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An improved model for calculating the optical rotation of simple saccharides

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Abstract

A calculational model for the optical rotation (OR) at the sodium D-line of simple saccharides has been developed that eliminates deficiencies of a previous model. Conformational conclusions based on the earlier model are not affected, as established by a recalculation of the OR φ,ψ-map of methyl 3-*O*-(α-D-mannopyranosyl)-α-D-mannopyranoside. The model relocates the strong long-wavelength σ–σ* circular dichroism (CD) component, which is mainly responsible for the Na_D OR from 160 to below 130 nm, where it is now known to occur. That correction allows future modeling of CD bands of different origins that appear in the 150–190 nm region. In order to demonstrate the utility of the revised model, it was applied to calculating the OR of methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside. The results provide experimental support for conformational conclusions derived from a molecular mechanics study of that molecule.

Keywords: Optical rotation, calculational model; Monosaccharides, optical rotation; Disaccharides, optical rotation; Disaccharides, conformation; Mannopyranosides; Rhamnopyranosides

1. Introduction

The properties of carbohydrates that make them important industrial materials [1] and give them biological significance [2] derive from their conformational behavior, but the detailed conformational analysis of even simple carbohydrates at times requires the use of more than one analytical technique because of difficulties posed by (a) flexibility of the interresidue linkages (there is often more than one stable conformation in solution), and (b) strong interactions with solvent. The first factor can present difficulties for NMR conformational analysis, where the time scale of the experiment requires that conformational heterogeneities be deconvoluted from other dynamic contributions. In the analysis of NMR data, recourse is sometimes made to the use of potential-energy surfaces derived from molecular modeling studies. Strong interactions with water molecules present a particular challenge for molecular modeling methods.

Optical rotation (OR) is often sensitive to molecular conformation [3] and can be used to complement other methods of conformational analysis, but the models required for extracting conformations from chiroptical measurements are not easily developed. Although the origins of molecular chirality have been understood at a fundamental level for many years, practical applications require that the theoretical equations of quantum mechanics be made tractable. Ab initio methods for cal-

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culating molecular chiroptical properties have been growing in scope [4], and it may be possible in the future to treat molecules as large as monosaccharides, but the computational requirements for ab initio calculations increase very rapidly with molecular size, so that applications for calculating the chiroptical properties of even disaccharides may still be far in the future. Semi-empirical approaches can be exploited in the meantime, and Kirkwood's model of interacting group polarizabilities [5], that we use here, remains one of the most fruitfully applied approaches, as exemplified recently in the application of it to systems as complex as proteins [6].

One semi-empirical OR method uses an algorithm (MOLROT), which computes the OR for specified saccharide geometries and compares the calculated values with experimental values [7]. The OR method can be useful in several situations, as when disaccharides have NMR-equivalent sugar residues. For example, the conformation of α,α-trehalose in solution, not readily determined by NMR, can clearly be shown by OR [8] to be the same as the solid-state crystal structure determined by X-ray diffraction. Or, in another application, maltose can be shown by OR [9] to take up a conformation in solution that is distinctly different from the conformation in the solid state, where crystal packing forces move the linkage geometry significantly away from the linkage geometry expected from the exoanomeric effect; OR clearly shows the predominance of the latter conformation in aqueous solution. In many disaccharides studied to date, the OR observed in solution can be accounted for in terms of a small number of putatively predominant linkage conformations, and the method can be applied to regular (helical) structures of simple polysaccharides [10].

We report here an improved model for describing the OR of simple saccharides, so that it can be used for purposes of conformational analysis. Its utility is demonstrated with calculations of the OR of methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside. Such α-(1→3)-linked dirhamnopyranoses are regularly found in outer membrane lipopolysaccharides of gram-negative cells.

