hand, photoelectron studies indicate that the interaction of the halide orbitals with the metal in the ground state molecule decrease in the order Cl > Br > I.[34]

Ligands such as triphenylphosphine, which are not capable of acting as relatively good π donors toward the metal following CO loss, are nevertheless observed to behave as cislabilizing ligands.[3,4] In these instances there may be some steric contribution to the rate enhancement.[35] Additional experimental work is required to separate electronic and steric factors. Calculations of the type performed here are not sufficiently reliable when applied to kinetics processes to permit distinctions between ligands such as various phosphines, or even between phosphines and CO.

References and Notes

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Application of ab Initio Molecular Orbital Calculations to the Structural Moieties of Carbohydrates. 3[1]

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Abstract: Ab initio RHF/4-31G level molecular orbital calculations have been carried out on dimethoxymethane as a model compound for the acetal moiety in methyl pyranosides. The calculations are consistent with the predictions of the *anomeric effect* and the *exo-anomeric effect*. They reproduce very successfully the differences in molecular geometry observed by x-ray and neutron diffraction of single crystals of the methyl α-D- and methyl β-D-pyranosides. Calculations carried out at the 6-31G* level for methanediol confirm the earlier calculations at the 4-31G level, with smaller energy differences between the four staggered conformations.

Dimethoxymethane as a Model Compound for the Acetal Moiety in Pyranosides

In pyranoses, pyranosides, pyranosyl halides, furanoses, furanosides, nucleosides, and nucleotides, two of the four atoms bonded to the anomeric carbon atom C(1) are more electronegative than carbon, and necessarily have lone-pair electrons. The electronic transfer, which arises from these electronegative differences, is compensated for by a feedback from the lone pairs to the antibonding (σ^*) orbitals of adjacent bonds, as

suggested by the application of Pauling's rule concerning the essential electroneutrality of atoms.[3] In consequence, there is a difference in the electronic structure between molecules with the α configuration, **1,** and those with the β configuration, **2,** at the anomeric center, C(1), because of the different geometrical relationship between the carbon 2p orbitals and the distribution of the lone pairs on the ring oxygen and the substituent X. This difference is believed to be responsible for the difference in the stability of pyranosides and furanosides to acid hydrolysis, the preferred α configurations in glycosyl fluoride
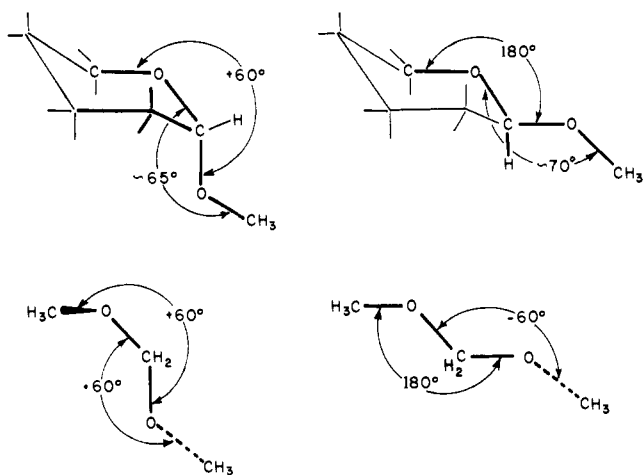
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Figure 1. Relation between conformations of pyranosides and dimethoxymethane.
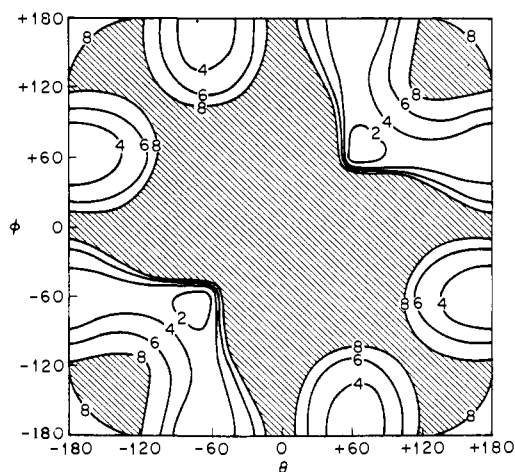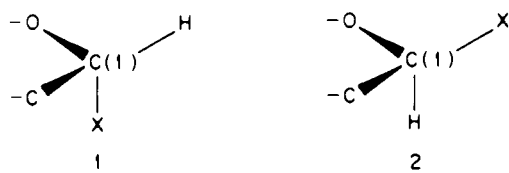

Figure 2. Potential energy surface for dimethoxymethane as a function of torsional angles θ and φ.

reaction products, and the preferred gauche conformations about glycosidic bonds in pyranosides. The first two observations are referred to as the *anomeric effect*, discovered by Edwards[4a] and by Lemieux.[4b] The third observation is referred to as the *exo-anomeric effect*.[4c]

In parts 1[5] and 2[6] of this series, we have discussed the use of methanediol and methoxymethanol as model compounds for interpreting the bond-length variations and preferred glycosidic conformations observed experimentally in the crystal structures of pyranoses, methyl pyranosides, disaccharides, and trisaccharides. We have also given in part 2 a more quantitative analysis of the roles that the internal bond rotation potentials and electrostatic lone-pair interactions play in determining the conformational energy.

