circular dichroism spectrum of hydrogen rotation alone. While one would not expect great changes, relaxation of the geometry to that optimal for conformations V and VI would inextricably tangle this with other effects. While this strategy is useful for the study of circular dichroism, it tends to produce spuriously large bathochromic shifts in the computed excitation energies of conformation V and VI. This is so for two primary reasons: (1) the ground-state energy of an unrelaxed conformer is rather higher than it would be at the equilibrium geometry and (2) the first ionization potential as judged by Koopman's theorem is rather smaller than it should be, i.e., the highest occupied orbital energy is a bit too high in energy. Since excitation is to a Rydberg-like orbital, these two effects combine to produce excitation energies which are somewhat too low. The bathochromic shifts shown in Tables III and IV relative to the excitation energies in Table II should therefore not be taken too seriously. It is to be expected, however, that the oscillator and rotational strengths are correctly represented for these conformations.

The CD rotational strength was calculated as described in an earlier study from this laboratory.[14]

IV. Discussion of Results

The first four unoccupied molecular orbitals of both basis set A and basis set B are primarily the 3s and 3p Rydberg components centered on the oxygen (MOs 17, 18, 19, and 20). In basis set A, the next four molecular orbitals (MOs 21, 22, 23, and 24) are

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largely the second set of s and p Rydbergs, also centered on the oxygen. In basis set B, the six molecular orbitals following the first s, p set (MOs 21, 22, 23, 24, 25, and 26) contain d character. The four final Rydberg molecular orbitals in basis set B have primarily s and p contributions from the second set of Rydberg s, p atomic orbitals centered on oxygen (MOs 27, 28, 29, and 30). MO number 16 is the nonbonding molecular orbital on oxygen.

For convenience, we divide the following discussion into two parts, the first for the results of basis set A and the second for the results of basis set B.

Basis Set A. In the spectra for 2-butanol presented in ref 5 (Figure 1 in this work), Snyder and Johnson assign the first transition in both the UV and CD spectra at 56 000 cm^{-1} as n → σ_{OH}. According to the spectra, this transition has a very small oscillator strength and an experimental rotational strength of 1.7 × 10^{-6} e^2 Å^2. In methanol, the lowest transition, at about 55 000 cm^{-1}[1,6] has an experimental oscillator strength of 0.005.[8]

In Table II, the minimum energy hydrogen conformation for basis set A, the lowest excited state, 16→17, is calculated at 7.1 eV (57 269 cm^{-1}), a number to be compared with the experimental maximum at 56 000 cm^{-1}. The calculated oscillator strength 0.005 is small, in agreement with the UV spectrum; this value agrees exactly with the experimental oscillator strength of 0.005 for the lowest transition of methanol.[8] The calculated rotational strength, 1.3 × 10^{-6} e^2 Å^2, is slightly smaller than the experimental CD value of 1.7 × 10^{-6} e^2 Å^2.[5] The calculated energies of the lowest transition in Tables III and IV (hydrogen conformations V and VI, respectively) fall at 6.69 eV (53 962 cm^{-1}) and 6.65 eV (53 639 cm^{-1}), respectively. These energies are well below the experimental value of 56 000 cm^{-1}. Although the calculated oscillator strengths, 0.001 and 0.009, are in reasonable agreement with experiment, the calculated rotational strengths do not appear reasonable. The rotational strength in Table III, −3.4 × 10^{-6} e^2 Å^2, is of the wrong sign, whereas the rotational strength in Table IV, 11.8 × 10^{-6} e^2 Å^2, is an order of magnitude too large.

The second band in the UV spectrum is centered around 64 000 cm^{-1} and is more strongly absorbing than is the first. Snyder and Johnson state, from the evidence of the CD spectrum, that this band is actually composed of two transitions, falling between 60 000 and 70 000 cm^{-1}.[5] The next two transitions in Table II, 16→18 and 16→19, are calculated at 7.68 eV (61 947 cm^{-1}) and 7.85 eV (63 318 cm^{-1}), respectively. The calculated oscillator strength, 0.005 for 16→18 and 0.021 for 16→19, could together give rise to the stronger UV band. A third transition, 16→20, calculated at 7.95 eV (64 125 cm^{-1}), may also be a contributor although its rotational and oscillator strengths are small. The rotational strengths in Table II for 16→18 and 16→19 are positive and negative respectively, in qualitative agreement with the CD spectrum. The magnitude of the rotational strength of the transition 16→18 (6.9 × 10^{-6} e^2 Å^2) agrees well with the experimental rotational strength of the second CD band (5.2 × 10^{-6} e^2 Å^2). According to Figure 1, the rotational strength of the negative band should be significantly larger than that of the second CD band. Our calculated value for 16→19, 4.3 × 10^{-6} e^2 Å^2, is much smaller.

