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(7) In contrast, a partial epimerization is observed for methyl ligand substitution in the reaction

$$\eta^5\text{-Cp-}\eta^5\text{-Cp'TiYCH}_3 \xrightarrow{\text{HCl}} \eta^5\text{-Cp}\eta^5\text{-Cp'TiYCl}$$

(Y = C_6F_5 or ortho $OC_6H_4CH_3$).
(8) NMR ($CDCl_3$): singlets at δ 1.22 ($-C(CH_3)_3$) and 6.30 (η^5-C_5H_5). Furthermore, the spectrum reveals traces of the bromo compound η^5-Cp-η^5-Cp'C_6F_5Br originated from Grignard's reagent (δ 6.35: η^5-C_5H_5). This impurity does not affect the following stages.
(9) This alcohol was prepared by $LiAlH_4$ reduction of (+)-(*S*)-2-phenylpropanoic acid (99% of optical purity).
(10) The racemic forms **2a** and **2b** (obtained from (±)-2-phenyl-1-propanol) melt respectively at 87 and 134°C. All new compounds gave satisfactory elemental analysis.
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Optical Rotatory Dispersion and Vacuum Ultraviolet Circular Dichroism of a Polysaccharide. ι-Carrageenan

Sir:

Many polysaccharides have no electronic transitions above 190 nm. Their optical rotatory dispersion (ORD) in the near-ultraviolet and visible regions is therefore of the normal type and Cotton effects are totally absent. Circular dichroism (CD) in that region is also completely absent. We report here the vacuum ultraviolet circular dichroism (VUCD) (155-200 nm) of ι-carrageenan; no polysaccharide CD has been reported previously below 190 nm. We also report a Drude equation analysis of the ORD of ι-carrageenan.

ι-Carrageenan was chosen for this study because it has been well-characterized by Rees and coworkers.[1-5] It approximates in structure an alternating copolymer $(A-B)_n$, in which B is a residue of β-D-galactose 4-sulfate and A of 3,6-anhydro-α-D-galactose 2-sulfate, with a mean residue weight of 271 for the potassium salts.[1,2] The glycoside linkages are A1→3B and B1→4A. In solution it undergoes a coil-to-helix transition as the temperature is decreased, with the helical form being more dextrarotatory than the unordered form.[3,4] Fiber X-ray studies indicated the presence of a helical structure.[5]

Figure 1 shows the ORD of a 0.5% ι-carrageenan solution in water at 22°C (curve 2) and in 0.05 *M* KCl at 24°C (curve 1) (measured on a Cary 60 spectropolarimeter). Curve 2 corresponds to the disordered form but in curve 1 the transition to helical form is not complete; the fully helical form is not achieved at temperatures above the freezing point of our solution (Chen and Yang, unpublished results). Both ORD spectra appear to be of the normal type[6] above 200 nm and obey the Drude equation: $[\alpha] = k/(\lambda^2 - \lambda_c^2)$ with $k = 18.9 \times 10^6$ and 13.9×10^6 when $\lambda_c = 155$ and 157 nm for curves 1 and 2, respectively. However, since the VUCD results (see below) show two bands, we can fit the same data with a two-term Drude equation:

$$[\alpha] = k_1/(\lambda^2 - \lambda_1^2) + k_2/(\lambda^2 - \lambda_2^2) \qquad (1)$$

A plot of $[\alpha](\lambda^2 - \lambda_1^2)$ vs. $(\lambda_2^2 - \lambda_1^2)/(\lambda^2 - \lambda_2^2)$ yields a straight line with λ_1 and λ_2 preset at 180 and 164 nm, respectively.[7] We find that $k_1 = -10.2 \times 10^6$ and -10.8×10^6 and $k_2 = 29.2 \times 10^6$ and 25.2×10^6, respectively, for curves 1 and 2. The fit is good over the wavelength range of 220-560 nm, except that the data points near 500 nm show some scatter. The fit is not unique; with $\lambda_1 = 180$ nm, lowering λ_2 to 160 or 150 nm would also give straight lines, but the magnitudes of both k_1 and k_2 decrease with decreasing λ_2; for instance, $k_1 = -5.9 \times 10^6$ and $k_2 = 24.9 \times 10^6$ with $\lambda_2 = 160$ nm (for curve 1).