In this paper, we carry this treatment one stage further by using dimethoxymethane, $H_3COCH_2OCH_3$, as a model compound for the acetal moiety in the α- and β-D-pyranosides, in order to explore, more completely than was previously attempted, the optimum dimensions of the acetal moiety in α- and β-pyranosides. As shown in Figure 1, the (+sc, +sc)
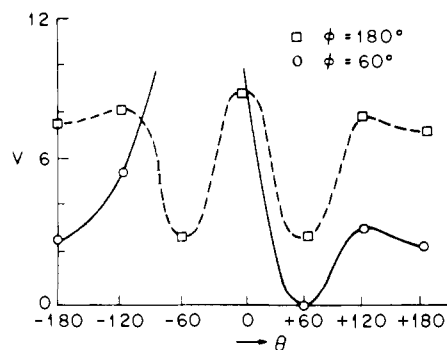

Figure 3. Sections, $V(\theta)$, of the potential surface for internal rotation in dimethoxymethane for fixed values of φ.

Table I. Potential Surfaces (RHF/4-31G) for Dimethoxymethane with Rigid Rotation[a] (kcal mol^{-1})

φ	θ						
	-180	-120	-60	0	60	120	180
180	7.68	8.05	2.59	8.95	2.59	8.05	7.68
120	8.05	10.39	5.64	11.47	3.28	8.49	8.05
60	2.59	5.64	18.93	18.70	0[b]	3.28	2.59
0	8.95	11.47	18.70	Large[c]	18.70	11.47	8.95

[a] The table can be extended to negative φ using $V(-\theta,-\varphi) = V(\theta,\varphi)$. [b] Total energy $-267.550\ 07$ hartrees. [c] Calculation not completed because of large overlap of methyl groups.

conformation of dimethoxymethane is a model for the preferred gauche conformation of a methyl α-D-pyranoside and the (ap, $-$sc) conformation is a model for that of a methyl β-D-pyranoside. The analogue of the third possible staggered conformation of the dimethoxymethane molecule (ap, ap) is not observed in methyl β-D-pyranosides in the crystalline state.[7]

Independently of our work, a theoretical study of dimethoxymethane has been carried out by Gorenstein and Kar,[8] using lower level molecular orbital techniques. Their results are compared with ours in the ensuing discussion.

The Molecular Orbital Calculations

As in the previous work on methanediol[5] and methoxymethanol,[6] we have mainly used closed shell Hartree–Fock theory[9] with the 4-31G basis[10] set (RHF/4-31G). The principal aim is to study internal rotation involving the O–C–O–CH$_3$ torsion angles θ and φ in structure **3**. In the first set of
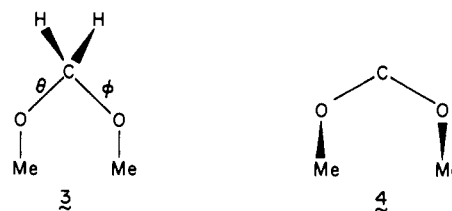
calculations, the potential surface $V(\theta, \varphi)$ was examined using fixed standard values[11] for all other geometrical parameters ($R_{CO} = 143$ pm, $R_{CH} = 109$ pm, $R_{OH} = 96$ pm, all bond angles tetrahedral, methyl groups staggered in H_3COC). The lowest energy (at a 60° grid) is found for the (+sc, +sc) structure **4**. Energies relative to this are listed in Table I. Figure 2 shows the corresponding contour diagram.

The results show some similarities to those previously obtained for methanediol and methoxymethanol. Of the four conformations **4–7** consistent with staggered bonds, **4** (+sc, +sc, $\theta = \varphi = 60°$) is the most stable. The symmetrically related conformation ($-$sc, $-$sc, $\theta = \varphi = -60°$) has the same energy.

Table II. Potential Surface (RHF/6-31G*) for Methanediol with Rigid Rotation[a] (kcal mol^{-1})

| φ	θ						
	−180	−120	−60	0	60	120	180
180	8.84	7.28	3.75	4.36	3.75	7.28	8.84
120	7.28	7.17	3.81	3.62	3.09	5.90	7.28
60	3.75	3.81	4.10	3.98	0[b]	3.09	3.75
0	4.36	3.62	3.98	10.36	3.98	3.62	4.36

[a] The table can be extended to negative φ using $V(-\theta,-\varphi) = V(\theta,\varphi)$.
[b] Total energy −189.895 53 hartrees.