2. Calculational methods

Since the original MOLROT model of saccharide OR was introduced, technical flaws in the algorithm have come to light: (1) the long-wavelength molecular circular dichroism (CD) component that dominates polarizability contributions to OR is calculated with MOLROT to occur near 160 nm, whereas CD measurements now place it below 130 nm [11]; (2) an ad hoc scaling parameter is necessary to bring calculated results into agreement with measurements on model compounds and it also corrects for an incorrectly scaled integral transform; (3) the wavelength parameter describing the unperturbed (group) σ–σ* transitions (70 nm) is shorter than the wavelength inferred from the literature [12], and (4) of lesser importance, parameterization of the model did not include consideration of *tg* methoxy conformers in pyranosides having an axial hydroxyl group at C-2, as in methyl α-D-mannopyranoside-$^4C_1$ (see also below). These flaws have not prevented the model's use as a practical interpretive device for OR, but they preclude its use in interpreting saccharide CD in the 150–190 nm region, which is becoming increasingly accessible. Specifically, the original model's inaccurate placement of the strong long-wavelength σ–σ* component near 160 nm interferes with modeling the CD bands of different origin that occur in that region [11].

Parameterization.—The present model, like the previous model, makes use of the 'excited state' matrix representation developed by Schellman and co-workers [13], which conveniently expresses the mechanisms by which CD and OR develop in an optically active molecule, as described earlier with perturbation theory by Tinoco [14]. Also, as in the previous model, the saccharide molecule is partitioned into C–H, C–C, C–O(acetal) and C–O(hydroxyl) groups; O–H groups are implicitly included through the C–O(hydroxyl) parameters by assuming free rotation about the C–O bond. Each group is assigned a set of three mutually perpendicular electronic transition moments (μ) positioned at the bond center; they represent the bond-localized high energy σ–σ* density of excited states. The

transition moment parameters are derived from the magnitudes and anisotropies of bond polarizability ellipsoids (α), through the following equations:

$$\mu^2 = \mu_{\|}^2 + 2\ \mu_{\perp}^2 = (3\ hc/2\ \lambda_0)\alpha \quad (1)$$

$$\mu_{\|}^2/\mu_{\perp}^2 = \alpha_{\|}/\alpha_{\perp}$$

where h is Planck's constant, c is the speed of light and λ_0 is the wavelength of the unperturbed group transitions, taken to be degenerate. $\alpha_{\|}$ and $\alpha_{\perp}$ are the longitudinal and transverse components of the bond polarizability; $\mu_{\|}$ and $\mu_{\perp}$ are the associated electric transition moments.

The group localized transition moments of the molecule, displayed as vectors, are coupled through their electrostatic interactions, which take the form of a matrix, **V**. The V_{ij} matrix elements are calculated in a distributed monopole (q_i) approximation of the moments [15] as $V_{ij} = q_i q_j / r_{ij}$, with the q values determined from:

$$|\mu| = |q|d \quad (2)$$

where d is the separation of the monopoles in each of the pairs, taken here to be 0.2 Å.

Diagonalization of the interaction matrix **V** allows the transformation of the unperturbed group moments into molecular moments, from which rotational strengths are calculated. In the MOLROT algorithm rotational strengths are calculated as

$$R_K = \mathrm{Im}[\pi/\lambda_0(\mathbf{C}_K \cdot \boldsymbol{\mu}_o) \cdot (\mathbf{C}_K \cdot (\mathbf{R} x \boldsymbol{\mu})_o)] = \mathrm{Im}\boldsymbol{\mu}_K \cdot \mathbf{M}_K \quad (3)$$

where $\mathbf{C}_K$ is the Kth column (eigenvector) of the transformation matrix, $\boldsymbol{\mu}_o$ and $(\mathbf{R}x\mu)_o$ are matrices describing the unperturbed group transition moments, and $\boldsymbol{\mu}_K$ and $\mathbf{M}_K$ represent the molecular transition moments.