Snyder and Johnson, in their theoretical treatment, report agreement with the experimental rotational strength of 5.2 × 10^{-6} e^2 Å^2 for the 62 000 cm^{-1} band.[5] Our calculated rotational strength of 6.9 × 10^{-6} e^2 Å^2 for the 16→18 transition also agrees well with experiment. According to Snyder and Johnson, if the experimental rotational strength of the negative bond is allowed to extend to only 66 000 cm^{-1}, its value is −4.4 × 10^{-6} e^2 Å^2.[5] Limiting the extent of this band is the only circumstance under which Snyder and Johnson's theoretical rotational strength obtains reasonable agreement with experiment. Indeed, our calculated rotational strength of −4.3 × 10^{-6} e^2 Å^2 for the third transition, 16→19, also agrees with experiment only if the third CD band is terminated at about 66 000 cm^{-1}. It should be noted that we could include the 16→20 transition as part of this band, but this would change nothing.

Snyder and Johnson considered the effect of contributions to the rotational strengths of the CD bands from a number of different hydrogen-rotation angles.[5] Even allowing for this, they were unable to theoretically account for the negative CD band in 2-butanol at energies higher than 66 000 cm^{-1}. Our inclusion of the results of other hydrogen conformations (Tables III and IV) were equally fruitless. Indeed an inspection of the data presented in Tables II–IV illustrates that no combination of the three different conformations can account for the large, negative CD band. We therefore conclude that the lowest energy conformer, conformation IV in Figure 2, is the preponderant contributor to the CD spectrum since all results from this conformation are in good agreement with all aspects of the experimental data with the exception of the large negative rotation at energies >66 000 cm^{-1}.

Conformation V in Figure 2 for 2-butanol is the equivalent of the 60° rotational conformer of the hydroxyl group in 1-borneol.[4,5] The ~3000-cm^{-1} bathochromic shift for the first three excited states of 1-borneol relative to 2-butanol is the usual result of an increasing complex hydrocarbon moiety. The calculated oscillator strengths of 2-butanol in this conformation are 0.001, 0.029, and 0.027 for 16→17, 16→18, and 16→19. These values are consistent with the gas-phase 1-borneol UV absorption spectrum, which shows weak absorption in the region of 52 000 cm^{-1}, stronger absorption at about 60 000 cm^{-1}, and increasing absorption thereafter.[4]

The reported experimental rotational strengths of the first two CD bands of 1-borneol are −8.6 × 10^{-6} and −27 × 10^{-6} e^2 Å^2, respectively. Although a value is not reported for the third CD transition, it appears from the spectrum to fall in magnitude between the rotational strengths of the first two transitions. The calculated rotational strengths of 2-butanol in conformation V (see Table III) of −3.4 × 10^{-6}, −9.2 × 10^{-6}, and −4.8 × 10^{-6} e^2 Å^2 are smaller than the 1-borneol values. Nevertheless, they do show the correct trend in accord with the fundamental assumption of transferability. For 1-borneol, the rotational strength of the second transition is about three times the first; in 2-butanol, the calculated rotational strength for the second transition is about two and a half times the first. In both cases, the magnitude of the third transition falls between that of the first two.

These results suggest that CI techniques like those employed for this work are capable of predicting the conformation of chromophore-containing molecules from experimental CD spectra. The absolute values of the calculated 2-butanol rotational strength are smaller than the experimental values for 1-borneol; indeed there is no reason to expect quantitative agreement across molecules. However, the calculated values show the correct trend and are therefore remarkably useful for predicting conformation.

Our conclusion that (+)-(*S*)-2-butanol is preponderantly in conformation IV while 1-borneol is preponderantly in conformation V is in agreement with the conclusion of Snyder and Johnson.[4,5]

Basis Set B. Because we could not duplicate the negative feature of the experimental CD spectrum above 66 000 cm^{-1} using basis set A, we hypothesized that a d Rydberg function with an exponent intermediate between the two s, p sets might provide additional negative rotational strength. The CI results for basis set B are shown in Table V. Indeed, adding the d Rydberg function led to six new low-energy transitions, 16→21 through 16→26. Inspection of the values of Table V, however, reveals that only two of these transitions, 16→26 and 16→24, have negative rotational strengths. Neither value is strong enough to account for the large negative CD band. Moreover, the two transitions are calculated at 69 000 and 70 000 cm^{-1} which is somewhat too high in energy.

The values for basis set B in Table V are in general agreement with those of basis set A in Table II. The lowest energy transition, 16→17, falls at 7.24 eV (58 398 cm^{-1}), somewhat higher than experiment. Its calculated oscillator strength of 0.004 and rotational strength of 3.0 × 10^{-6} e^2 Å^2 are in the right range. The next two transitions, 16→18 and 16→19, fall at 7.72 (62 270 cm^{-1}) and 7.91 eV (63 802 cm−^{1}), respectively. Their oscillator and rotational strengths show the same general pattern as the corresponding transitions in Table II.