Table III. Relative Energies of Methanediol Conformations at RHF/4-31G and RHF/6-31G* (kcal mol^{-1})

	RHF/4-31G	RHF/6-31G*
+sc,+sc	0[a]	0
+sc,ap	4.73	3.75
+sc,−sc	5.37	4.10
ap,ap	11.74	8.84

[a] Total energy −189.624 99 hartrees.
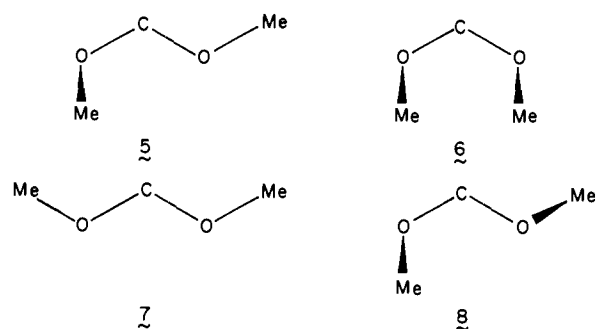
The (+sc, ap) conformation **5** lies 2.6 kcal mol^{-1} higher in energy than (+sc, +sc). This is a rather smaller separation than in methanediol where the corresponding energy difference is 4.7 kcal mol^{-1}. The (+sc, −sc) structure **6** is unstable, presumably because of steric repulsion between the methyl groups. The fully extended (ap, ap) conformation **7** is less stable than (+sc, +sc) or (+sc, ap). The energy of this relative to (+sc, +sc) is 7.7 kcal mol^{-1}, rather less than the value of 11.2 kcal mol^{-1} found for methanediol.

A more detailed examination of the potential indicates some differences from methanediol. Figure 3 shows sections with one dihedral angle held fixed. If $\varphi = 60°$ (+sc), there is one principal minimum (now $\theta = 60°$) but there is an indication of a slight barrier to conversion to the (+sc, ap) form. This was not found for methanediol. If $\varphi = 180°$, the two equivalent minima near $\theta = \pm60°$ are separated by a high barrier, whereas the corresponding barrier for methanediol was quite small. The fully extended (ap, ap) form is found to be a local minimum on the surface, unlike methanediol, but only a small activation is needed for conversion to ($\pm$sc, ap).

At this point, we note that Gorenstein and Kar[8] found the ordering

$$V(+sc,+sc) < V(+sc,ap) < V(ap,ap)$$

to depend on the value of the OCO bond angle. However, their work used either the semiempirical CNDO method or the smaller STO-3G basis set. We shall discuss the angle variation later in this section, but at this stage, it is clear that the above energy ordering holds at the RHF/4-31G level with rigid rotation and tetrahedral valence angles.

It would, of course, be desirable to test the potential surface with an even higher level of basis set including polarization functions. This is not possible for dimethoxymethane with
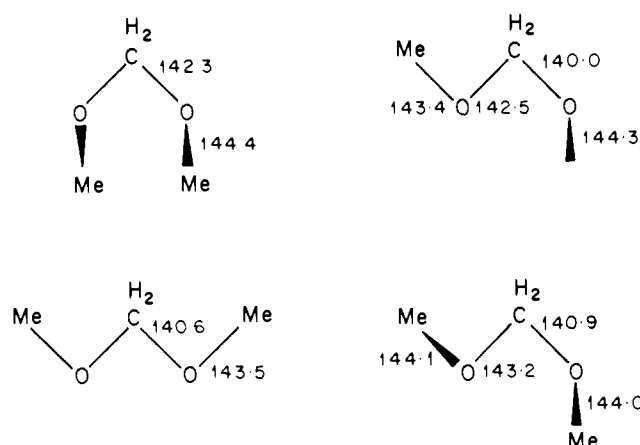
Figure 4. Calculated bond lengths (RHF/4-31G) for various conformations of dimethoxymethane.

Table IV. Energies of Dimethoxymethane with Optimized CO Lengths

Conformation		Total energy, hartrees	Rel energy, kcal mol^{-1}
2	+sc,+sc	−267.550 41	0.0
3	+sc,ap	−267.546 62	2.38
6	+sc,−sc	−267.545 27	3.23
5	ap,ap	−267.538 56	7.44

present computing facilities. However, we may further test the validity of the methanediol rigid rotation surfaces using the 6-31G* basis (RHF/6-31G* method).[12] This basis set includes d functions on nonhydrogen atoms. The results of such calculations are given in Table II. They are close to those obtained previously at the RHF/4-31G level but do show some reduction in the energy separations between the various forms. Table III compares relative energies of methanediol at those two levels for the four conformations consistent with staggered arrangements about all single bonds. The energies relative to (+sc,+sc) are reduced by about 1 kcal mol^{-1}. If similar reductions applied to the larger molecule dimethoxymethane, the energies of (+sc,ap) and (ap,ap) relative to (+sc,+sc) would be about 1.6 and 7.6 kcal mol^{-1}, rigid rotation still being assumed.