To allow for future extension of the model to include 150–190 nm CD bands arising from oxygen-centered Rydberg-like transitions, we converted to a representation that Bayley et al. [13b] have shown is required with non-degenerate transitions in order to avoid an origin dependence in calculating rotational strengths. (The original MOLROT algorithm included only one set of degenerate σ–σ* electronic transitions, so the question of origin dependence did not arise.) The net effect in the present case is to replace λ_0 in Eq. (3) with λ_K, the wavelength of the Kth eigenvalue.

The molar rotation $[M]_D$ can be calculated from the R_K either as a Kronig–Kramers transform of a Gaussian CD or as the sum of Drude-like terms based on the rotational strengths. The latter form is essentially a Kronig–Kramers transform of the line (δ function lineshape) spectrum CD [16]. For wavelengths sufficiently removed from the CD, such as that of the D-line of sodium (589 nm), and for the bandwidths we have used the two calculated molar rotations are essentially the same [17]. The $[M]_D$ values are then multiplied by the Lorentz–Lorenz refractive index correction for water, $(n^2+2)/3 = 1.26$ [17].

By introducing a dielectric parameter (ε) into the denominator of the V_{ij} matrix elements, we have found a self-consistent set of parameters which (1) produces the lowest energy molecular σ–σ* component at wavelengths consistent with experimental observations (near 125 nm) [11]; (2) eliminates the need for an empirical 'scale factor' (the dielectric parameter takes its place); (3) places λ_o at a wavelength (80 nm) more consistent with literature estimates [12]; (4) retains the consistency of polarizability parameters (the q_i) with literature values [18]; (5) incorporates a dielectric parameter value ($\varepsilon = 3.65$) similar to values used in some molecular mechanics methods and other types of calculation, and (6) reproduces well the observed OR for the canonical set of model saccharides used in the optimization.

Six methyl pyranosides (the α and β anomers of methyl D-glucopyranoside, methyl D-galactopyranoside, and methyl D-mannopyranoside) were used in the optimization. The parameterization was also constrained to be consistent with the observed OR of the relatively inflexible α,α-trehalose molecule, previously found to be restricted in solution to its X-ray determined structure [8], and with the observed OR of β-maltose, previously analyzed in detail [9]. Coordinates for the $^4C_1$ ring conformations were adapted from Ref. [19].

The exocyclic hydroxymethyl group on each residue was successively fixed at each of the three stable energy minimum conformations (*gg*, *gt* and *tg*) and the OR calculated for each

molecular conformation. The letters *g* and *t* describe O-6 as gauche or trans relative to O-5 (first letter) or relative to C-4 (second letter). Statistical weights for the molecular conformers were kept in the range consistent with NMR measurements [20]: α-D-glucopyranoside (0.60 *gg*, 0.40 *gt*), β-D-glucopyranoside (0.50 *gg*, 0.50 *gt*), α-D-galactopyranoside (0.17 *gg*, 0.65 *gt*, 0.18 *tg*), β-D-galactopyranoside (0.20 *gg*, 0.60 *gt*, 0.20 *tg*), α-D-mannopyranoside (0.30 *gg*, 0.70 *gt*) and β-D-mannopyranoside (0.50 *gg*, 0.50 *gt*). The reported OR values are values averaged over conformers.

For methyl α-D-mannopyranoside, two conformations of the methoxy group were included in the averaged OR, with weightings of 0.80 (*gt*) and 0.20 (*tg*), where *g* and *t* describe the methoxy carbon atom as gauche or trans relative to O-5 (first letter) or relative to C-2 (second letter). As indicated by NMR [21], the axial hydroxyl group at C-2 makes the *tg* conformation less precluded than in cases where the C-2 hydroxyl group is equatorial, but the weighting chosen here is an estimate (see also below).