Our efforts to theoretically duplicate the third negative CD band in the spectrum were not successful, and we conclude that it is caused by something other than (+)-(S)-2-butanol. Snyder and Johnson's attribution of this rotational strength to the hydrocarbon σ–σ^* transitions[5] must be ruled out since all such possible transitions were considered in our calculation.

Although we cannot predict the exact quantitative features of the CD spectrum of 2-butanol, we can make some general qualitative comments on its form. When the data of Table II are used, the first CD band should be very small and positive (16→17). The second CD band would be larger and also positive (16→18). The next three transitions 16→19, 16→20, and 15→17 fall in the same energy range; the CD spectrum should exhibit a small, negative band. The region above about 69 000 cm^{-1} would be dominated by a very large positive band; it would include contributions from the transitions 16→21 and 14→17.

V. Conclusions

We have calculated the singlet Rydberg excited states of 2-butanol in the energy range of 7–9 eV in two basis sets. The CI calculations, which include the generation of more than a million distinct spatial configurations, are probably among the largest ever performed. The energies and oscillator strengths of the lowest states agree well with the experimental UV spectrum. The calculated rotational strengths represent the two lowest bands of the CD spectrum reasonably. The calculations do not entirely reproduce the third, large, negative CD band observed experimentally. They do, in accord with the transferability hypothesis, correctly predict the observed CD spectrum of 1-borneol for all three bands, and it is our belief that these calculations correctly represent the CD spectrum of the first three UV bands of 2-butanol in particular and, in a more qualitative sense, alcohols in general.

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Mechanistic Studies of the Selective Oxygen Oxidation of Sulfides to Sulfoxides Catalyzed by Dihaloruthenium(II) Complexes

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Abstract: The selective and facile molecular oxygen oxidation of dialkyl sulfides to their sulfoxides can be effectively catalyzed by neutral ruthenium(II) complexes of the type *cis*- or *trans*-$RuX_2(Me_2SO)_4$. The results of kinetic studies for two of these catalysts, *cis*-$RuCl_2(Me_2SO)_4$ and *trans*-$RuBr_2(Me_2SO)_4$, show that these catalytic oxidations are first order with respect to total catalyst concentration, less than first order in oxygen concentration, zero order in the sulfide substrate, and approximately first order in alcohol. These and other observations plus ^{18}O-labeling studies support a mechanism involving oxidation of a "Ru(II)" species to give an oxidized metal species, probably "Ru(IV)" and peroxide. The active sulfide oxidant is peroxide, whose concentration is approximated by the steady-state assumption. The reductant of the oxidized metal is the solvent alcohol, thus completing the catalytic cycle.

For several years we have been investigating the possibility of using metal-based catalysts to promote the selective air oxidation of dialkyl sulfides to their sulfoxides. There are only a very few examples of metal-based sulfide oxidation catalysts that utilize O_2 as the oxidant, and these catalysts suffer from poor selectivities and very slow rates.[1] In contrast to the sulfide dioxygen oxidation, a large number of transition-metal complexes are known to function as homogeneous catalysts for the molecular oxygen oxidation of phosphines to phosphine oxides. Using such catalyzed phosphine oxidation reactions as models for the sulfide oxidation, we screened all of the metal complexes known to us to catalyze the oxidation of phosphines to phosphine oxides[2-4] or to form metal–O_2 adducts.[2,5] There was no activity associated with any of these complexes for the oxidation of sulfides. For many of these complexes, such results are perhaps not unexpected since from the work of Halpern et al.[3a] it is known that the dioxygen oxidation of phosphines to phosphine oxides catalyzed with $Pt^{\circ}(PPh_3)_4$ generates peroxide as the active oxidant. These catalysts form inner-sphere peroxide complexes (O_2 adducts); thus for an oxidation to occur the substrate must be able to displace peroxide from the coordination sphere. Phosphines are excellent ligands and are able to displace O_2^{2-}, but sulfides are generally considered to be poorer ligands and are apparently not able to displace peroxide.

For this reason we believed that to achieve effective dioxygen catalysis with substrates that are poor ligands, such as sulfides, it would be essential to use metal complexes that can undergo outer-sphere electron transfer to give free peroxide in solution. We chose to investigate ruthenium(II) complexes as potential catalysts, since there are a number of Ru(II) compounds known to undergo outer-sphere oxidation with molecular oxygen to yield peroxide and Ru(III)[6,7] or Ru(IV).[8] Our choice of ruthenium(II)

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