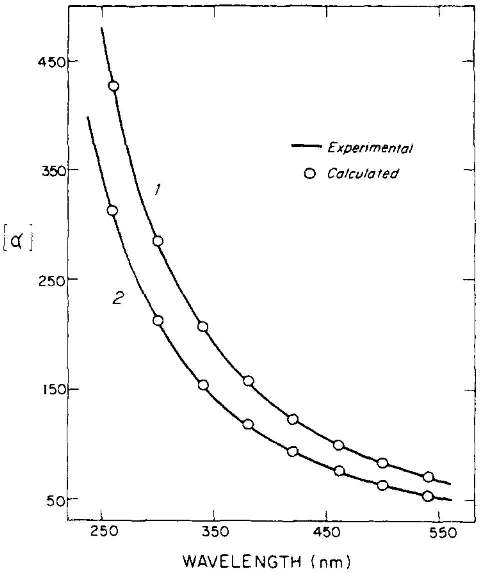

Figure 1. Optical rotatory dispersion of ι-carrageenan in solution: curve 1, 0.5% in 0.05 *M* KCl at 24°C, and 2, 0.5% in water at 22°C (pH 5). The circles are calculated values based on a two-term Drude equation. See text for details.

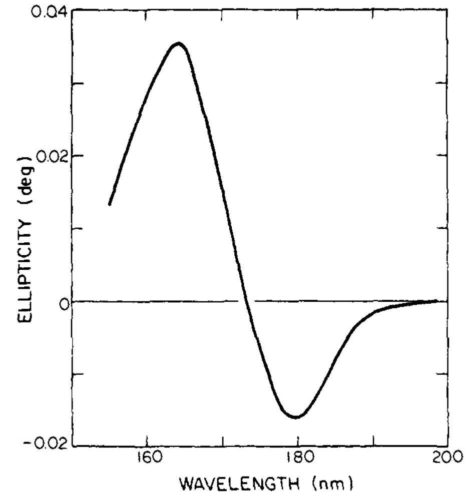

Figure 2. Vacuum ultraviolet circular dichroism of ι-carrageenan film prepared from aqueous solution.

ι-Carrageenan has no optical transitions above 190 nm and the CD spectrum measured on commercial instruments (not shown) indicates only the onset of negative dichroism as the instrumental wavelength limit is reached near 190 nm. Figure 2 shows the VUCD of ι-carrageenan from 155 to 200 nm. For the VUCD study a film of ι-carrageenan was prepared on a 1 mm CaF_2 disk by evaporation to dryness of an aqueous solution. The spectrometer[8] was operated with a spectral width of 1.66 nm, a time constant of 10 sec and a scan rate of 2 nm/min. Rotation of the film about the optical axis had no effect on the signal, and there was no indication of flattening of the CD bands. The data in Figure 2 have been corrected by subtraction of a wavelength dependent scattering contribution to the signal. The wavelength dependence of the correction was determined by measuring the scattering contribution to the signal measured with a film of poly(D,L-alanine). The wavelength positions of the two bands observed in the VUCD spectrum and the signs of those bands, together with the ORD data, are sufficient information to preclude the possibility that a third CD band at higher energy is contributing significantly to the ORD in the near-ultraviolet region. In this case it is therefore possible to use the ORD data to determine the proper scattering correction for the VUCD data, by scaling the correction to give the relative band areas extracted from the Drude analysis ($|k_1/k_2|$ = 10.2/29.2). At 164 nm the scattering correction is twice the noise level, and the signal-to-noise ratio is 10:1.

Assuming that the CD bands are Gaussian, we can calculate from k_1 and k_2 mean residue rotational strengths[9] of approximately -9×10^{-40} and 32×10^{-40} erg cm^3 rad, respectively (or mean residue ellipticities of $[\theta]_{180} \simeq -23000$ and $[\theta]_{164} \simeq 48000°$ cm^2 dmol^{-1}, respectively), for curve 1 in Figure 1. These are rough estimates since (a) the conformation in solution under our experimental conditions is not completely helical, and (b) we used a CD correction factor derived from the partially ordered conformation although the film is almost completely in the helical form (P. Lillford, private communication). Nevertheless we can conclude that the ORD changes observed during the helix-coil transition[2-4] must be determined by changes in the magnitudes, and also possibly in the positions, of the two CD bands we observe.