Table 1
Optimized parameters for σ–σ* contributions ($\varepsilon = 3.65$, $\lambda_o =$ 80 nm)

Bond	α (Å^3)	$\alpha_{\|}/\alpha_{\perp}$	$\pm q_{\|}$ (10^{-10} esu)	$\pm q_{\perp}$ (10^{-10} esu)
CH	0.0348	1.38	3.64	3.10
CC	0.2553	2.64	11.63	7.16
CO(H)	0.7296	2.64	19.67	12.10
CO(C)	0.6159	5.28	20.40	8.88

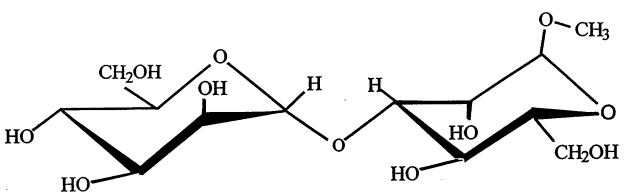

Fig. 1. Methyl 3-*O*-(α-D-mannopyranosyl)-α-D-mannopyranoside (**1**).

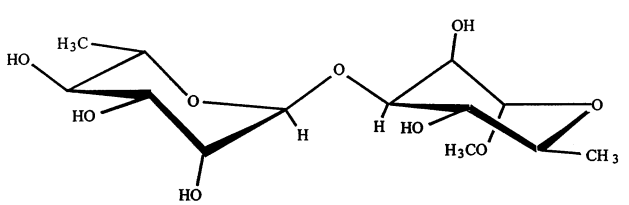

Fig. 2. Methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**2**).

The reparameterization began with the original set of polarizabilities. A grid search was carried out with the dielectric parameter (ε) ranging from unity to 10, and λ_0 from 70 to 100 nm. When the lowest energy molecular σ–σ* component occurred at a wavelength less than 130 nm, polarizability parameters were individually varied until the rms error in the calculated OR was minimized for the set of model compounds. The procedure was repeated varying ε and λ_0. The final parameters (Table 1) satisfy the criteria set as the goal of the parameter search (above); they are not necessarily globally optimized. Additional details of the model development are given in Ref. [22].

The program CARBROT (FORTRAN) is available for downloading at http://www.chem.binghamton.edu/STEVENS/CARBROT.TXT. It calculates the OR of a single fixed geometry from user-generated input files. The OR of one monosaccharide conformer can be calculated with a typically configured PC in a few seconds.

Applications.—To determine the effect of the revised parameters on previously published OR φ,ψ-maps and conformational analyses, the complete OR φ,ψ-map for methyl 3-*O*-(α-D-mannopyranosyl)-α-D-mannopyranoside (**1**) (Fig. 1), reported earlier [10c], was recalculated.

In order to demonstrate the utility of the model, we applied the revised parameters to methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**2**) (Fig. 2). Hardy et al. [23] have reported a molecular mechanics conformational analysis of that compound. They also applied the MOLROT algorithm to their results in an attempt to account for its observed OR. They found that a combination of conformations favored in the molecular mechanics calculations could account for the observed OR, but also found

Table 2
Calculated and observed optical rotations (deg cm^2 dmol^{-1})

Compound	$[M]_D$, calc	$[M]_D$, obs^{25}
Methyl α-D-glucopyranoside	307	309
Methyl β-D-glucopyranoside	−87	−66
Methyl α-D-galactopyranoside	386	380
Methyl β-D-galactopyranoside	−2	0
Methyl α-D-mannopyranoside	153	154
Methyl β-D-mannopyranoside	−134	−136

that ad hoc adjustments to the calculated values of OR were necessary, and suggested a need for further development of the algorithm. Coordinates for the monomer, methyl α-L-rhamnopyranoside, were taken from the crystal structure of Shalaby et al. [24] and modified to give both *gt* and *tg* methoxy conformers (see above); the crystal structure is predominantly *gt*. We used weightings for those conformers that result from Hardy et al.'s molecular mechanics calculations with a dielectric constant of 5; the *gt*:*tg* methoxy ratio in the dominant disaccharide conformer is 31:19 (Ref. [23], Table III).