Bond Length Calculations. In the second set of calculations the C–O bond lengths were varied, the bond angles being maintained at standard values. Attention was focused on the staggered conformations **4** (+60,+60), **5** (60,180), and **7** (180,180) and the partly eclipsed conformation **8** with $\theta = 60°$ and $\varphi = 120°$. The resulting lengths are shown in Figure 4 and the total energies in Table IV. The lengths should be compared with the corresponding value for methanol (143.7 pm).

These results indicate that the C–O bonds in the O–C–O segment of dimethoxymethane have lengths which are shorter than that in methanol and close to those for the corresponding conformations of methanediol and methoxymethanol. As explained in ref 5 and 6, this shortening arises because of the acquisition of double-bond character by virtue of back-donation of p-type nonbonded oxygen electrons into the antibonding (σ^*) orbital of the neighboring bond. This effect is strongest in the +sc bond of the (+sc,ap) structure **5**. Also notable is the fact that the terminal C–O bonds in the (+sc,+sc) conformation **4** are lengthened relative to methanol. The same is true for the terminal C–O bond attached to the shorter central C–O bond in the (sc,ap) conformation **5**. This lengthening effect, which was also found in methoxymethanol, is interpreted as the result of competition for the back-donation of the oxygen p-type lone pair electrons; if the central C–O bond has more
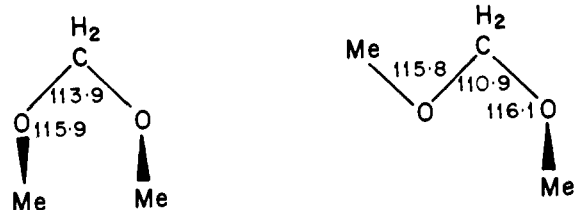
Figure 5. Calculated bond angles (RHF/4-31G) for two conformations of dimethoxymethane.

Table V. Energies of Dimethoxymethane with Optimized OCO and COC Angles

Conformation	Total energy, hartrees	Rel energy, kcal mol^{-1}
2 +sc,+sc	−267.555 41	0.00
3 +sc,ap	−267.550 34	3.18

double-bond character, the terminal C–O must correspondingly have less double-bond character and thus be longer.

Bond Angle Calculations. In the third set of calculations, the O–C–O and C–O–C angles were varied for the (+sc,+sc) and (+sc,ap) conformations, the bond lengths being held at the

optimum values shown in Figure 4. The angles so obtained are shown in Figure 5 and corresponding energies are given in Table V. The most marked difference between the two conformations is the fact that the OCO angle is 3.0° larger in (+sc,+sc) than in (+sc,ap). This parallels results obtained by Gorenstein and Kar using the minimal STO-3G basis. They obtained 114.7 and 109.4°. The COC bond angles are similar and probably too large (a general feature of split-valence basis sets for oxygen angles). The energy difference between the structures is increased to 3.2 kcal mol^{-1}. Again, we note that this is without inclusion of polarization functions; evidence from methanediol (Table III) suggests that this correction will lower the energy separation to a best estimate of 2.2 kcal mol^{-1}.

Comparison of Theory with Experiment

The *anomeric effect* postulates that of the two configurations about the anomeric center and three staggered conformations about the glycosidic bond for the acetal moiety in pyranosides [i.e., (+sc,+sc), (+sc,−sc), and (+sc,+ap) in the α-D-pyranosides, and (ap,+sc), (ap,−sc), and (ap,ap) in β-D-pyranosides], the α-D-pyranoside in the (+sc,+sc) conformation is the most stable. An electron diffraction study of dimethoxymethane has shown[13] that the corresponding (+sc,+sc) conformation is indeed the major constituent of the

