Reaction of Perfluoroallyl Iodide with Oxygen.—Perfluoroallyl iodide (5.16 g., 0.02 mole), oxygen (0.64 g., 0.02 mole), nitrogen (0.84 g., 0.03 mole), and mercury (70 ml.) were shaken together in the dark for 1 hr. in a 2-l. flask. The only organic material isolated was 4.7 g. of unchanged perfluoroallyl iodide (91% recovery).

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Ring Conformation in Methyl α- and β-D-Xylothiapyranosides as Demonstrated by Nuclear Magnetic Resonance[1]

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The recent synthesis of sugars in which the ring oxygen is replaced by a sulfur atom[2] makes possible an experimental attack on many interesting questions relative to both chemical and physical–chemical properties of the carbohydrates. However, one question which must be answered before certain other results can be interpreted without ambiguity is that of whether there is a direct effect of this substitution on the ring conformation. The D-xylopyranosides have been shown to exist in the Cl conformation by optical rotatory studies,[3] by stability considerations,[4,5] and by X-ray analysis.[6] It has also been shown in D-xylopyranose tetraacetates that the spin–spin coupling constants observed by n.m.r. are as required for the Cl conformation.[7] The purpose of the present work is to determine if replacement of the ring oxygen by sulfur in D-xylothiapyranose and the methyl D-xylothiapyranosides produces a change in the ring conformation.

The proton magnetic resonance spectra of the various compounds were determined at 60 Mc.p.s. with a Varian A-60 n.m.r. spectrometer using 10–20% by weight solutions of the carbohydrates in deuterium oxide. The assignment of τ values were made by taking the water peak (5.2 τ) as an internal standard. The dihedral angles between the anomeric proton and the proton on the adjacent carbon atom C-2 were calculated from the magnitude of the splitting of the corresponding absorption peak using the modified Karplus equation.[8,9]

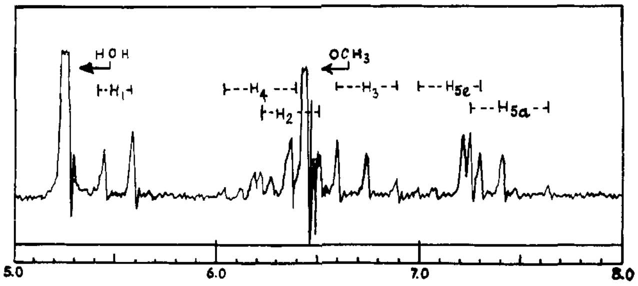

Fig. 1.—N.m.r. spectrum of methyl β-D-xylothiapyranoside in deuterium oxide at 60 Mc., with chemical shifts given in τ values.

It has been shown that the signal due to the anomeric proton of sugars appears at a lower field than that of any of the other carbon-bonded hydrogen atoms.[7,9,10] Further, the signal for an equatorial anomeric proton occurs at a somewhat lower field than for an axial proton. From Table I it is evident that the signal in methyl α-D-xylothiapyranoside appears at a lower field than for the corresponding β-anomer. In all cases the peak corresponding to the anomeric proton is split due to coupling with the proton on C-2. The large values of this coupling constant for methyl β-D-xylopyranoside and methyl β-D-xylothiapyranoside (7.2 and 8.4 c.p.s., respectively) are of the expected order of magnitude for an axial–axial orientation. Similarly the low values for the α-anomers indicate an axial–equatorial situation. The calculated values of the dihedral angles are in reasonable agreement with the expected values for the Cl conformation (60° and 180° for α- and β- anomers, respectively).

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR ANOMERIC PROTONS

	Chemical shifts (τ values)		Coupling constant JH_1H_2, cycles/-sec.	Dihedral angle, deg.
	H_{1e}	H_{1a}		
D-Xylose[a]	4.82	...	2.2	60
	...	5.45	7.2	148
Methyl β-D-xylopyranoside	...	5.62	7.2	148
D-Xylothiapyranose	5.0	...	2.5	57
	...	5.25	8.2	154
Methyl α-D-xylothiapyranoside	5.35	...	2.8	55
Methyl β-D-xylothiapyranoside	...	5.52	8.4	156

[a] Data from ref. 9.

The spectra of both D-xylopyranosides and D-xylothiapyranosides show additional fine structure. The spectrum of methyl β-D-xylothiapyranoside is presented in Fig. 1. The splitting pattern in the region 5.8–6.5 τ has been identified as due to the proton at C-2. This indicates that it is coupled to protons at C-1 and C-3 with J values 8.4 and 8.6, respectively. These large values indicate that the C-2 proton is in axial–axial orientation with the protons at C-1 and C-3. The triplet in the region 6.6–6.9 τ is assigned to the C-3 proton. The splitting pattern shows that the C-3 proton is coupled with

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TABLE II

COUPLING CONSTANTS OF METHYL β-D-THIAXYLOPYRANOSIDE (C.P.S.)