These two CD bands must reflect two separate monomeric transitions, since they are too far apart to be accounted for in terms of an exciton splitting mechanism. Nelson and Johnson[10] observed, in an equilibrium mixture of D-galactose anomers, a negative band near 177 nm, and increasing negative dichroism to 164 nm, the wavelength limit of that study. Tetrahydropyran in the vapor phase has two vacuum ultraviolet absorption bands, at approximately 189 and 173 nm, attributed to excitation of the unshared electrons of the oxygen atom.[11] The CD bands we see here may well have a similar origin, and the 9-nm blue shift in each of the transitions may reflect the difference between the ether and the acetal chromophores.

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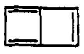
The Generation and Trapping of Butalene

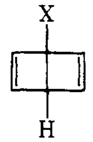
Sir:

Among conjugated fused-ring systems those with two 4n π electron rings, which thus have overall $4n + 2$ π electrons, are particularly interesting. The question of whether they reflect the instability of their component antiaromatic rings or the stability of their overall $4n + 2$ π electrons has been the subject of several experimental and theoretical studies.[1] A fundamental structure in this regard is that of butalene (**1**), a 1,4-dehydrobenzene. In 1965 Berry reported[2] the detection of a relatively long-lived species C_6H_4 of undetermined structure from the flash thermolysis of benzenediazonium-4-carboxylate. More recently, Bergman[3] has described the trapping of 1,4-benzenediyl (**2**) from the thermolysis of diethynylethylene at 200°. He also reported[4] our preliminary observation that a different 1,4-dehydrobenzene, butalene (**1**), can apparently be trapped at low temperature. Dewar has calculated[5] using MINDO 3 that both **1** and **2** should be energy minima, with **1** being 19 kcal/mol less stable than **2**; only a 4.6 kcal/mol barrier was predicted for the isomerization of **1** to **2**. We now wish to describe our evidence[6] that butalene (**1**) can indeed be generated and trapped somewhat below room temperature.

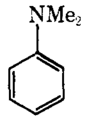


1

2



3, X = Cl
6. X = NMe$_2$



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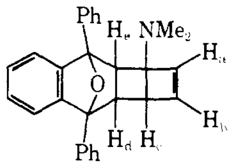

5

The starting material for the work was 3-chloro[2.2.0]bicyclohexadiene[7] (**3**). This compound is quite stable to most strong bases,[6] but with 0.1 *M* LiNMe$_2$ in HNMe$_2$-THF at 0° for 45 min, **3** is quantitatively converted to *N,N*-dimethylaniline (**4**). When DNMe$_2$ is used, the product **4** is 25% d_1, 38% d_2, 22% d_3, and only 6.3% d_0. The NMR spectrum, clarified with the use of Eu(fod)$_3$, showed that **4** is 76% para deuterated, 15% meta deuterated, and 48% (of 2 protons) ortho deuterated. When tetramethylethylenediamine is added to the above reaction mixture, the process can be carried out at −35° with quantitative conversion of **3** to **4** and 76, 5, and 25% deuteration of the para, meta, and ortho protons of **4** respectively. Under these same conditions, in the presence of a fivefold excess of diphenylisobenzofuran (DPIBF), the adduct **5** can be isolated in 10–15% yield. The structure of **5** follows from the mass spectrum (*m/e* 391) and NMR spectrum. Signals at δ 6.29, 6.21, 2.98, 2.60, and 2.45 are found for H's a–e, respectively; the assignments were confirmed by appropriate decoupling experiments (J_{ab} = 1.5 Hz, J_{bc} = 1.0 Hz, J_{cd} = 1.6 Hz, J_{de} = 3.0 Hz). When DNMe$_2$ is used rather than HNMe$_2$ the isolated adduct **5** contains 90% deuterium at H$_c$; within the 10% limits of experimental accuracy no deuterium is observed at any other position regardless of whether H_2O or D_2O work-up is employed.

Several controls help to establish that butalene is an intermediate in these reactions. Thus, **3** does not isomerize to chlorobenzene at these temperatures, and chlorobenzene is not converted to **4** under these conditions. Furthermore, **3**