Table VI. Acetal Geometry in α-D-Aldopyranosides

	Bond distances, pm C(5)—O(5)$_\alpha$—C(1)$_\beta$—O(1)$_\gamma$—C (θ)				Torsion angle, deg θ	Valance angles, deg			Ref
	C(5)	O(5)	C(1)	O(1)		α	β	γ	
X-Ray Data									
Methyl α-pyranosides									
(β-D)-Arabino[a]	143.4	141.8	139.3	142.3	69	112.8	112.9	113.1	b
Xylo (mol 1)	141.8	141.4	140.0	142.5	71	113.0	112.2	113.5	b
Xylo (mol 2)	143.4	141.3	139.1	142.7	63	111.5	112.5	113.1	b
Gluco	143.4	141.4	141.1	143.0	63	114.0	112.6	113.0	c
Galacto	143.9	141.8	140.5	143.7	64	113.8	111.3	113.0	d
Manno	145.0	142.1	140.7	144.2	61	114.3	111.7	113.4	e
Altro	144.0	141.6	140.5	142.8	64	113.9	112.1	113.2	f
4-Deoxy-4-fluorogluco	143.4	141.6	140.9	143.2	66	113.7	112.2	113.0	g
Exptl mean	143.54	141.63	140.44	143.05		113.4	112.3	113.1	
α-Glycosidic linkages[h]									
Methyl β-maltoside	144.1	140.8	141.5	143.7	110	114.7	111.4	117.6	i
Isomaltose	143.1	142.7	139.8	143.2	77	113.8	111.9	115.5	j
Planteose	143.0	141.6	141.5	144.0	109	114.5	109.8	118.9	k
Raffinose	143.6	142.3	142.8	144.2	72	113.2	111.1	111.4	l
Melezitose	143.4	141.6	140.8	142.3	92	114.4	110.8	116.9	m
Exptl mean	143.44	141.80	140.75	143.48		114.1	111.2	115.0	
α-Cyclohexamylose[n] (propanol adduct)	144.63	140.67	140.83	143.30	100–111	113.8	111.3	119.2	o
Neutron Data									
Methyl α-pyranosides									
Gluco	142.8	141.4	140.1	142.2	63	113.5	113.0	113.9	p
Manno	143.9	141.8	140.1	142.2	61	114.3	112.4	113.9	p
Altro	143.9	141.3	140.0	140.7	64	113.9	112.0	114.0	q
Exptl mean	143.53	141.57	140.07	141.70		113.9	112.5	113.9	
α-Glycosidic linkages									
β-Maltose	143.4	140.3	141.4	141;9	122	113.8	110.7	117.8	r
Sucrose	143.7	141.1	142.2	142.9	108	116.0	110.9	114.3	s
Theory	144.4	142.3	(142.3)	(144.4)	60	115.9	113.9	(115.9)	

[a] Has the α configuration at C(1), with C(5)–O(5)–C(1)–O(1) + sc. [b] G. A. Jeffrey and S. Takagi, unpublished work. [c] H. M. Berman and S. H Kim, *Acta Crystallogr.*, **24**, 897 (1968). [d] B. M. Gatehouse and B. J. Poppleton, *Acta Crystallogr., Sect. B*, **27**, 654 (1971). [e] B. M. Gatehouse and B. J. Poppleton, *ibid.*, **26**, 1761 (1970). [f] B. M. Gatehouse and B. J. Poppleton, *ibid.*, **27**, 871 (1971). [g] W. Choong, N. C. Stephenson, and J. D. Stevens, *Cryst. Struct. Commun.*, **4**, 491 (1975). [h] Omitting those with a C–O–C–O–C sequence. [i] S. S. C. Chu and G. A. Jeffrey, *Acta Crystallogr.*, **23**, 1038 (1967). [j] W. Dreissig and P. Luger, *Acta Crystallogr., Sect. B*, **29**, 514 (1973). [k] D. C. Rohrer, *ibid.*, **28**, 425 (1972). [l] H. M. Berman, *ibid.*, **26**, 290 (1970). [m] K. Horotsu and S. Shimada, *Chem. Lett.*, 83 (1973). [n] Mean value for six linkages. [o] W. Saenger, R. K. McMullan, J. Fayos, and D. Mootz, *Acta Crystallogr., Sect. B*, **30**, 2019 (1974). [p] G. A. Jeffrey, R. K. McMullan, and S. Takagi, *ibid.*, **33**, 728 (1977). [q] B. J. Poppleton, G. A. Jeffrey, and G. J. B. Williams, *ibid.*, **31**, 2400 (1975). [r] M. E. Gress and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, **33**, 2490 (1977). [s] G. M. Brown and H. A. Levy, *ibid.*, **29**, 790 (1973).

Table VII. Acetal Geometry in β-D-Aldopyranosides [C(5)-O(5)-C(1)-O(1) ≈ 180°]

	Bond distances, pm				Torsion angle, deg	Valence angles, deg			
	C(5)—O(5) [α]	C(1) [β]	θ	O(1) [γ] C	θ	α	β	γ	Ref
X-Ray Data									
Methyl β-D-pyranosides									
(α-L)-Arabino[a]	143.2	143.4	137.5	143.4	−80	112.7	107.4	114.4	b
Xylo	142.6	142.1	139.0	142.7	−72	110.6	107.0	113.3	c
Gluco	144.0	143.3	138.0	143.0	−73	111.5	108.1	113.1	d
Galacto	143.9	142.4	139.0	142.3	−78	111.1	107.4	113.0	e
6-O-Acetylgluco	142.9	142.9	138.4	142.8	−70	110.8	106.9	112.4	f
6-O-Acetylgalacto	142.7	143.7	137.4	142.8	−82	112.6	107.3	114.4	g
3,4-Ethylidenegalacto	144.2	142.3	139.3	142.1	−70	110.6	107.9	113.5	h
Maltoside	142.8	142.4	137.7	142.5	−69	111.5	107.1	113.2	i
Exptl mean	143.29	142.81	138.29	142.70		111.4	107.9	113.4	
β linkages									
Cellobiose	143.6	142.5	139.7	144.6	−76	112.2	107.5	116.1	j
Galacto-L-rhamnitol	143.9	142.6	138.4	144.1	−71	111.2	107.7	115.8	k
α-Lactose-H₂O	144.8	142.7	138.7	143.6	−94	112.2	106.9	117.3	l
Exptl mean	144.1	142.6	138.9	144.1		111.9	107.4	116.4	
Neutron Data									
Methyl β-pyranosides	C(5)——O(5)	——C(1)——	O(1)——	CH₃					
Xylo	142.1	142.7	138.1	142.6	−72	111.1	107.4	113.0	m
Theory	143.4	142.5	140.0	144.3	60	115.8	110.9	116.1	

