Optical Activity of a Chiral Bicyclic Orthoester

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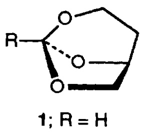
The circular dichroism (CD) spectra of two optically active bicyclic orthoesters have been measured in the vacuum UV (VUV) region; transitions to 3s, 3p and 3d Rydberg states are detected in the CD spectra; no indication for excitonic interaction between the three non-identical oxygen chromophores is observed.

The extension of circular dichroism (CD) measurements to the vacuum UV (VUV) region has enabled the investigation of chromophores absorbing in this wavelength region. Cyclic ethers are examples of such chromophores which have been extensively studied, both experimentally[1–7] and theoretically.[2,8,9] The special interest in these molecules arises from the fact that because of their rigid skeletons their chiroptical properties can be easily calculated. Thus the CD of oxiranes,[1–3] oxetanes,[4] furans,[10] pyrans[10] and dioxolanes[11] have been reported in the gas phase.

The optically active orthoesters (*R*)-(−)-R-2,7,8-trioxabicyclo[3.2.1]octanes (R = H, Me and Ph) have recently been synthesized and their chiroptical properties measured.[12]

Molar rotation calculations resulted in the correct sign for all three molecules studied. The magnitudes of the calculated molar rotations, however, were larger than the experimental values and did not vary with the substituent on C-1. Moreover, the calculated rotation for the phenyl derivative showed no sensitivity to rotation of the phenyl group about the C–C bond.[12]

In this study we report on the absorption and CD spectra of (*R*)-(−)-R-2,7,8-trioxabicyclo[3.2.1]octane **1** and of (*R*)-(−)-1-methyl-2,7,8-trioxabicyclo[3.2.1]octanes **2** in the gas phase. The absorption spectra of cyclic ethers are known to be dominated by Rydberg transitions which undergo blue shifts when the molecule is embedded in a solvent,[13] thus to avoid this complication and to obtain the information related to the isolated molecule, the measurements were carried out in the gas phase.



1; R = H
2; R = Me

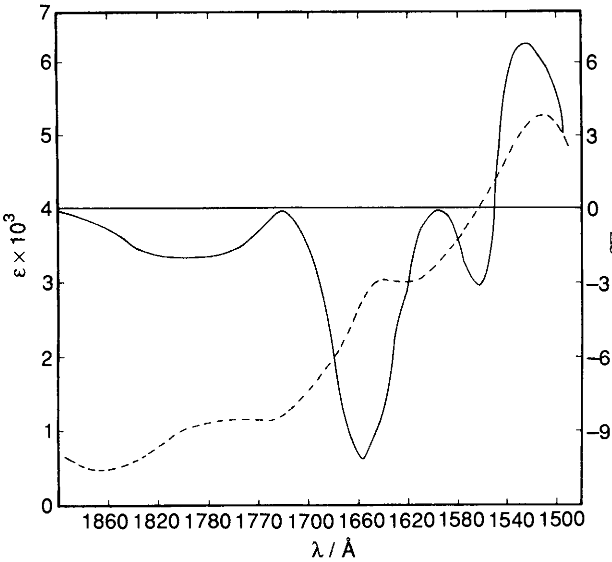


Fig. 1 Absorption (- - -) and CD (———) of (*R*)-(−)-R,2,7,8-trioxabicyclo[3.2.1]octane in the gas phase. The spectral resolution is 16 Å; the units of ε and Δε are l mol⁻¹ cm⁻¹.