In specifying disaccharide linkage conformations about C-1–O-1–C-3′, we use dihedral angles φ = O-5–C-1–O-1–C-3′ and ψ = C-1–O-1–C-3′–C-2′. The dihedral angle is 0° in the eclipsed conformation and is positive if, when viewed along the central bond, the front bond has to be rotated in a clockwise sense in order to eclipse the rear bond.

In the rhamnopyranoside disaccharide (**2**), conformers of types A (50°, −40°), B (50°, 30°), and C (−40°, 0°) represent three primary low energy conformations in the calculated potential energy surface of Hardy et al. [23]. To calculate conformer-averaged OR values, we used population distributions calculated from their conformer energies (Ref. [23], Table III). For $\varepsilon = 5$, the fractional populations are 0.339 A(*gt*), 0.208 A(*tg*), 0.211 B(*gt*), 0.060 B(*tg*), 0.148 C(*gt*) and 0.035 C(*tg*). The *gt* conformer energies do not strongly depend on dielectric constant, but the energies of all *tg* conformers increase with decreasing dielectric constant, such that they are significantly less populated at, e.g., a dielectric constant of 1.

3. Results

Methyl pyranosides.—Calculated molar rotations $[M]_D$ are shown in Table 2. The calculated OR is associated almost entirely with CD components at wavelengths shorter than 125 nm. The rms difference between the calculated and experimental [25] values is 10 deg cm^2 dmol^{-1}.

Methyl 3-O-(α-D-mannopyranosyl)-α-D-mannopyranoside (**1**).—The OR φ,ψ-map of **1** calculated with the new parameterization [22] is generally similar to the one calculated previously [10c], and the earlier conclusions remain valid: the presence of large-OR A type conformations requires the presence of small-OR C type conformations to maintain consistency with the observed OR of 333 deg cm^2 dmol^{-1} [26]; i.e., multiple conformers exist in solution and the linkage is flexible.

Moreover, a previously examined molecular dynamics simulation of the disaccharide [27], in which the relative populations of regions A, B, and C were approximately 31, 55, and 14, was found here to be consistent with the observed OR, as was also previously found to be; the weighted average OR calculated for such a trajectory with the current parameters is 355 deg cm^2 dmol^{-1}, not significantly different from the observed OR given the uncertainty of the models.

Methyl 3-O-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**2**).—The calculated OR of the monomer, methyl α-L-rhamnopyranoside, averaged over the *gt* and *tg* methoxy conformations (−213 and 29 deg cm^2 dmol^{-1}, respectively), is −121 deg cm^2 dmol^{-1}, comparable with the observed value [25] of −111 deg cm^2 dmol^{-1}.

The calculated OR values for the A, B, and C disaccharide conformers [22] (in deg cm^2 dmol^{-1}) are −274 (A), −377 (B) and −193 (C). The observed OR for the disaccharide in aqueous solution [23] is −266 deg cm^2 dmol^{-1}, close to what is expected for A conformers. Any significant population of B conformers requires the presence of C conformers to match the observed OR value. Fig. 3 is a linkage conformation distribution map, with the solid line depicting those distributions that would generate the observed OR. The dotted

lines represent the 2σ (± 20 deg cm^2 dmol^{-1}) estimated uncertainty in the model. The population distributions calculated from Hardy et al.'s results [23] for dielectric constants of 1, 3, and 5 are also shown. The molecular mechanics results generate linkage distributions that are consistent with the observed OR.

In all of the calculations the lowest energy CD component responsible for the OR is at wavelengths shorter than 130 nm. Fig. 4 illustrates that result for methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**2**). For presentation purposes, rotational strength components were given Gaussian bandshapes, with bandwidths increasing from 13 nm for the longest wavelength component at λ_0, in increments of 3.5 ($\lambda_i - \lambda_0$), to a maximum of 23 nm. Guidance came partially from the empirical CD deconvolution in Ref. [11].