[a]Has the β configuration at C(1) with C(5)-O(5)-C(1)-O(1) ap. [b]See ref b, Table VI. [c]C. J. Brown, G. Cox, and F. J. Llewellyn, *J. Chem. Soc.*, 922 (1966). [d]G. A. Jeffrey and S. Takagi, *Acta Crystallogr., Sect. B*, 33, 738 (1977). [e]G. A. Jeffrey and S. Takagi, *Acta Crystallogr.*, in press. [f]K. B. Lindberg, *Acta Crystallogr., Sect. B*, 32, 642 (1976). [g]K. B. Lindberg, *ibid.*, 32, 645 (1976). [h]K. B. Lindberg, *ibid.*, 32, 639 (1976). [i]See ref i, Table VI. [j]S. S. C. Chu and G. A. Jeffrey, *Acta Crystallogr.*, 24, 830 (1968). [k]G. A. Jeffrey and S. Takagi, *ibid.*, 33, 2377 (1977). [l]D. C. Fries, S. T. Rao, and M. Sundaralingam, *Acta Crystallogr., Sect. B*, 27, 994 (1971). [m]S. Takagi and G. A. Jeffrey *ibid.*, 33, 3033 (1977).

Table VIII. Hemiacetal Geometry in α-D-Aldopyranoses

	Bond distances, pm				Torsion angle, deg	Valence angles, deg			
	C(5)—O(5) [α]	C(1) [β]	θ	O(1) [γ] H	θ	α	β	γ	Ref
X-Ray Data[a]									
α-D-Xylose	144.2	142.6	139.6			112.4	112.0		b
	144.9	142.8	139.3			112.4	111.5		c
β-DL-Arabinose[d]	145.0	143.5	139.5			113.5	112.8		e
β-L-Arabinose[d]	144.0	142.1	138.2			112.7	113.1		f
α-D-Galactose	143.1	144.5	140.9			114.1	110.9		g
	142.6	143.3	140.0			114.2	111.8		h
α-Fucose	148.1	141.2	138.2			112.1	111.6		i
α-L-Rhamnose-H₂O	144.4	142.2	140.1			115.0	111.9		j
α-DL-Mannose	144.4	144.7	139.5			112.8	111.8		k
α-D-Mannose (mol 1)	144.0	141.2	140.4			114.8	111.9		l
(mol 2)	144.8	141.5	142.1			115.5	111.6		l
α-Talose	144.5	143.5	140.0			113.5	111.9		m
Exptl mean	144.48	142.77	138.53			113.7	111.9		
Neutron Data									
α-D-Glucose	142.7	142.5	138.9	96.8	+75	113.8	111.6	107.8	n
β-L-Arabinose[d]	143.2	141.8	139.8	95.2	+64	113.4	109.8	109.2	o
α-L-Rhamnose	143.9	141.9	140.4	97.9	−98	114.7	111.9	107.4	p
Theory	144.4	142.1	141.7	(96.0)		(109.5)	(109.5)	(109.5)	

[a]θ and γ values are omitted for the x-ray data because of their low accuracy. [b]E. Morild, private communication. [c]A. Hordvik, *Acta Chem. Scand.*, 25, 2175 (1971). [d]Has the α configuration with the C(5)-O(5)-C(1)-O(1) torsion angle = +61°. [e]S. H. Kim and G. A. Jeffrey, *Acta Crystallogr.*, 22, 527 (1967). [f]A. Hordvik, *Acta Chem. Scand.*, 15, 16 (1961). [g]J. Ohanessian and H. Gillier-Pandraud, *Acta Crystallogr.,Sect. B*, 32, 2810 (1976). [h]B. Sheldrick, *ibid.*, 32, 1016 (1976). [i]F. Longchambon, J. Ohanessian, D. Avenel, and A. Neuman, *ibid.*, 31, 2623 (1975). [j]R. C. G. Killean, J. L. Lawrence, and V. C. Sharma, *ibid.*, 27, 1707 (1971). [k]F. Planinsek and R. D. Rosenstein, Abstract N10, American Crystallographic Association Meeting, Aug 1967. [l]F. Longchambon, D. Avenel, and A. Neuman, *Acta Crystallogr., Sect. B*, 32, 1822 (1976). [m] J. Ohanessian, D. Avenel, J. A. Kanters, and D. Smits, *ibid.*, 33, 1063 (1977). [n]G. M. Brown and H. A. Levy, *Science*, 147, 1038 (1965). [o]See ref m, Table VII. [p]G. A. Jeffrey and S. Takagi, *Acta Crystallogr.*, in press.

conformational species in the gas phase. The *exo-anomeric effect* postulates that for a molecule with the α-D configuration the (+sc,+sc) conformation is the most stable; for a molecule with the β-D configuration, the most stable conformation will be (ap,±sc).