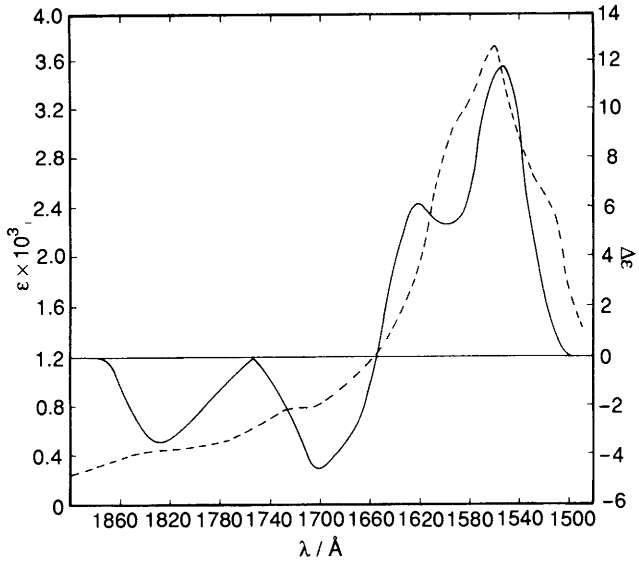


Fig. 2 Absorption (- - -) and CD (———) of (*R*)-(−)-1-methyl-2,7,8-trioxabicyclo[3.2.1]octane in the gas phase. The spectral resolution is 16 Å; the units of ε and Δε are l mol⁻¹ cm⁻¹.

The VUVCD instrument used in this study has been described previously.[14] The absorption and CD measurements were carried out in an 11 cm cell. The vapour pressure was measured using a Wallace and Tiernan absolute pressure gauge. The optically active compounds were prepared according to a procedure described elsewhere.[12]

The adsorption and CD spectra of compounds **1** and **2** are depicted in Figs. 1 and 2, respectively. The first absorption bands are observed as shoulders at 1770 and 1800 Å for **1** and **2**, respectively. The CD bands corresponding to this transition have a better shaped contour with more distinct peaks at 1800 and 1830 Å for **1** and **2**, respectively. The first excited state in cyclic ethers was assigned as the n(o) → 3s Rydberg transition.[15] This assignment is based on a comparison of the gas phase absorption spectrum and a solution spectrum of ethylene oxide in hexafluoroisopropanol.[15] We adopt Basch's[15] interpretation and assign the first excited state in compounds **1** and **2** as a 3s Rydberg state. The observed red shift of 30 Å, which is obtained when a hydrogen atom is substituted by a methyl group, is also typical for a 3s Rydberg transition.[2,15] The same red shifts are observed for methyloxirane[1] and methyloxetane.[4] The term value of a 3s Rydberg reaches a limit of 22 000–24 000 cm^{-1} when the chromophore is embedded in a molecule containing 6–8 carbon or heteroatoms.[16] We can therefore use the 24 000 cm^{-1} as an upper limit for the ionization potential and obtain a value of 9.98 eV.

The second excited state also reveals a negative CD signal, with peaks at 1656 and 1700 Å for compounds **1** and **2**, respectively. The second transition is assigned as the n(o) → 3p Rydberg excitation. The 3p Rydberg manifold consists of three components. In oxirane or in any other molecule with C_{2v} symmetry, the $3p_y$ component has A_2 symmetry and is electrically dipole forbidden from the ground state.[3] It is, however, magnetically dipole allowed from the ground state and should therefore show a strong CD signal, while its absorption should be negligible. We therefore assign the positive CD band at 1620 Å in **2** and the negative trough at 1600 Å in **1** as the n(o) → $3p_y$ transition. This peak does not have a corresponding absorption band. Similar behaviour was detected recently in dideuteriooxirane.[6] The positive CD signal at 1525 Å in **1** and at 1545 Å in **2** is assigned as the n(o) → 3d Rydberg transition on the basis of term value arguments. If we assume an ionization potential of 9.98 eV for **1**, the term value for the 3d Rydberg is 14 920 cm^{-1}. Taking into consideration that the 9.98 eV value is an upper limit for the ionization potential, the magnitude obtained is very reasonable.

The CD spectrum does not reveal any excitonic interaction,[17] and although the three oxygen chromophores are not identical substituents, they can still interact as a nondegenerate system whose three different chromophores have similar λ_{max} values. The reason for this lack of behaviour in the orthoesters is attributable to their relatively small extinction coefficient (the largest ε is 6000).

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