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The origin of circular dichroism in unsubstituted carbohydrate polymers

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Abstract

Molecular modeling calculations support assignment of the circular dichroism (CD) of unsubstituted saccharides and polysaccharides to oxygen-centered transitions of the acetal chromophore. The results are in agreement with an empirical CD-based assignment, which treated the acetal chromophore as two weakly coupled ether chromophores. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The circular dichroism (CD) of unsubstituted polysaccharides (Arndt & Stevens, 1994; Arndt & Stevens, 1996a; Balcerski, Pysh, Chen & Yang, 1975; Buffington, Stevens, Morris & Rees, 1980; Stipanovic & Stevens, 1981) and their monomers (Arndt & Stevens, 1996b; Arndt & Stevens, 1997; Listowsky & Englard, 1968; Nelson & Johnson, 1976) lies at wavelengths shorter than 200 nm; CD bands have been observed in the 150–190 nm region. Until recently the origin of that CD has been assigned only in general terms to the acetal chromophore. Arndt and Stevens (1993) proposed a more detailed assignment to specific electronic transitions, based on an analysis of CD observed in monosaccharides. In that picture the acetal chromophore is treated as two weakly coupled ether (C_{2v}) chromophores. Two principal features of the CD spectra were assigned to oxygen centered transitions, $1^1A_1 \rightarrow 2^1B_1$ (i.e. $2pb_1 \rightarrow 3pa_1$) and $1^1A_1 \rightarrow 1^1A_2$ (i.e. $2pb_1 \rightarrow 3pb_2$), with the former having a lower energy than the latter. That ordering is the opposite of the known ordering in the water molecule which has been well studied (Buenker & Peyerimhoff, 1974; Winter, Goddard & Bobrowicz, 1975).

We report here molecular modeling calculations that support the empirical assignments, using dimethyl ether as a prototypic C_{2v} molecule. We find an inversion of the energy ordering of the two states of interest in going from water to dimethyl ether. As we were also interested in characterizing the Rydberg nature of the excited states and relevant magnetic dipole transition moments, we sought approximate wave functions as well as excitation energies, and therefore adopted a configuration interaction (CI) approach.

Our aim has been to provide a basis for developing a calculational model for polysaccharide CD which may prove useful for purposes of conformational analysis.

2. Methods

We used the GAMESS (General Atomic and Molecular Electronic Structure System) program (Schmidt et al., 1993), implemented either on a Silicon Graphics Indigo 2 workstation, or the National Center for Supercomputer Applications (NCSA) Silicon Graphics Power Challenge Array.

Restricted Hartree–Fock (RHF) ground state calculations were carried out first, with a DZV basis set (Dunning & Hay, 1977) augmented with Rydberg and “diffuse” orbitals according to the calculation performed. Rydberg orbitals on oxygen were included in all calculations, with exponents of 0.032 and 0.028 for the 3s and 3p orbitals, respectively. When carbon 3s and 3p orbitals were added, the corresponding exponents were 0.023 and 0.021; an s diffuse function added to hydrogen in one case was given an exponent of 0.036 (Dunning & Hay, 1977). (For hydrogen, the DZV basis set in the GAMESS library uses inner/outer scale factors for the exponents of 1.2 and 1.15, respectively, as opposed to the usual 1.2 scaling throughout.) The core electrons, 1s in oxygen and carbon, were frozen at all times.

The symmetry types and relative energies of the resulting RHF MOs are shown in Table 1. In the RHF ground state, the virtual Rydberg orbitals were clearly distinguished and

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Table 1
CH_3OCH_3 RHF MOs in order of increasing energy; doubly occupied MOs in boldface; MOs predominantly oxygen Rydberg orbitals in parentheses

$1a_1$[a]	**$1b_2$**[a]	**$2a_1$**[a]	**$3a_1$**	**$2b_2$**	**$4a_1$**	**$1b_1$**	**$5a_1$**	**$3b_2$**
$1a_2$	**$4b_2$**	**$6a_1$**	**$2b_1$**	($7a_1$)	($5b_2$)	($3b_1$)	($8a_1$)	$9a_1$
$6b_2$	$10a_1$	$4b_1$	$2a_2$	$7b_2$	$11a_1$	$8b_2$	$3a_2$	$12a_1$
$5b_1$	$9b_2$	$10b_2$	$13a_1$	$14a_1$	$6b_1$	$15a_1$	$11b_2$	$7b_1$
$12b_2$	$16a_1$	$4a_2$	$17a_1$	$13b_2$	$14b_2$	$18a_1$		

[a] Frozen core MOs.

separated from the remaining virtual orbitals by an energy of about 200 millihartrees (mh).

The dimethyl ether RHF MOs were then used in CI calculations, without any further optimization, to generate configuration state functions (CSFs). NVAL, the number of virtual orbitals available to generate CSFs, was set to 18. All singly, doubly and triply excited CSFs were generated. In one calculation, carbon polarization functions were added to the basis set.

For comparison, calculations on the water molecule were also carried out, using the complete set of 12 empty RHF orbitals to generate the CSFs. In one calculation diffuse s orbitals were added to the hydrogen atoms. Calculations on water were also performed to determine the effect of bond angle variation on the ordering of excited states. In this case, complete active space (CAS) calculations were performed with the standard DZV + Rydbergs basis set and NVAL = 10, increasing the bond angle in steps of 1° from 104.5 to 111.7°, the latter being the bond angle in dimethyl ether.