The energy calculations discussed in the previous section and reported in Tables I–V and Figure 2 are completely consistent with both these hypotheses. In addition to these energy differences, there are small but significant differences in the molecular geometry associated with the acetal moieties in α-

Table IX. Hemiacetal Geometry in β-D-Aldopyranoses

	Bond distances, pm			Torsion angle, deg θ	Valence angles, deg			Ref
	C(5)—O(5) α	C(1) β	O(1)—H γ		α	β	γ	
			X-Ray Data[a]					
β-L-Lyxose	142.6	142.9	138.4		112.4	107.2		b
β-D-Glucose	143.7	143.3	138.4		112.7	107.0		c
β-D-Galactose	144.0	142.2	139.6		111.5	106.7		d
	143.7	141.3	139.5		111.9	107.1		e
2-Deoxy-2-fluoro-β-D-mannose	143.0	142.9	139.9		112.0	106.2		f
Exptl mean	143.40	142.52	139.36		112.0	106.8		
Theory	143.5	142.4	139.8		(109.5)	(109.5)		

[a] See ref a, Table VIII. [b] See ref b, Table VIII. [c] See ref j, Table VII. [d] See ref i, Table VIII. [e] See ref h, Table VIII. [f] W. Choong, D. C. Craig, N. C. Stephenson, and J. D. Stevens, *Cryst. Struct. Commun.*, 4, 111 (1975).

and β-pyranosides which are now well established to a high degree of accuracy, by both x-ray and neutron diffraction single crystal studies. These data are given in Table VI for the α-D-pyranosides and Table VII for the β-D-pyranosides.

In the α-methyl pyranosides, the glycosidic torsion angles lie in a surprisingly narrow range of 61–71°, in view of the fact that every molecule has a different crystal field environment. This is in agreement with the relatively steep slope to the potential energy curves given in Figure 2. In the β-methyl pyranosides, the range is 69–82°. The electron diffraction study of dimethoxymethane[13] gave a C–O–C–O torsion angle of 63.3°.

In the α and β linkages of the oligosaccharides the variation in the glycosidic torsion angles is greater. This is due to the effect of intramolecular factors, such as hydrogen bonds and steric interactions between substituents of the adjacent pyranose rings.

In the experimental bond lengths and valence angles there is a very consistent pattern to the dimensions of these molecules. The electron diffraction results[13] on $CH_3OCH_2OCH_3$ favored unequal C–O bonds over equal bonds, but the results were not decisive. The best fit with the experimental data was obtained with the two inner bonds at 138.2 pm and the two outer bonds at 143.2 pm. The central O–C–O valence angle was 114.3° and the C–O–C angles were 114.6°.

The bond lengths and valence angles from the x-ray and neutron diffraction studies of the methyl pyranosides and some of the di- and trisaccharides are shown in Tables VI and VII. In the α-pyranosides, the two inner bonds are shorter than the two outer bonds of the acetal sequence by 2.5 pm. The glycosidic bond is slightly shorter than the ring bond to the anomeric carbon by the order of 1 pm, which we believe is significant. This difference may be sensitive to the glycosidic torsion angle, since the difference between the lengths of the two inner bonds tends to disappear in the oligosaccharides when the glycosidic torsion angle is closer to 90° than 60°. All three valence angles are greater than tetrahedral, that at C(1) being smaller than those at the oxygen.

The neutron diffraction data agree well with the x-ray data. In comparing x-ray and neutron diffraction data on the same crystal structures[14] a trend was observed for the C–O bond distances to be systematically shorter by about 1 pm. This is interpreted as a consequence of the displacement of the lone-pair electrons from the oxygen nucleus, when averaged by the thermal motion.

In the β-pyranosides, a different pattern of bond lengths is observed. In that configuration the bond shortening is concentrated in the glycosidic bond. The bond from the ring oxygen to the anomeric carbon atom is only slightly shorter than the two external bonds of the acetal group. Again this may be sensitive to the torsion angle, since this difference appears to be greater in the disaccharides, where the glycosidic angle

Table X. Comparison of C–H Bond Lengths from Neutron Diffraction Data

Structure	Anomeric C–H, pm	Range of nonanomeric C–H, pm[a]	Ref
α-D-Glucose	109.5	109.2–110.7	b
β-L-Arabinose	110.2	109.2–110.2	c
Methyl α-glucose	110.9	109.2–109.5	d
Methyl α-mannose	110.2	110.1–110.5	d
Methyl α-altrose	110.5	109.4–110.5	e
Methyl β-xylose	109.5	109.2–110.2	c

[a] These values exclude those on primary alcohol groups because of differences in thermal motion, which affect the bond lengths due to the riding motion effect. [b] See ref n, Table VIII. [c] See ref m, Table VII. [d] See ref p, Table VI. [e] See ref q, Table VI.

is close to 90°, than in the methyl pyranosides. Another marked feature of the β configuration is the closure of the anomeric O–C–O valence angle below the tetrahedral value, and the difference of 2° between the angles at the ring and glycosidic oxygen.