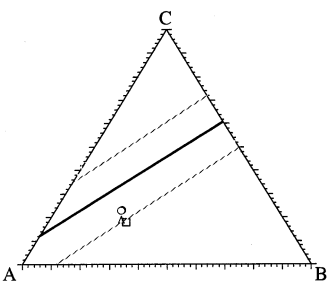

Fig. 3. Linkage populations that reproduce the observed aqueous solution $[M]_D$ for methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**2**) (solid line). The dashed line indicates the uncertainty in the calculational model. Also shown are the A, B, and C population distributions calculated from conformer energies in Ref. [23], at various dielectric constants [○ ($\varepsilon = 1$), △ ($\varepsilon = 3$), □ ($\varepsilon = 5$)].

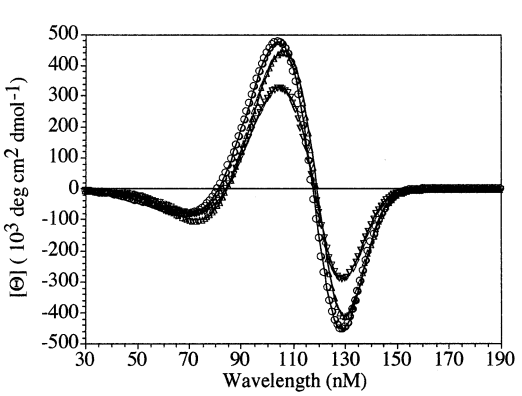

Fig. 4. Calculated CD of methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**2**) for conformers A (Δ), B (○), and C (▽).

4. Discussion

The major improvement in the model is the decrease in the wavelength of the lowest energy σ–σ* component from near 160 nm in the original parameterization to approximately 125 nm (Fig. 4), a value more consistent with experimental data [11]. Relocating the lowest energy σ–σ* component allows future modeling of CD bands arising from oxygen-centered Rydberg-like transitions that are observed in the 150–190 nm region [11]. Assignment of the 150–190 nm CD bands in unsubstituted saccharides to Rydberg-like oxygen-centered transitions has recently received support from ab initio calculations [28]. The second major improvement in the model is that no ad hoc scaling factor is required, a result of the improved approximation of the monopole interaction energy. Also, a more satisfactory, longer wavelength results for the λ_0 parameter.

In spite of the change in the model from a degenerate to non-degenerate formalism, the final polarizability parameters are not markedly different from the original model, and are well within the range of values suggested in the literature [18]. The dielectric screening factor, responsible for much of the model's improvement, has a value of 3.65, typical of values used in some molecular mechanics calculations, but that value represents only an empirical approximation of complex interactions, so that the value found here has no direct bearing on related parameters used in different applications.

The improved parameterization is not expected to change the conclusions resulting from earlier applications of the original parameterization, as indicated by the results reported here for methyl 3-*O*-(α-D-mannopyranosyl)-α-D-mannopyranoside (**1**). The model improvement places the conclusions of previous OR analyses on firmer grounds, and indicates that future analyses may benefit from the more accurate calculation of linkage contributions to disaccharide OR.

To illustrate the significance of the improved model it was applied to methyl 3-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**2**). The calculated OR of the monomer,

methyl α-L-rhamnopyranoside, successfully reproduced the observed rotation. Applied to the disaccharide, the model reproduces the observed OR for equilibrium conformer distributions predicted from the molecular mechanics modeling calculations of Hardy et al. [23]. The corollary support for molecular modeling calculations, via a test for consistency of putative conformation distributions with OR measurements, constitutes one of the useful applications of the present model.

5. Conclusions

A newly parameterized calculational model for the Na_D optical rotation of simple saccharides reproduces experimental results semi-quantitatively for a number of compounds. The improved model corrects the previous model by relocating the strong long-wavelength $\sigma-\sigma^*$ CD component from 160 to below 130 nm, where it is now known to occur [11], thereby allowing a modeling of the CD bands of different origin that are observed in the 150–190 nm region [11,28]. It also provides a firmer theoretical basis for describing the optical rotation of saccharides and can be applied to the conformational analysis of simple saccharides, complementing other methods.

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