For an additional comparison, calculations on the methanol molecule were also carried out.

Atomic coordinates were obtained from the literature (Aung, Pitzer & Chan, 1968; Blukis, Kasai & Myers, 1963; Yadav, Yadav & Poirier, 1989).

3. Results

Dimethyl ether results (Table 2) indicate that the 2^1B_1 state lies at a lower energy than the 1^1A_2 state, representing a reordering of those excitations relative to water. Addition of polarization functions to the carbon atoms did not significantly affect the results. Previous calculations on dimethyl ether (Wadt & Goddard, 1976) included an empirical scaling parameter, but provided the basis for similar assignments (Bremner, Curtis & Walker, 1991).

Table 2
Excitation energies in mh for CH_3OCH_3

State	Energy	Exp[a]
1^1B_1	277	247
2^1B_1	300	270
2^1A_1	303	280
1^1A_2	305	290
3^1A_1	338	325

[a] From Bremner et al. (1991). Only the transition energies are experimental, not the assignments.

Calculations on H_2O, carried out with the same protocol, reproduced the experimentally observed energy ordering of the first five excited states (Buenker & Peyerimhoff, 1974; Winter et al., 1975); excitation energies were reproduced with an rms error of 5 mh. Diffuse s orbitals on the hydrogen atoms had no effect on the transition energies, their relative ordering, or the rms error. Calculations on H_2O in which the bond angle was varied indicate that the reordering of state energies in dimethyl ether is not simply a result of different bond angles in the two molecules. Calculations on methanol gave the same ordering of the states of interest as the ordering in water.

The CI wavefunctions were examined to evaluate what part of each excitation can be described as being localized on the oxygen atom. From the coefficients of the CSFs contributing to each of the excited state wavefunctions, and the coefficients of the atomic orbitals contributing to the RHF molecular orbitals, it was found that approximately 26% of the $1^1A_1 \rightarrow 2^1B_1$ excitation is represented by an oxygen centered $2pb_1 \rightarrow 3pa_1$ component, and 20% by a $2pb_1 \rightarrow 3s$ component; there is strong 3s, $3pa_1$ mixing. Also, approximately 48% of the $1^1A_1 \rightarrow 1^1A_2$ transition is represented by an oxygen centered $2pb_1 \rightarrow 3pb_2$ component. The Rydberg components of the low lying excitations in the water, methanol and dimethyl ether molecules have been discussed by Robin (1974).

4. Discussion

The present calculations were motivated by empirical assignments of the 150–190 nm CD spectra of monosaccharides (Arndt & Stevens, 1993) in which the acetal chromophore is treated as two weakly coupled ether (C_{2v}) chromophores. Briefly, a 183 nm CD band, easily assigned to an $^1A_1 \rightarrow {}^1B_1$ transition, is followed by a band at 171 nm that consistently has the same sign as the 183 nm band for an entire set of canonical sugar structures, which argues for assignment of the 171 nm band to a transition of the same symmetry as the 183 nm band. The third CD band (168 nm), consistently having a sign opposite to that of the 171 nm band, was assigned to an $^1A_1 \rightarrow {}^1A_2$ transition on the basis of its magnetically allowed character. The $^1B_1$ and $^1A_2$ states are approximately described in an LCAO-MO picture as having parentage in components of the 3p oxygen manifold. As the $^1B_1$ state is the higher energy state of the two in H_2O, which has been well studied, we have sought calculational grounds that their ordering is reversed in an ether chromophore.

The present calculations show a reordering of the 2^1B_1 and 1^1A_2 excited states in dimethyl ether, relative to the known ordering in water, with the 2^1B_1 state at a lower energy in dimethyl ether. The differences in bond angle alone do not seem to account for this reordering (Parra, 1999). The present results, therefore, provide calculational support for the assignment of the low energy CD of unsubstituted saccharides and polysaccharides to oxygen-centered transitions, in which the excited states have significant Rydberg character.

Transitions to both excited states are magnetically allowed, and those intrinsic magnetic transition moments may play a role in determining the intensity of the CD of saccharides in the 150–190 nm region. There is, therefore, some interest in estimating those moments from the CI wavefunctions determined here; there have been no experimental determinations. The contribution from the oxygen-centered components of the CI wavefunction (see above) were combined with the oxygen 2p → 3p overlap integral (0.127) to produce an estimate of approximately $0.06\mu_B$ for the $1^1A_1 \rightarrow 1^1A_2$ transition and approximately half that value for the $1^1A_1 \rightarrow 2^1B_1$ transition (for details, see Parra, 1999).

The 150–190 nm CD of unsubstituted saccharides was described in early work as being responsible for the Na_D optical rotation, through a Kramers–Kronig transform, implying an assignment of that CD to strong σ–σ^* valence transitions localized on the acetal chromophore. Although the low energy CD can be confirmed by the present work as arising from transitions localized on the oxygen atoms of the acetal chromophore, the generally low CD intensity in the 150–190 nm region is not sufficient to account for the observed Na_D optical rotation. Experiments have now shown (Arndt & Stevens, 1993) that the strong high energy σ–σ^* CD responsible for the Na_D optical rotation occurs at wavelengths shorter than 130 nm. The 150–190 nm CD intensity in polysaccharides, although not significantly responsible for Na_D optical rotation, nevertheless shows considerable dependence on conformation and may provide a measure of conformational order in carbohydrates (Stevens, 1996).

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