$J_{1a,2a}$	8.4
$J_{2a,3a}$	8.6
$J_{3a,4a}$	8.6
$J_{4a,5e}$	3.3
$J_{4a,5a}$	11.2
$J_{5a,5e}$	13.5

C-2 and C-4 protons with J values of 8.6, which confirms the axial–axial relation between C-2 and C-3 protons and further indicates that the C-3 proton is in axial–axial orientation with the C-4 proton.

The two quartets in the region 7.0–7.7 τ are assigned to the C-5 protons. This is due to the coupling among themselves and with the neighboring proton at C-4. Part of the splitting pattern of the C-4 proton is overlapped by the signals due to the C-2 proton and the methyl hydrogens. This is treated as an ABX-type[11] spectrum, and the values of the various coupling constants which can be deduced from these spectral features are summarized in Table II. The large coupling constant $J_{5e}J_{5a}$ is expected for the interaction of axial and equatorial protons on the same carbon atom.[9] The small J value for the coupling of the equatorial proton on C-5 with the proton on C-4, and the corresponding large value for the coupling of the axial proton on C-5 with this same proton, show beyond a doubt that the proton on C-4 is in an axial orientation.

In summary, the n.m.r. spectra show no evidence for any important alterations in ring conformation due to the replacement of the ring oxygen of D-xylopyranose by sulfur. Furthermore, the spectra of methyl β-D-thiaxylopyranoside are in accord with the Cl ring conformation.

Acknowledgment.—We are indebted to the Corn Industries Research Foundation for financial support of this work.

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[11] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 6.

Dipole Moments of Two Nitrogen Analogs of Sesquifulvalene

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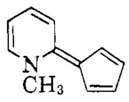
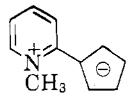
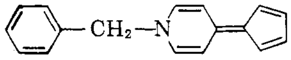
The dipole moments of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (I) and 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (II) are of interest because of possible large contributions of resonance forms with a separation of charge, Ia and IIa, which would cause these molecules to have large dipole moments.[1-5]



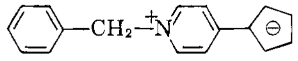
I



Ia



II



IIa

The moment of compound I has not been reported and although that of II has been reported to be 9.7 D.,[1] no experimental details were given. If the electronic polarization was calculated from atomic refraction constants, the reported moment would be high because of the likely exaltation in such a compound.

Results and Discussion

The results are given in Table I. Compound I was sufficiently soluble so solutions up to the usual concentration range of about 1% could be measured and in this range the ϵ_{12}–ω_2 points still fell on a straight line giving no evidence of association. The $P_{E_{20}}$ from the refractive index of the solutions was about 22 units higher than the MRD value, indicating considerable exaltation as expected from this type of compound. The dipole moment of 5.20 ± 0.6 D. gives evidence of approximately a 25% contribution from the forms with a separation of charge Ia and IIa. This calculation was made without taking into account the small moment possessed by the normal forms I and II of the compound since the direction of this small moment is not known with regard to the resultant moment coming mainly from the contribution of the forms with a separation of charge.

Since the solubility of compound II was less than 10 mg. in 10 ml. of benzene, only very dilute solutions could be measured. The density of these solutions was indistinguishable from that of benzene, but dielectric constant differences were significant. More concen-

TABLE I

DIPOLE MOMENTS IN BENZENE AT 25°

1-METHYL-2-CYCLOPENTADIENYLIDENE-1,2-DIHYDROPYRIDINE

ω_2	ϵ_{12}	ν_{12}
0.0	2.2725	1.14025
.0021995	2.3156	1.13935
.0046113	2.3593	1.13830
.0074636	2.4168	1.13726
.0102930	2.4702	1.13636
.0127364	2.5301	1.13532

$\epsilon_1 = 2.2702$ $\alpha = 19.9269$ $\nu_1 = 1.14017$

$\beta = -0.38057$ $P_{20} = 3.96391$ $P_{20} = 623.205$

$P_{E_{20}} = 69.70$ from refractive index of solutions

$MR_D = 47.75$

$\mu = 5.20 \pm 0.06$ D.

1-BENZYL-4-CYCLOPENTADIENYLIDENE-1,4-DIHYDROPYRIDINE

ω_2	ϵ_{12}	ν_{12}
0.0	2.2756	1.141947
.00012881	2.2792	1.141947
.00028457	2.2859	1.141947
.00058901	2.2975	1.141947

$\epsilon_1 = 2.2750$ $\alpha = 37.9034$ $\nu_1 = 1.14195$

$\beta = 0.0$ $P_{20} = 7.4455$ $P_{20} = 1736.97$

$P_{E_{20}} = 108.57$ from refractive index of solutions

$MR_D = 70.07$

$\mu = 8.93 \pm 0.18$ D.

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