The majority of these features are reproduced very closely by the theoretical calculations as shown in Tables VI and VII. In the (+sc,+sc) conformation, the model molecule necessarily has a twofold axis of symmetry, so that small differences which could arise because of the difference between the ring carbon and the methyl carbon in the α-pyranosides cannot be reproduced.

There is a trend for the theoretical valence angles to be 2–3° greater than those observed experimentally. This is not unexpected as noted above. In Tables VIII and IX, we give the most recent data available on the α-D- and β-D-pyranose sugars, with a comparable comparison with the earlier calculations on methoxymethane where the valence angles were not optimized. An interesting feature is that the difference in bond length distribution about the C(1)–O bonds, which was very apparent in the comparison of the α- and β-methyl pyranosides, disappears in the experimental data on free sugars, but is partially retained in the theoretical results.

It was thought that the unique character of the electron density distribution in the region of the anomeric carbon might also be reflected in differences between the C(1)–H bond lengths and those of other C–H bonds in carbohydrate molecules. The recent neutron diffraction data shown in Table X show this not to be the case.

References and Notes

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Molecular Structures and Potential Functions for the Deformation of Cyclopropane, Cyclopropene, Cyclobutane, and Cyclopentadiene

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Abstract: Cyclopropane, cyclopropene, cyclobutane, and cyclopentadiene have been chosen as models to study angular deformations for higher hydrocarbons (e.g., spiro hydrocarbons). To this end, ab initio molecular orbital theory has been used to examine the structural and energetic changes accompanying distortion of an exocyclic HCH angle in these molecules. Results are compared with previous studies on methane. Although methane is confirmed to be a reasonable model in most respects, the structural variations found in C–C bonds are significantly larger than those found for the C–H bonds in methane, a result which is consistent with the difference in bond strength between C–C and C–H bonds. The structural and energetic consequences of angular deformation are usefully analyzed in terms of Walsh–Mulliken diagrams of the several highest bonding molecular orbitals. The calculated dipole moments and the HOMO energies (for cyclopropene and cyclopentadiene) are shown to be sensitive to the deformed exocyclic HCH angle.

Introduction

Molecular deformations are of particular interest to chemists because molecules with different bond angles may differ appreciably in both physical and chemical properties. In the past, attention has mainly been focused on small angular deformations which are of interest in connection with studies of molecular vibrations. Relatively little work has been carried out which deals with the potential functions and the geometric changes that are associated with highly distorted structures.

Recently, however, the angular deformation of methane has been extensively studied using ab initio orbital theory.[1,2] The structural simplicity and inherent symmetry of methane make it an economical model for investigating angular deformation at tetracoordinate carbon for higher hydrocarbons. However, it has not yet been established whether distorted methane provides a reliable and realistic model for making detailed predictions concerning the properties of larger distorted molecules (e.g., cyclohydrocarbons, spiro hydrocarbons). In particular, it is not clear whether the greater effective nuclear charge on carbon (compared with hydrogen) can be compensated by the greater C–C (compared with C–H) bond length. The effect of differing C–C and C–H bond strengths also needs to be assessed.

In order to provide a better understanding of angular deformations in higher hydrocarbons and to learn how well methane can serve as a model for these molecules, studies of additional larger systems are desirable. In this paper, angular deformations in cyclopropane, cyclopropene, cyclobutane, and cyclopentadiene have been studied using ab initio molecular

orbital theory. The structural and energetic variations are interpreted in terms of Walsh–Mulliken diagrams. Comparison is made with results obtained from the previous model studies[1,2] of methane.

Method

Standard ab initio LCAO SCF molecular orbital calculations were carried out using a modified version of the Gaussian 70 system of programs.[3] Geometry optimizations were performed with the STO-3G basis set[4] and a gradient optimization procedure.[5] Single calculations on optimized structures were carried out with the 4-31G basis set[6] which is somewhat more reliable for energetic comparisons.[6,7]

The STO-3G optimized equilibrium structures for cyclopropane, cyclopropene, and planar cyclobutane[8] have been reported previously.[9,10] We report here for the first time the fully optimized STO-3G structure for cyclopentadiene.

Structural and energetic variations accompanying distortion of the exocyclic HCH angle (ϕ, see **1**) have been studied by

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